Secretary:
Prof. Michael Cunningham

Queen’s University
Department of Chemical Engineering
Queen’s University
Kingston, Ontario
K7L 6T5
Canada
Fax: 613-533-6637

Email: michael.cunningham@chee.queensu.ca

IPCG

INTERNATIONAL POLYMER AND COLLOIDS GROUP
NEWSLETTER

Conference Announcements and Future Meetings:

Macro 2010 '43rd IUPAC World Polymer Congress'

July 11-16, 2010
Scottish Exhibition and Conference Centre (SECC), Glasgow, United Kingdom
Webpage: www.Macro2010.org
Contact: Prof. Peter Lovell, University of Manchester (Chair)
E-mail: Macro2010@rsc.org

Pacifichem 2010

December 15-20, 2010
Honolulu, Hawaii, USA
Webpage: http://www.pacifichem.org/

IPCG Conference on Polymer Colloids (mark your calendar!)

June 26-July 1, 2011
University of New Hampshire, Durham, New Hampshire, USA
Chair persons: Prof. Michael Cunningham (Michael.Cunningham@chee.queensu.ca)
Dr. Dieter Urban, BASF (Dieter.Urban@basf.com)

4th ASEPFPM, Hong Kong, China

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

Industrial Short Courses:

Lehigh EPI: Advances in Emulsion Polymerization and Latex Technology
Lehigh University, USA, June 7-11, 2010
https://fp1.cc.lehigh.edu/inemuls/epi/Lehigh_sc.htm

UNH Latex Morphology Control Workshop
University of New Hampshire, USA, June 7-10, 2010
http://www.unh.edu/prg/workshop.html

Lehigh EPI: Advances in Emulsion Polymerization and Latex Technology
Davos, Switzerland, August 2-6, 2010
http://www.davoscourse.com/

POLYMAT Course on Emulsion Polymerization Processes
September 6-10, 2010
http://www.sc.ehu.es/qpwilp/EPP_2010.htm

MEMBERSHIP LIST

Prof. H-J Adler TU Dresden Professur für Makromolekulare Chemie D-01062 Dresden Tel.: ++49 (0) 351 463 3 3782 bzw ++49 (0) 351 463 3 7676 Hans-juergen.adler@chemie.tu-dresden.de http://www.chm.tu-dresden.de/mtc1/hj_adler.shtml	**Dr. S.P. Armes** The University of Sheffield Department of Chemistry, Room C83 Western Bank Sheffield S10 2TN UNITED KINGDOM Tel. +44 -114-222-9342 Fax. +44- 114-222-9346 s.p.armes@sheffield.ac.uk http://armesresearch.group.shef.ac.uk/
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 qppasgoj@sq.ehu.es http://www.sc.ehu.es/powgep99/polymat/homepagi.html	**Prof. Dr. M. Ballauff** F-I2 Soft Matter and Functional Materials Helmholtz-Zentrum Berlin für Materialien und Energie GmbH Glienicker Straße 100, 14109 Berlin AND Humboldt University Berlin Department of Physics Newtonstr. 15, 12489 Berlin GERMANY Tel: +49 30 8062-3071 Fax: +49 30 8062 2308 matthias.ballauff@helmholtz-berlin.de http://www.helmholtz-berlin.de/pubbin/vkart.pl?v=kzunu
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 bartsch@aak.chemie.uni-mainz.de http://www.colloids.uni-freiburg.de/Bartsch	**Dr. D.R. Bassett** *(RETIRED MEMBER)* Dow 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 http://www2.warwick.ac.uk/fac/sci/chemistry/research/materialschemistry/bon/	**Dr. E. Bourgeat-Lami** LCPP-CNRS/ESCPE-Lyon 43 Blvd du 11 Novembre 1918 B.P. 2077 69616 Villeurbanne Cedex FRANCE Fax: +33- 4 72 43 17 68 bourgeat@lcpp.cpe.fr http://www.lcpp-cpe.com/staff.php?name=bourgeat-lami
Dr. F. Candau *(RETIRED MEMBER)* (CRM-EAHP) Institute Charles Sadron 6 Rue Boussingault Strasbourg Cedex 67083 FRANCE Fax: +33-388-41-4099 candau@ics.u-strasbg.fr	**Dr. P. Chan** PCTS Specialty Chemicals PTE, Nippon Paint Ltd. 16 Joo Koon Crescent Singapore 629018 SINGAPORE Fax: peterchan@pcts.com.sg http://snic.org.sg/people/profile_peter_chan.htm
Dr. B. Charleux Professeur à l' UCB Lyon 1 Membre senior de l'IUF - promotion 2009 C2P2 / LCPP - UMR 5265 (UCBL - CNRS - CPE) CPE Lyon - Bât 308 43 Bd du 11 Novembre 1918 BP 2077 69616 Villeurbanne Cedex - France E-mail: bernadette.charleux@lcpp.cpe.fr Phone: 33 (0)4 72 43 17 75 Fax: 33 (0)4 72 43 17 68 http://www.c2p2-cpe.com/	**Prof.Dr. S.Choe** R&D Center, Okong Corporation 426-1 Yonghyun 3 dong Namgu, Incheon 402-023, Republic of Korea AND Inha University, Dep. of Chemical Engineering 253 Yonghyundong, Namgu Incheon 402-751 REPUBLIC OF KOREA Fax: +82-32-876-7467 sjchoe@inha.ac.kr http://whs.inha.ac.kr/~k1031/home.htm
Prof. Dr. J.P. Claverie University of Québec at Montréal Director of Nanoqam Department of Chemistry and Biochemistry Succursale Centre Ville Montréal, Québec, H3C 3P8 CANADA Tel. +1-514 987 3000 / 6143 Fax: +1- 514 987 4054 claverie.jerome@uqam.ca http://www.nanoqam.uqam.ca/?page_id=17&language=fr	Dr. Catheline Colard *(NEW MEMBER)* Postdoctoral Researcher Ghent University Polymer Chemistry Research Group Department of Organic Chemistry Krijgslaan 281, S4bis 9000 Gent, Belgium Phone: (+32)9264-4489 Fax: (+32)9264-4972 colardcatheline@gmail.com http://www.pcr.ugent.be/

Prof M. Cunningham
Queen’s University
Department of Chemical Engineering
99 University Avenue
Kingston, Ontario K7L 3N6
CANADA
Fax: +1 613 533-6637
cunning@chee.queensu.ca
http://chemeng.queensu.ca/people/faculty/cunningham/index.php

Dr. F. D’ Agosto
LCPP-CNRS/ ESCPE
Bât. F308, B.P. 2077
43 Bd du 11 Nov. 1918
69616 Villeurbanne cedex
FRANCE
Tel.: +33 472 43 1770
Fax:
Franck.dagosto@lcpp.cpe.fr
http://www.lcpp-cpe.com/staff.php?name=dagosto

Prof. Dr. J. DeSimone
Department of Chemistry
Campus Box 3290
Caudill 257
The University of North Carolina at Chapel Hill
Chapel Hill, NC 27599-3290
Tel: 919-962-2166
Fax: 919-962-5467
desimone@email.unc.edu
http://www.chem.unc.edu/people/faculty/desimone/

Dr. M. do Amaral
Accenture
Manager
Av. Chile 500, 18 andar
Rio de Janeiro, RJ
BRAZIL
Tel : +55-21-45019560
Fax:
marcelo.do.amaral@accenture.com
doamaral.marcelo@gmail.com

Dr. M.S. El-Aasser
EPI, Lehigh University
111 Research Drive,
Bethlehem PA 18015-4732
USA
Fax: +1-610-758-5880
mse0@lehigh.edu
https://fp2.cc.lehigh.edu/inemuls/MEAhome.htm

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

Dr. J. Forcada
The University of the Basque Country
Institute for Polymer Materials "POLYMAT"
Avenida de Tolosa 72
20018 Donostia-San Sebastián
SPAIN
Phone: + 34-943-018181
Fax: + 34-943-017065
jacqueline.forcada@ehu.es
http://www.sc.ehu.es/powgep99/polymat/homepagi.html

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
http://chem.okstate.edu/index.php?option=com_content&task=view&id=40&Itemid=124

Dr. F. Ganachaud Laboratoire de Chimie Macromoléculaire UMR 5076 CNRS/ENSCM Ecole Nationale Supérieure de Chimie de Montpellier 8 rue de l'école normale 34296 Montpellier cedex 5 FRANCE Fax: +33 -4-67 1472 96/20 ganachau@enscm.fr fganachaud@yahoo.fr	**Dr. A.P. Gast** Lehigh University 27 Memorial Drive West Bethlehem, PA. 18015 USA tel: 610.758.3157 fax: 610.758.3154 apg206@lehigh.edu gast@mit.edu http://www3.lehigh.edu/inauguration/bio.html http://web.mit.edu/gastlab/www/index.shtml
Prof.Dr. A.L. German *(RETIRED MEMBER)* 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.german@chello.nl http://w3.chem.tue.nl/nl/people_pages/?script=showemp.php&pid=496	**Dr. J.W. Goodwin** Interfacial Dynamics Corp. PO Box 3284 Tualatin OR 97062 USA Fax: +1-503- 684-4559 jimgoodwin@compuserve.com
Dr. F.K. Hansen University of Oslo Department of Chemistry PO Box 1033 Blindern 0315 OSLO NORWAY Fax: +47-228-55542 f.k.hansen@kjemi.uio.no http://www.kjemi.uio.no/forskning/pol/fhansen/english.html	**Dr. Brian Hawkett** School of Chemistry Sydney University NSW 2006 Key Centre for Polymer Colloids Chemistry F11 NSW 2006 AUSTRALIA Tel. +61 2 9351 6973 Fax: +61 2 9351 8651 b.hawkett@chem.usyd.edu.au http://www.kcpc.usyd.edu.au/Brian_Hawkett.html
Dr. W.D. Hergeth Wacker Chemie AG LEP, PK 14 Johannes Hess Strasse 24 Burghausen, D-84489 GERMANY Tel: +49-8677-83 1148 Fax: +49-8677-866 1148 wolf-dieter.hergeth@wacker.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 http://www.avcr.cz/o_avcr/struktura/pracoviste/ziva/UMCH.html

Dr. C-C Ho
Universiti Tunku Abdul Rahman
Faculty of Engineering & Science
No. 13 Jalan 13/6, 46200 Petaling Jaya
Selangor D.E., Malaysia
Tel: 603-7958-2628 ext. 8204
Fax: 603-7955-8209
ccho@utar.edu.my
cchoho2001@yahoo.com
http://research.utar.edu.my/utargrn/icp/HoCheeCheong/index.jsp

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

Prof. Dr. D. Johannsmann
Technische Universität Clausthal
Institut für Physikalische Chemie
Arnold-Sommerfeld-Str. 4
D-38678 Clausthal Zellerfeld
GERMANY
Tel.: +49 (0) 5323 - 72 3768
Fax: +49 (0) 5323 - 72 4835
johannsmann@pc.tu-clausthal.de
http://www.pc.tu-clausthal.de/forschung/ak-johannsmann/mitarbeiter/d-johannsmann/

Dr. O. Karlsson
Lund University
Department of Physical Chemistry 1
P.O. Box 124
Lund SE-221 00
SWEDEN
Fax: +46-4622-24-413
ola.karlsson@fkem1.lu.se
http://www.fkem1.lu.se/staff/asp/detail.asp?person_id=251&val=senior&valtext=Senior+Scientists%2FTeachers

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
http://www.lcc.keio.ac.jp/cgi-bin/public/display.cgi?table_id=2&data_id=88&je=1

Dr. J. Keddie
Department of Physics
University of Surrey
Guildford, Surrey GU2 7XH
UNITED KINGDOM
Fax: +44 1483 686781
j.keddie@surrey.ac.uk
http://www2.surrey.ac.uk/physics/people/joseph_keddie/

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

Prof. J.H. 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
http://www.nanotech.or.kr/eng/people01.php

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

Dr. P. Lacroix-Desmazes
Chargé de Recherche au CNRS
Ecole Nationale Supérieure de Chimie de Montpellier
Equipe "Ingénierie et Architectures Macromoléculaires"
UMR 5253 - Institut Charles Gerhardt
8, rue de l'Ecole Normale
34296 MONTPELLIER CEDEX 5 (FRANCE)
Tél: + 33-4-67-14-72-05
Fax: + 33-4-67-14-72-20
Patrick.Lacroix-Desmazes@enscm.fr
http://www.iam.icgm.fr or http://www.icgm.fr/

Dr. Do Ik Lee
Western Michigan University
College of Engineering and Applied Science
Kalamazoo, MI 49008-5462
USA
Tel: 989-631-6127
Fax: 269-276-3501
doiklee@aol.com
http://www.wmich.edu/pci/faculty/lee_N.htm

Prof. J. Leiza
The University of the Basque Country
Institute for Polymer Materials "POLYMAT"
Avenida de Tolosa 72, 20018 Donostia-San Sebastián, Spain
Phone: + 34-943-018181
Fax: + 34-943-017065
jrleiza@ehu.es
http://www.sc.ehu.es/powgep99/polymat/homepagi.html

Dr. Pei Li
Hong Kong Polytechnic University
Department of Applied Biology and Chemical Technology
Office : Y845
Hung Hom, Kowloon, Hong Kong
CHINA
Tel : (852) 3400 8721
Fax : (852) 2364 9932
bcpeili@polyu.edu.hk
http://www.polyu.edu.hk/abct/staff_lipei.php

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 pal@umist.ac.uk
http://www.materials.manchester.ac.uk/aboutus/staff/peterlovell/

Prof. Dr. A. Lyon
Georgia Institute of Technology
School of Chemistry and Biochemistry
Office: Molecular Science & Engineering, Room 1100K
901 Atlantic Drive, NW
Atlanta, GA 30332-0400
Phone: 404-894-4090
Fax: 404-894-7452
lyon@gatech.edu
http://www.chemistry.gatech.edu/faculty/Lyon/

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

M.S. Ahmed (*NEW MEMBER*) Manager, WB Research Nuplex Resins LLC 4730 Crittenden Drive Louisville, KY 40209 USA Phone: 502-375-5309 Fax: 502-375-5580 maqsood.ahbed@nuplexresins.com	**Dr. C.J. McDonald** Consultant 45 Rattle Hill Road Southhampton, MA 01073 USA Fax: cjm@cjmcdonald.com
Prof. Dr.Timothy F. McKenna Queen's University Department of Chemical Engineering 19 Division St Kingston, Ontario K7L 3N6 CANADA Fax: +1 613 533-6637 tim.mckenna@chee.queensu.ca http://chemeng.queensu.ca/people/faculty/mckenna/index.php	**Prof. A.Y. Menshikova** Institute of Macromolecular Compounds of Russian Academy of Sciences Bol'shoi Prospect 31 199004 St. Petersburg, RUSSIA Fax: +7 812 328 68 69 asya@hq.macro.ru mensh_asya@yahoo.com http://www.macro.ru/en/1.html
Dr. D. Mestach Nuplex Resins BV P.O. Box 79 4600 AB Bergen op Zoom THE NETHERLANDS Tel: +31 164 276582 Fax: +31 164 276502 dirk.mestach@NuplexResins.com http://www.nuplexresins.com/	**Prof. Dr. A. Mueller** Universität Bayreuth Makromolekulare Chemie II Universitaetsstrasse 30 NW II 95440, Bayreuth GERMANY Tel. +49 (921) 553399 Fax. +49 (921) 553393 axel.mueller@uni-bayreuth.de http://www.chemie.uni-bayreuth.de/mcii/
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 http://www.fukui-u.ac.jp/en/	**Prof. Dr. M. Okubo** Department of Chemical Science and Engineering, Graduate School of Engineering, Kobe University, Kobe 657-8501, Japan Tel/Fax +81-78-803-6161 okubo@kobe-u.ac.jp
Dr. D. Ou-Yang Lehigh University, Physics Department 16, Derning Lewis Lab 18015 Bethlehem, PA USA Tel. 001 610 7583920 Fax. 1 610 7585730 hdo0@lehigh.edu http://www.lehigh.edu/~influids/index.html	**Dr. K. Ouzineb** Cytec Specialty Chemicals- R&D Acrylics Anderlechtstraat, 33 B-1620 Drogenbos BELGIUM Tel: + 32-(0)2.334.51.94 Fax: keltoum.ouzineb@cytec.com

Prof. Dr. R. Pelton
McMaster University, Dept of Chem. Engineering
SENTINEL- Bioactive Paper Network
1280 Main Street West
Hamilton, Ontario
CANADA   L8S 4L7
Tel.: + 1 905 529 7070 ext. 27045
Fax: +1 905 528-5114
Website: www.papersci.mcmaster.ca
peltonrh@mcmaster.ca

Jose Carlos Pinto (*NEW MEMBER*)
Programa de Engenharia Quimica / COPPE
Universidade Federal do Rio de
Janeiro Cidade Universitaria - CP: 68502 Rio de Janeiro
- 21945-970 RJ – Brasil
pinto@peq.coppe.ufrj.br
Fone:55-21-25628337 FAX:55-21-25628300
Internet:
http://www.peq.coppe.ufrj.br/Pessoal/Professores/pinto/

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

Prof. Dr. W. Richtering
Lehrstuhl für Physikalische Chemie II
RWTH Aachen University
Landoltweg 2, D-52056 Aachen
GERMANY
Tel +49(0)241 80 94760 / 761
Fax +49(0)241 80 92327
richtering@rwth-aachen.de
http://www.ipc.rwth-aachen.de/groups/ipc-rwth/ak-richtering/home.html

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
G.Riess@uha.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
http://www.polymercentre.org.uk/staff/member.php?id=54

Prof. Dr. A. Ritcey
Universite Laval
Department of Chemistry,
Quebec City,
Quebec, G1K7P4
CANADA
Tel: 1-418-656-2368
E-mail: anna.ritcey@chm.ulaval.ca
http://www.chm.ulaval.ca/sections/ficheritcey.html

Dr. W.B. Russel
Dept of Chem. Engineering
Princeton University
Olden Street
Princeton, NJ 08544   USA
Fax: +1 609 258-0211
wbrussel@princeton.edu
http://www.princeton.edu/che/people/faculty/russel/

Dr. C. Schellenberg
Ciba Specialty Chemicals Inc.
K-147.2.58
4002 Basel
SWITZERLAND
Fax: +41 61 63 62730
carsten.schellenberg@basf.com
http://www.ciba.com/cmp-ww-ch-car-myf-contacts.htm

Prof. F.J. Schork
University of Maryland
Dept. of Chemical & Biomolecular Engineering
2113E Chemical Engineering Bldg 090
College Park, MD 20742 USA
Fax: +1 301 405-0523
joseph.schork@chbe.gatech.edu
http://www.chbe.umd.edu/facstaff/chair.html

Dr. K-V. Schubert Kai-Volker.Schubert@usa.dupont.com	**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 http://www.cbmm.lodz.pl/en/slomkowski.html
Prof. J. Snuparek Department of Polymeric Materials University of Pardubice 532 10 Pardubice CZECH REPUBLIC Fax: +420-46-603-7068 Jaromir.Snuparek@upce.cz http://www.upce.cz/lideUPa.html?id=5067D87F-A63C-4F2A-BCF7-C998AFC6B15F#z1	**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 dcs@christa.unh.edu http://www.unh.edu/apl/	**Dr. K. Tauer** Max-Planck-Institut für Kolloid- und Grenzflächenforschung Abteilung Kolloidchemie Wissenschaftspark Potsdam-Golm D-14424 Potsdam Tel: +49-(0)331-567-9511 Fax: +49-(0)331-567-9512 Room: K-2.114 klaus.tauer@mpikg-golm.mpg.de http://www.mpikg-golm.mpg.de/kolloidchemie/arbGruppen/Heterophasenpolymerisation/MitarbeiterInnen/Dr__Klaus_Tauer/index.html
Prof. Dr. A. van Blaaderen Debye Institute for NanoMaterials Science Utrecht University, Ornstein Lab. (062) Princeton Plein 5 3584 CC Utrecht THE NETHERLANDS Tel: +31-30-2532204 / 2952 Fax: +31-30-2532706 A.vanBlaaderen@uu.nl http://www.debye.uu.nl/	**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 tgtkah@chem.tue.nl http://w3.chem.tue.nl/nl/people_pages/?script=showemp.php&pid=372

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 http://www.che.udel.edu/directory/facultyprofile.html?id=452
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 http://www.chem.utoronto.ca/staff/MAW/group.html
Prof. Alexander Zaichenko Department of Pharmacia and Biotechnology Department of Organic Chemistry Lviv Polytechnic National University 12 S. Bandera St. Lviv 79013 UKRAINE Tel: +38 032 2582390 Fax: +38 032 2375089 zaichenk@polynet.lviv.ua alzaich@i.ua	**Prof. Dr. P.B. Zetterlund** The University of New South Wales Sydney AUSTRALIA Tel: +61 2 9385 4331 Fax: +61 2 9385 6250 pbzetterlund@hotmail.com p.zetterlund@unsw.edu.au http://www.camd.unsw.edu.au/index.php?option=com_content&view=article&id=128&Itemid=58

MEMBER CONTRIBUTIONS

Contribution to the IPCG newsletter (October 2010)

Jacqueline Forcada

The University of the Basque Country/EHU

Accepted papers:

Cationic Polymer Nanoparticles and Nanogels: From Synthesis to Biomedical Applications

Jose Ramos, Ainara Imaz, Jacqueline Forcada, and Roque Hidalgo-Álvarez

CHEMICAL REVIEWS

Proposal ID: cr-2010-00021a: ACCEPTED

ABSTRACT: In this review, syntheses of cationic polymer nanoparticles and nanogels by emulsion polymerization will be updated. An in-deep study on the kinetics of the cationic systems will be detailed and compared to that of the well-known anionic systems. Then, polymeric and colloidal features of the cationic nanoparticles/nanogels will be revised, and finally biomedical applications of cationic nanoparticles/nanogels will be described in detail.

Recently published papers:

Use of Hydrophobically Modified Inulin for the Preparation of Polymethyl Methacrylate/Polybutyl Acrylate Latex Particles Using a Semicontinuous Reactor

Marc Obiols-Rabasa, Jose Ramos, Jacqueline Forcada, Jordi Esquena, Conxita Solans, Bart Levecke, Karl Booten, and Tharwat F. Tadros

LANGMUIR 26(11), 7717-7724 (2010)

ABSTRACT: The seeded semicontinuous emulsion copolymerization of methyl methacrylate (MMA) and butyl acrylate (BuA) stabilized with a graft polymeric surfactant based on inulin, INUTEC SP1, as well as its mixture with sodium lauryl sulfate (SLS) is described. The mixture of SLS and Brij58 (alcohol ethoxylated) and the mixture of SLS and Pluronic P85 (block copolymer PEO-PPO-PEO) are also used as surfactant systems. The addition of methacrylic acid (MAA) or acrylic acid (AA) as comonomers is also studied. Previous results proved this inulin-derivative surfactant, INUTEC SP1, to be very effective on synthesizing latexes using a very low surfactant concentration. The kinetic features of the emulsion polymerization (instantaneous conversion and total conversion) were gravimetrically determined along the reactions. Latex dispersions were characterized by photon correlation spectroscopy (PCS) and transmission electron microscopy (TEM) to obtain the average particle size, the particle size distributions (PSDs) as well as the polydispersity index (PdI). The stability was determined by turbidimetry measurements and expressed in terms of critical coagulation concentration. The results showed that the use of the graft polymeric surfactant allowed obtaining highly stable nanoparticles, at low surfactant concentrations and high solid contents (up to 37 wt %). This is an improvement with respect to previous works, in which a mixture of the graft polymeric surfactant with another surfactant was required to obtain stable nanoparticles with low polydispersity, at high solid content. In the present work, low polydispersity was achieved using INUTEC as the only emulsifier, which was related to the absence of secondary nucleations. When a mixture of INUTEC SP1 and SLS is used, a wider PSD is obtained due to secondary nucleations. Replacing INUTEC SP1 by other nonionic surfactants such as Brij58 or Pluronic P85 leads to an increase of average particle size and wider PSD.

The Role of Cationic Monomers in Emulsion Polymerization
Jose Ramos and Jacqueline Forcada
EUROPEAN POLYMER JOURNAL 46(5), 1106-1110 (2010)

ABSTRACT: [2-(methacryloyloxy)ethyl] trimethylammonium chloride (MATMAC), and vinylbenzyl trimethyl ammonium chloride (VBTMAC) were chosen to be used as ionic comonomers in the emulsion polymerization of styrene. The cationic nature of the two comonomers is the same (quaternary ammonium salts), however the styrene derivate (VBTMAC) is more hydrophobic than the methacrylic one (MATMAC). With the more hydrophobic cationic comonomer (VBTMAC) higher conversions were obtained due to the in situ creation of an amphiphilic copolymer with styrene and faster rates of polymerization were observed by increasing the cationic comonomer concentration. The same behavior was observed with the more hydrophilic cationic comonomer (MATMAC) at concentrations up to 0.012 M. At higher concentrations the ionic strength controls the colloidal stability of the system and coagulation occurs.

Small-Amplitude Oscillatory Shear Magnetorheology of Inverse Ferrofluids
Jose Ramos, Juan de Vicente, and Roque Hidalgo-Álvarez
LANGMUIR 26(12), 9334-9341 (2010)

ABSTRACT: A comprehensive investigation is performed on highly monodisperse silica-based inverse ferrofluids under small-amplitude oscillatory shear in the presence of external magnetic fields up to 1 Tesla. The effect of particle volume fraction and continuous medium Newtonian viscosity is thoroughly investigated. Experimental results for storage modulus are used to validate existing micromechanical magneto-rheological models assuming different particle-level field-induced structures.

Preparation of Carboxylic Magnetic Polymeric Composite Particles by Miniemulsion Polymerization in the Absence of Hydrophobe
Shulai Lu, Rongjun Qu, and Jacqueline Forcada
MATERIALS LETTERS 63, 2539-2541 (2009)

ABSTRACT: Carboxylic magnetic polymeric composite particles (C-MPCPs) were prepared by miniemulsion polymerizationin the absence of hydrophobe using styrene (St) as monomer, methacrylic acid (MAA) as comonomer, sodium dodecyl sulfate (SDS) as emulsifier, and azodiisobutyronitrile (AIBN) as initiator in the presence ofhydrophobic magnetite particles. For comparison, non-carboxylic magnetic polymeric composite particles (N-MPCPs) were also prepared under the same conditions as C-MPCPs but without MAA as comonomer. Microscopic morphology of resulting C-MPCPs and N-MPCPs was observed by Transmission Electron Microscopy (TEM). Magnetic properties of C-MPCPs in dry condition were investigated by vibrating sample magnetometer (VSM). The results showed that the encapsulation of magnetite to prepare C-MPCPs by miniemulsion in the absence of hydrophobe was successful but not totally successful in the preparation of NMPCPs, and the resultant C-MPCPs exhibited a broad practical size distribution, superparamagnetism and a certain level of magnetic response. The mechanism of miniemulsion polymerization to encapsulate magnetite particles successfully in the absence of hydrophobes was hypothesized that the hydrophobic magnetite particles could act as a hydrophobe and MAA could enhance the hydrophobicity of magnetite particles by ensuring oleic acid adsorption on magnetite particles' surface in acid form instead of salt form.

Book chapters:

Encapsulation of Inorganic Nanoparticles by Miniemulsion Polymerization
Jacqueline Forcada and Jose Ramos
in MINIEMULSION POLYMERIZATION: RECENT ADVANCES. Vikas Mittal Ed. Scrivener Publishing, USA, 2010, Chapter nº 4, Pages: 71-96. **ISBN: 978-470-62596-5**

ABSTRACT: Miniemulsion polymerization is a powerful approach to encapsulate inorganic nanoparticles into a polymer shell. However, prior to carry out the miniemulsion process, the surface of inorganic nanoparticles must be made more hydrophobic with surface modifiers or coupling agents. The type of surface modifier used depends strongly on the type of inorganic nanoparticle to encapsulate. Special attention will be paid to the encapsulation of silica and magnetite nanoparticles by miniemulsion polymerization using different surface modifiers. The use of the right combination of surface modifiers together with the adequate miniemulsion process (single or double) are the key factors to obtain a high encapsulation degree of inorganic nanoparticles with a well-controlled morphology of the hybrid nanocolloids.

Patents:

*Spanish Patent Application:
Inventors: Jacqueline Forcada, Ainara Imaz, Andoni San Martín, J.P.A. Heuts, A.M. van Herk, Jose Ramos
NANOGELES CATIÓNICOS Y SUS APLICACIONES BIOTECNOLÓGICAS
Patentability positive report: P5462ES00
Application Number: **P201030399**
Priority Country: Spain
Priority Date: 2010-03-18

* US Patent Application:
Inventors: Ainara Imaz, Jose Ramos, Jacqueline Forcada
BIOCOMPATIBLE MICROGELS AND APPLICATIONS THEREOF
Application Number: **US 12/601,618**
Priority Country: USA
Priority Date: 2007-05-25
Publication Number: **US 2010/0172990 A1**
Publication Date: Jul. 8, 2010

Contributions to the Second International Soft Matter Conference 2010
Granada, 5-8 July 2010

Temperature and pH effects on the average hydrodynamic diameters and electrophoretic mobilities of acrylic acid containing Poly(N-vinylcaprolactam)-based nanogels
Ainara Imaz and Jacqueline Forcada

Synthesis of Well-Defined Hybrid Nanogels
Jose Ramos, Ainara Imaz, Jacqueline Forcada, and Roque Hidalgo-Álvarez

Unexpected temperature-response of Poly(N-vinylcaprolactam)-based cationic nanogels
Andoni San Martín, Ainara Imaz, and Jacqueline Forcada

The relationship between reinforcement and chain/filler structure in silica-latex model nanocomposites
Mouna Tatou, Isabelle Grillo, Ralf Schweins, Ainara Imaz, Anne Caroline Genix, and Julian Oberdisse

Small-amplitude oscillatory shear magnetorheology of inverse ferrofluids
Jose Ramos, Juan de Vicente, and Roque Hidalgo-Álvarez

Nanoparticle deposits formed at driven contact lines
Carmen Lucía Moraila-Martínez, Jose Ramos, Miguel Cabrerizo-Vílchez, and Miguel Ángel Rodríguez-Valverde

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

For abstracts see our website: www.mcii.de

1. W. Zhang, A. H. E. Müller
   Synthesis of Tadpole-shaped POSS-containing Hybrid Polymers via "Click Chemistry"
   Polymer **51**, 2133 (2010), DOI: 10.1016/j.polymer.2010.03.028
2. A. S. Goldmann, C. Schödel, A. Walther, J. Yuan, K. Loos A. H. E. Müller
   Biomimetic Mussel Adhesive Inspired Clickable Anchors Applied to the Functionalization of Fe_3O_4 Nanoparticles (Cover Article)
   Macromol. Rapid Commun. **31**, 1608 (2010), DOI: 10.1002/marc.201000193
3. Y. Xu, A. Walther, A. H. E. Müller
   Direct Synthesis of Poly(potassium 3-sulfopropyl methacrylate) Cylindrical Polymer Brushes via ATRP Using a Supramolecular Complex with Crown Ether
   Macromol. Rapid Commun. **31** (2010) published online on July 14, 2010, DOI: 10.1002/marc.201000157
4. A. Walther, C. Barner-Kowollik, A. H. E. Müller
   Mixed, multicompartment or Janus micelles? A systematic study of thermo-responsive bis-hydrophilic block terpolymers
   Langmuir **26,** 12237 (2010), DOI: 10.1021/la101173b
5. J. Yuan, A- H. E. Müller
   One-Dimensional Organic-Inorganic Hybrid Nanomaterials (Feature Article)
   Polymer **51**, 4015 (2010). DOI: 10.1016/j.polymer.2010.06.064
6. J. Yuan, A. Walther, A, H. E. Müller
   Template-directed Synthesis of Hybrid Nanowires and Nanorods
   Phys. Stat. Sol. B, published online on August 16, 2010, DOI: 10.1002/pssb.201046176
7. P.-E. Millard, L. Barner, J. Reinhardt, M. H. Stenzel, M. R. Buchmeiser, C. Barner-Kowollik, A. H. E. Müller
   Synthesis of Water-Soluble Polymers by RAFT Polymerization under γ-Irradiation in Aqueous Media
   Polymer **51**, 4319 (2010), DOI: 10.1016/j.polymer.2010.07.017
8. M. Junginger, K. Kita-Tokarczyk, Th. Schuster, J. Reiche, F. Schacher, A. H.E. Müller, A. Taubert
   Calcium phosphate mineralization beneath a polycationic monolayer at the air-water interface
   Macromol. Biosci. in press
9. M. Junginger, K. Bleek, K. Kita-Tokarczyk, J. Reiche, A. Shkilnyy, F. Schacher, A.H.E. Müller, A Taubert
   Calcium phosphate growth beneath a polycationic monolayer at the air-water interface: effects of oscillating surface pressure on mineralization
   Nanoscale in press

10. Y. Xu, J. Yuan, B. Fang, M. Drechsler, M. Müllner, S. Bolisetty, M. Ballauff, A. H. E. Müller
Hybrids of magnetic nanoparticles with double-hydrophilic core-shell cylindrical polymer brushes and their alignment in a magnetic field
Adv. Funct. Mater., published online on September 7, 2010, DOI: 10.1002/adfm201000769
11. A. Pfaff, A. H. E. Müller, A. M. Granville
Surface Modification of Polymeric Microspheres using Glycopolymers for Biorecognition
Eur. Polym. J., accepted
12. D. V. Pergushov, O. V. Borisov, A. B. Zezin, A. H. E. Müller
Interpolyelectrolyte complexes based on polyionic species of branched topology
Adv. Polym. Sci. in press
13. M. Ballauff, A. H. E. Müller, F. A. M. Leermakers, O. V. Borisov
Conformations and counterion localization in solutions of star-like polyelectrolytes
Adv. Polym. Sci., in press
14. J. Yuan, A. H. E. Müller
Cylindrical polymer brushes
in: " *Synthesis of Polymers*", A.D. Schlüter, C.J. Hawker, M. Sawamoto, Eds., Wiley-VCH, Weinheim, in press

In revision

15. A. Pfaff, V.S. Shinde, Y. Lu, A. Wittemann, M. Ballauff, A. H. E. Müller
Glycopolymer Grafted Polystyrene Nanospheres
Macromol. Biosci. in revision
16. M. Müllner, J. Yuan, S. Weiss, A. Walther, M. Förtsch, M. Drechsler, A. H. E. Müller
Water-Soluble Organo-Silica Hybrid Nanotubes Templated by Cylindrical Polymer Brushes
J. Am. Chem. Soc. in revision

submitted

17. J. Yuan, Y. Xu, A. H. E. Müller
One-dimensional Magnetic Inorganic-Organic Hybrid Nanomaterials
submitted to *Chem. Soc. Rev*.
18. F. Schacher, T. Rudolph, M. Drechsler, A. H. E. Müller
Core-Crosslinked Compartmentalized Cylinders
submitted to *Nanoscale*

Konig, A. M.; Johannsmann, D., Stress Fluctuations in Drying Polymer Dispersions. *Langmuir* **2010***,* 26, (12), 9437-9441.
Drying polymer dispersions usually experience tensile stress, induced by the reduction in volume and by the rigid substrate. Due to edge-in drying, the stress is usually heterogeneous over the film. Stress peaks play a decisive role in the formation of cracks. This work relies on membrane bending, a technique that provides spatially resolved stress maps. In the experiments reported here, stress fluctuations on the order of 10% on the time scale of a few seconds were found. The stress fluctuations occur coherently over the entire drying front. Fluctuations go back to slight fluctuations in humidity of the environment (as opposed to local stress relaxations due to reorganizations of the particle network). The stress fluctuations disappear when covering the sample with a lid. They can be enhanced by blowing humid or dry air across the sample surface. Modeling builds on the assumption that all stresses go back to capillary pressure created at the menisci in between different spheres at the film air interface. The local radius of curvature changes in response to slight variations in ambient humidity according to the Kelvin equation. The fluctuations are observed under a wide variety of drying conditions and should be included in film formation models.

Nikiforow, I.; Adams, J.; Konig, A. M.; Langhoff, A.; Pohl, K.; Turshatov, A.; Johannsmann, D., Selfstratification during film formation from latex blends driven by differences in collective diffusivity. *Langmuir* **2010***,* 26, (16), 13162-7.
Coatings with vertical gradients in composition were produced by drying an aqueous polymer dispersion containing both charged and neutral particles. After drying, the neutral component was enriched at the film/air interface. The spontaneous vertical segregation between the two types of particles goes back to a difference in collective diffusivity. As the film dries, a layer enriched in polymer develops at the top. Due to their mutual repulsion, charged spheres escape from this layer more quickly than their neutral counterparts. Provided that the total time of drying is between the times of diffusion for the two types of particles (similar to H-0(2)/D-c with H-0 the initial film thickness and De the collective diffusivity of the respective species), a concentration gradient persists after the film has turned dry. This effect can be used to create a functionally graded material (FGM) in a single coating step.

Konig, A. M.; Bourgeat-Lami, E.; Mellon, V.; von der Ehe, K.; Routh, A. F.; Johannsmann, D., Dilational Lateral Stress in Drying Latex Films. *Langmuir* **2010,** 26, (6), 3815-3820.
Drying latex films usually experience tensile stress due to the reduction in volume. While an unconstrained film would shrink affinely in all three dimensions, it coating can only shrink along the vertical and therefore exerts tensile stress onto the substrate. Using an instrument capable of producing maps of the stress distribution, we found that dilational stress sometimes develops as well. The inplane stress was monitored by spreading the latex dispersion oil a flexible membrane. Usually, the membrane bends upward under the tensile stress exerted by the film, but it may also bend downward. Dilational stress was only found with samples showing a strong coffee stain effect, that is, samples in which there is a significant lateral flow from the center to the edge while the film dries. During drying, particles consolidate first at the edge because of the lower height in this region. Continued evaporation from the consolidated region results in it water flow toward the edge, exerting it force onto the latex particles. At the time, when the network is formed, any single sphere must be in it force-balance condition: the network must exert an elastic force onto the sphere which just compensates the viscous drag, Pictorially speaking, a spring (all elastic network) is created while an external force acts onto it. Once the flow stops, the drag force vanishes and the internal stress, which previously compensated the drag, expands the film laterally. This phenomenon can lead to buckling. Given that lateral now of liquid while films dry is a rather common Occurrence, this mode of structure formation should be widespread. It requires lateral flow in conjunction with elastic recovery of the particle network.

LCPP

Laboratoire de Chimie, Catalyse, Polymères et Procédés

Equipe Chimie et Procédés de Polymérisation
(LCPP-CNRS) Lyon-France. www.lcpp-cpe.com

Contribution to IPCG Newsletter

Submitted by :	B. Charleux	charleux@lcpp.cpe.fr
	E. Bourgeat-Lami	bourgeat@lcpp.cpe.fr
	F. D'Agosto	dagosto@lcpp.cpe.fr
	M. Lansalot	lansalot@lcpp.cpe.fr

1. Recently published papers. * Corresponding author

- *Macromolecular Rapid Communications* DOI: 10/1002/marc.201000305 **(2010)**

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

E. Bourgeat-Lami,[1]* T. Rodrigues Guimarães,[2] A. M. Cenacchi Pereira,[1,2] G. Maria Alves,[2] J. C. Moreira,[2] J-L. Putaux,[3] A. Martins dos Santos[2]*

[1]Université de Lyon, Université Lyon 1, CPE Lyon, CNRS, UMR 5265, Laboratoire de Chimie, Catalyse, Polymères et Procédés (C2P2), LCPP group, 43, Bd. du 11 Novembre 1918, F-69616 Villeurbanne, France. [2]Laboratory of Polymer, Department of Chemical Engineering, Lorena Engineering School, University of São Paulo, Estrada Municipal do Campinho, S/N, 12.602.810, Lorena (SP), Brazil. [3]Centre de Recherches sur les Macromolécules Végétales (CERMAV-CNRS), BP 53, F-38041 Grenoble Cedex 9, France - affiliated with Université Joseph Fourier and member of the Institut de Chimie Moléculaire de Grenoble.

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

- *Polymer* DOI: 10/1016/j.polymer.2010.07.028 **(2010)**

Polymer/clay nanocomposites: impact of *in-situ* polymerization processes on the interphase characteristics

Jenny Faucheu[1], Catherine Gauthier[1*], Laurent Chazeau[1], Jean-Yves Cavaillé[1], Véronique Mellon[2], Elodie Bourgeat Lami[2]

[1]MATEIS, INSA-LYON, 7 avenue Jean Capelle 69621 Villeurbanne Cedex, France. [2]Université de Lyon, Univ. Lyon 1, CPE Lyon, CNRS UMR 5265, Laboratoire de Chimie, Catalyse, Polymères et Procédés (C2P2), LCPP group, 43 Boulevard du 11 Novembre 1918, F-69616, Villeurbanne, France

> This article refers to the side-effects of *in-situ* polymerization in the presence of modified clays. The clay modifications intend to render the clay surface compatible with the monomer-polymer and/or reactive during polymerization. Samples issued from two *in-situ* polymerization mechanisms have been compared to simple blends of latex/unmodified clays in terms of shifts in relaxation temperature (assessed by Dynamic Mechanical Analysis) and shifts in monomer ratio in the copolymer (assessed by Nuclear Magnetic Resonance analysis).

- *Adv. Polym. Sci.* (A. Van Herk & K. Landfester Eds) DOI: 10.1007/12_2010_60 **(2010)**

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

E. Bourgeat-Lami*, M. Lansalot*

Université de Lyon, Univ. Lyon 1, CPE Lyon, CNRS UMR5265, Laboratoire de Chimie, Catalyse, Polymères et Procédés (C2P2), LCPP group, 43 Bd du 11 Novembre 1918, F-69616, Villeurbanne, France.

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

- *Polymer* DOI: 10.1016/j.polymer.2010.08.035 **(2010)**

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

H. Sardon[1,2], L. Irusta[1], M.J. Fernández-Berridi[1*], M. Lansalot[2], E. Bourgeat-Lami[2]

[1]Departamento de Ciencia y Tecnología de Polímeros e Instituto de Materiales Poliméricos (POLYMAT), Facultad de Química UPV/EHU P.O.Box 1072 20018-Donostia. [2]Université de Lyon, Univ. Lyon 1, CPE Lyon, CNRS UMR 5265, Laboratoire de Chimie, Catalyse, Polymères et Procédés (C2P2), LCPP team, 43 Bd du 11 Novembre 1918, F-69616, Villeurbanne, France

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

- *Polymer Chemistry* DOI:10.1039/C0PY00237B **(2010)**

Controlled radical polymerization of styrene in miniemulsion mediated by PEO-based trithiocarbonate macromolecular RAFT agents
T. Boursier,[a] I. Chaduc,[a] J. Rieger,[b] F. D'Agosto,[a]* M. Lansalot,[a]* B. Charleux[a]

[a] Université de Lyon, Univ. Lyon 1, CPE Lyon, CNRS UMR 5265, Laboratoire de Chimie Catalyse Polymères et Procédés (C2P2), Equipe LCPP Bat 308F, 43 Bd du 11 novembre 1918, F-69616 Villeurbanne, France [b] UPMC Univ. Paris 6 and CNRS, Laboratoire de Chimie des Polymères, UMR 7610, 4 place Jussieu, Tour 44-54, 75252 Paris Cedex 05, France

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

- *In "Polymer Nanocomposites par Emulsion and Suspension"* V. Mittal (Ed), The Royal Society of Chemistry, UK, Chap. 13. pp. 269-311 **(2010)**

Polymer/clay nanocomposite particles and soap-free latexes stabilized by clay platelets: state of the art and recent advances
E. Bourgeat-Lami,[1]* N. Sheibat-Othman,[2] A. Martins dos Santos[3]

[1]Université de Lyon, Université Lyon 1, CPE Lyon, CNRS, UMR 5265, Laboratoire de Chimie, Catalyse, Polymères et Procédés (C2P2), LCPP group, 43, Bd. du 11 Novembre 1918, F-

69616 Villeurbanne, France. [2]Université de Lyon, Univ. Lyon 1, CNRS, CPE Lyon, UMR 5007, Laboratoire d'Automatique et de Génie des Procédés (LAGEP), 43 Bd du 11 Novembre 1918, F-69622 Villeurbanne, France. [3]Laboratory of Polymer, Department of Chemical Engineering, Lorena Engineering School, University of São Paulo, Estrada Municipal do Campinho, S/N, 12.602.810, Lorena (SP), Brazil.

Recent advances in synthesis of polymer/clay nanocomposites by heterophase polymerisation in aqueous dispersed media are briefly reviewed in this chapter. Particular emphasis is given to emulsion polymerisation and to the ability to produce polymer/clay nanocomposites with controlled nanostructures. A focus is also given on the influence of these nanostructures on the final properties of the composite materials. Besides conventional emulsion polymerisation, increasing interest into the synthesis of clay-armoured latexes produced in the absence of surfactant has emerged in the recent literature. This review highlights recent developments in this area which have contributed to a deeper understanding of the mechanism of particle formation. Important breakthroughs including the production of high solids content latexes and latex films with enhanced mechanical properties are reported and discussed. Finally, process features and modelling are introduced to show their interest in the comprehension of the reaction mechanisms and the optimisation of the operating conditions.

- *Langmuir* **26**, 3815-3820 (2010)

Dilational lateral stress in drying latex films

A. M. Konig,[1] E. Bourgeat-Lami,[2] V. Mellon, [2] K. Von Der Ehe,[1] A. F. Routh,[3] D. Johannsmann[1*]

[1]Institute of Physical Chemistry, Clausthal University of Technology, Arnold-Sommerfeld-Str. 4, D-38678 Clausthal-Zellerfeld, Germany. [2]Université de Lyon, Univ. Lyon 1, CPE Lyon, CNRS UMR 5265, Laboratoire de Chimie, Catalyse, Polymères et Procédés (C2P2), LCPP group, 43 Bd du 11 Novembre 1918, F-69616, Villeurbanne, France. [3]Department of Chemical Engineering and Biotechnology, University of Cambridge, Pembroke Street, Cambridge, UK, CB2 3RA

Drying latex films usually experience tensile stress, induced by the fact that the reduction in volume is constrained to a uniaxial shrinkage by the rigid substrate. Tensile stress entails the danger of cracking, which is one of the classical failure scenarios of the film formation process. We report on a related defect pattern, where unrelaxed stress causes wrinkles, rather than cracks. The stress in these cases is dilational, not tensile. The in-plane stress was monitored by spreading a drop of the latex dispersion on a flexible membrane. Usually, the membrane bends upward, but it may also bend downward in special cases. Photon correlation spectroscopy on such drying films revealed that the time when dilational stress was observed coincided with the time when Brownian motion arrested, that is, when the sample first formed an elastically coupled network. Dilational stress is mostly found with materials containing rigid inorganic components. We explain the phenomenon in the frame of the coffee stain effect. Since evaporation is fastest at the edge of the drop, water moves towards the rim, exerting a force onto the latex particles. At the time, when the network is formed, the spheres must be in a force-balance condition: the network then exerts a (dilational) stress, compensating the viscous drag. Once the flow stops, the network is out of balance and warping results. This phenomenon leads to an uneven film surface. Given that lateral flow of liquid while it dries is rather common, this mode of structure formation should be widespread.

- *Actualité Chimique* **340,** 14-17, Avril 2010

Les particules mettent les formes. Quand le Dieu romain Janus inspire les scientifiques
A. Perro[1], S. Reculusa[1,2], E. Bourgeat-Lami[3], S. Ravaine[1], E. Duguet [2*]

[1]CNRS, Université de Bordeaux,CRPP, 33600 Pessac, France. [2]CNRS, Université de Bordeaux, ICMCB, 33608 Pessac Cedex, France. [3]Chimie Catalyse Polymères Procédés - UMR 5265 CNRS/CPE/UCBL, ESCPE, 69616 Villeurbanne Cedex, France

> Because the roman god Janus was usually represented with two heads placed back to back, the term Janus is used for the description of particles whose surfaces of both hemispheres are different from a chemical view point. Original properties and applications are expected. Moreover, they could be used as building blocks for supraparticular assemblies. This review deals with the great and imaginative efforts which were devoted to the synthesis of Janus particles.

- *Actualité Chimique* **340,** 18-21, Avril 2010

Les particules mettent les formes. Des atomes aux molécules colloïdales
A. Perro[1], D. NGuyen[2], E. Bourgeat-Lami[3], S. Ravaine[1], E. Duguet [2*]

[1]CNRS, Université de Bordeaux,CRPP, 33600 Pessac, France. [2]CNRS, Université de Bordeaux, ICMCB, 33608 Pessac Cedex, France. [3]Chimie Catalyse Polymères Procédés - UMR 5265 CNRS/CPE/UCBL, ESCPE, 69616 Villeurbanne Cedex, France

> The concept of colloidal molecules was first evoked by van Blaaderen in 2003 for describing small non-spherical colloids made of the aggregation of a small number of particles. He predicted original morphologies to the complex assembly of such colloids, in particular optics. This paper deals with the first successful elaboration routes of such new building bricks.

- *Adv. Polym. Sci.* (A. Van Herk and K. Landfester Editors)

Preparation of Hybrid Latex Particles and Core-Shell Particles Through the Use of Controlled Radical Polymerization Techniques in Aqueous Media.
B. Charleux,[1*] F. D'Agosto,[1] G. Delaittre[2]

[1] Université de Lyon, Univ. Lyon 1, CPE Lyon, CNRS UMR5265, Laboratoire de Chimie, Catalyse, Polymères et Procédés (C2P2), LCPP group, 43 Bd du 11 Novembre 1918, F-69616, Villeurbanne, France. [2] Institute for Molecules and Materials, Radboud University Nijmegen, Heyendaalseweg 135, 6525ED Nijmegen, The Netherlands

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

- *Chem. Commun* **46**, 1950-1952 (2010)

Amphiphilic Block Copolymer Nano-fibers via RAFT-Mediated Polymerization in Aqueous Dispersed System

Stéphanie Boissé,[a,b] Jutta Rieger,*[a] Khaled Belal,[a] Aurélie Di-Cicco,[b] Patricia Beaunier,[c]
Min-Hui Li[b] and Bernadette Charleux*[a,d]

[a] UPMC Univ. Paris 6 and CNRS, Laboratoire de Chimie des Polymères, UMR 7610, 4 place Jussieu, Tour 44-54, 75252 Paris cedex 05, France. Fax : 33 1 44277089, Tel: 33 1 44275137; E-mail: jutta.rieger@upmc.fr. [b] Institut Curie, CNRS, UPMC, Laboratoire Physico-Chimie Curie,UMR 168, 26 rue d'Ulm, 75248 Paris cedex 05, France. [c]UPMC Univ. Paris 6 and CNRS, Laboratoire de Réactivité de Surface, UMR 7197, 4 place Jussieu, 75252 Paris cedex 05, France. [d] Université de Lyon, Univ. Lyon 1, CPE Lyon, CNRS UMR 5265, C2P2, Team LCPP Bat 308F, 43 Bd du 11 novembre 1918, 69616 Villeurbanne, France; E-mail : bernadette.charleux@lcpp.cpe.fr

Self-assembled polymeric nanofibers are attractive materials for multiple applications. We propose here a novel, very simple and straightforward method to prepare polymeric nanofibers at high solids contents directly in water. It is based on an aqueous emulsion polymerization process performed under living radical polymerization conditions, using the RAFT method.

- *Polymer Chemistry* **1**, 720-729 (2010)

Nitroxide-mediated copolymerization of methacrylic acid with sodium 4-styrene sulfonate: Toward new water-soluble macroalkoxyamines for the synthesis of amphiphilic block copolymers and nanoparticles.

Ségolène Brusseau,[1] Joël Belleney,[1] Stéphanie Magnet,[2] Laurence Couvreur,[3] Bernadette Charleux* [1,4]

[1]UPMC Univ. Paris 6, CNRS, UMR 7610, Laboratoire de Chimie des Polymères, 4 place Jussieu, 75252 Paris cedex 05, France. [2]ARKEMA, Groupement de Recherches de Lacq, RN 117, B.P. n°34, 64170, Lacq, France. [3]ARKEMA, 420, rue d'Estienne d'Orves, 92705, Colombes, France. [4]Université de Lyon, Univ. Lyon 1, CPE Lyon, CNRS UMR 5265, Laboratoire de Chimie Catalyse Polymères et Procédés (C2P2), Equipe LCPP Bat 308F, 43 Bd du 11 novembre 1918, 69616 Villeurbanne, France.

The SG1-mediated copolymerization of methacrylic acid (MAA) and 4-styrene sulfonate (SS) was studied in dimethylsulfoxide solution at 76 °C, first, to determine the reactivity ratios in such conditions and second, to check the living character of the reaction at low molar fraction of SS. The reactivity ratios in the terminal model were rMAA = 0.44 and rSS = 1.34 indicating a favored incorporation of SS at the beginning of the copolymerization. All characteristics of a controlled/living system were observed, in good agreement with an efficient deactivation of the propagating radicals by the nitroxide SG1, most probably via formation of an SS terminal subunit-based alkoxyamine. The method was shown to be particularly well-suited for the design of living polymers intended to be used as hydrophilic macroinitiators for the synthesis of amphiphilic block copolymers. This was demonstrated in both solution polymerization and ab initio, batch emulsion polymerization. The latter process allowed well-defined block copolymer nanoparticles to be formed at low temperature, in a single step, by simultaneous chain growth and self-assembling.

- *Journal of Polymer Science. Part A. Polymer Chemistry* **48**, 2329-2339 (2010)

New ethyl cellulose/acrylic hybrid latexes and coatings via miniemulsion polymerization

R. Chen,[1, 2] F. Chu,[2] C. Gauthier, [3] L. Chazeau,[3] I. Chaduc,[1] E. Bourgeat-Lami,[1*] M. Lansalot[1*]

[1] *Université de Lyon, Univ. Lyon 1, CPE Lyon, CNRS UMR 5265, Laboratoire de Chimie, Catalyse, Polymères et Procédés (C2P2), LCPP group, 43 Bd. du 11 Novembre 1918, F-69616, Villeurbanne, France.*[2] *Institute of Chemical Industry of Forest Products, Chinese Academy of Forestry, 16 Suo Jin Wucun, 210042 Nanjing, China.* [3] *MATEIS, INSA-Lyon, 7 avenue Jean Capelle 69621 Villeurbanne Cedex, France*

Ethyl cellulose (EC) was incorporated into copolymer latexes via miniemulsion polymerization. The effects of EC viscosity and EC content on droplet size, particle size and polymerization kinetics were investigated. The higher the EC content and viscosity, the larger the droplet size and the less stable the latex suspension. Small droplets that could be efficiently nucleated were formed for the lower-viscosity EC but the latex still showed limited colloidal stability. This was attributed to some phase-incompatibility between EC and the acrylic polymer. These stability issues were overcome by using an oil-soluble initiator and a cross-linker. The later enabled to physically entrap EC inside the polymer particles while the former allowed *in situ* grafting of the growing acrylic radicals to the EC backbone decreasing thereby the extent of phase separation. Thermal-mechanical analyses evidenced that the films obtained from the hybrid latexes displayed better properties than the EC-free latex films or the physical blends. This supports the hypothesis of formation of hybrid latexes that synergistically combine the properties of the acrylic matrix and the EC polymer. Interestingly, a significant increase of the elastic modulus was observed between 50-90°C. This mechanical reinforcement was tentatively attributed to the formation of a percolating EC-based hybrid phase.

- *Chemistry of Materials* **22**, 2822-2828 (2010)

Latex-templated silica films: tailoring the pore structure to get highly stable dielectric properties

F. Guillemot[1,2], T. Gacoin[1], J.-P. Boilot[1*], E. Barthel[2], A. Brunet-Bruneau[3], E. Bourgeat-Lami[4]

[1]*Groupe de Chimie du Solide, Laboratoire de Physique de la Matière Condensée, UMR CNRS 7643, Ecole Polytechnique, 91128 Palaiseau, France.* [2] *Surface du Verre et Interfaces (CNRS/Saint-Gobain) UMR 125, 39 quai Lucien Lefranc, F-93303, Aubervilliers, France,* [3] *Institut des Nanosciences de Paris, UMR 7601, Université Paris 6, Campus Boucicaut, 140 rue de Lourmel, case 80, 75015 Paris, France, and* [4]*Laboratoire de Chimie, Catalyse, Polymères et Procédés (C2P2), UMR 5265 Univ. Lyon 1, CPE Lyon, CNRS, Bâtiment 308 F, 43 boulevard du 11 novembre 1918, BP 2077, 69616 Villeurbanne Cedex, France*

Porous sol-gel silica films have been prepared using different PMMA latex nanoparticles, 30-80 nm in diameter, as sacrificial templates. By changing the size and the content of the latex particles in the deposited silica sol, it was possible for the first time to tailor the pore structure of the sol-gel films (uniform pore size and porous fraction from 0.10 to 0.74) independently of their thickness. This is the consequence of the absence of a significant microporosity in the silica walls as shown by the equivalence between the measured porous fraction after calcination and the starting latex volume fraction. No capillary condensation occurred in these films before high partial pressure (above 0.9) leading to very stable dielectric properties, such as a low refractive index that could be tuned in a large range (from 1.15 to 1.40 at 600 nm) corresponding to k values ranging from 1.5 to 4.5. A porosity percolation transition with the opening of the pore interconnection was observed at a pore fraction threshold of about 0.40 for different sizes of the initial template. Below the threshold, the films showed a closed porosity structure with a low refractive index (up to 1.29 at 600 nm), which is promising for antireflective applications. These new sol-gel coatings appear very promising for applications in optics and microelectronics.

- *Langmuir* **26**, 6086-6090 (2010)

An easy way to control the morphology of colloidal polymer-oxide clusters through seeded dispersion polymerization

D. NGuyen[1,2], E. Duguet[2], E. Bourgeat-Lami[3], S. Ravaine[1*]

[1]CNRS, Université de Bordeaux,CRPP, 33600 Pessac, France. [2]CNRS, Université de Bordeaux, ICMCB, 33608 Pessac Cedex, France. [3]Chimie Catalyse Polymères Procédés - UMR 5265 CNRS/CPE/UCBL, ESCPE, 69616 Villeurbanne Cedex, France

> Biphasic colloidal particles were obtained by a dispersion polymerization of styrene in presence of silica seeds in a water/ethanol medium. By simply varying the water content, the morphology of the clusters can be modulated from core-shell to raspberry-like entities.

- *Macromolecular Symposia* **289**, 129-134 (2010)

Synthesis of polyacrylic/silica nanocomposite latexes using static mixer

G. Farzi[1], T. F.L. McKenna [1,2*], E. Bourgeat-Lami[1]

[1]CNRS-LCPP/ CPE-LYON, BP 2007, Université Claude Bernard Lyon 1, Villeurbanne, 69616, France. [2]Department of Chemical Engineering, Queen's University, Kingston, Ontario, Canada

> Static mixers (Sulzer Chemtech; SMX) were used to prepare silica/ MMA-co-BA miniemulsions that were polymerized to produce nanocomposite latexes. Acceptable conditions for the formulation of polymerizable nanodroplets were found. and subsequently used to produce silica/poly(MMA-co-BA) nanocomposites by introducing silica-loaded monomers and preparation of silica-loaded miniemulsions. The droplet size distribution of the resulting miniemulsions was narrow enough that it could be successfully polymerized. It was found that the droplet size depends on the silica content and increases with increasing the silica concentration. It was also shown that there is a relationship between the droplet size and the viscosity of the dispersed phase. The majority of droplets were nucleated upon polymerization when less than 15% silica was used. However, when the silica content exceeded 15%, the ratio of the number of particles in the final latex to the number of droplets (Np/Nd) increased to value much higher than 1 indicating the occurrence of homogeneous nucleation.

- *J. Am. Chem. Soc.* **132**, 10796–10801 (2010)

End-Functionalised Tetrathiafulvalene Poly(N-isopropylacrylamide): A New Class of Amphiphilic Polymer for the Creation of Multi-stimuli Responsive Micelles

Julien Bigot,† Bernadette Charleux, ‡ Graeme Cooke, §* François Delattre, David Fournier,† Joël Lyskawa,† Léna Sambe,† François Stoffelbach, Patrice Woisel†*

† Univ Lille Nord de France, F-59000 Lille, France USTL, Unité des Matériaux Et Transformations (UMET, UMR 8207), Team "Ingénierie des Systèmes Polymères" (ISP), 59650 Villeneuve d'Ascq Cedex, France. ‡ Université de Lyon, Univ. Lyon 1, CPE Lyon, CNRS UMR 5265, Laboratoire de Chimie Catalyse Polymères et Procédés (C2P2), Equipe LCPP Bat 308F, 43 Bd du11 novembre 1918, F-69616 Villeurbanne, France§ Glasgow Centre for Physical Organic Chemistry, WestCHEM, Department of Chemistry, Joseph Black Building, University of Glasgow, Glasgow, UK, G12 8QQ, UK. LSOE, EA2599 Université du Littoral Côte d'Opale, Avenue M.Schumann 59140 Dunkerque, France. UPMC-CNRS Univ. Paris 6, UMR 7610 Laboratoire de Chimie des Polymères, 4 Place Jussieu, Tour 44-54, 75252 Paris Cedex 05, France.

In this article we report the formation of micelles from a tetrathiafulvalene (TTF) end-functionalised poly(N-isopropylacrylamide) (poly(NIPAM)) derivative 1. We have determined the critical aggregation concentration (CAC) and average diameter of the micelles using fluorescence spectroscopy and dynamic light scattering experiments, respectively. We have exploited the NIPAM backbone of the polymer to thermally transform the swollen hydrophilic poly(NIPAM) derivative to a more globular hydrophobic state at the lower critical solution temperature (LCST). Finally, we have shown that we can exploit the chemical oxidation and complexation properties of the TTF unit to disrupt the micelle architecture to release the hydrophobic dye Nile Red from the hydrophobic interior of the micelle.

- *Macromolecules* **43**, 6302–6310 (2010)

Surfactant-free RAFT emulsion polymerization using poly(N,N-dimethylacrylamide) trithiocarbonate macromolecular chain transfer agents.
J. Rieger*, W. Zhang , F. Stoffelbach1, B. Charleux*

[1]UPMC Univ. Paris 6 and CNRS, Laboratoire de Chimie des Polymères, UMR 7610, 4 place Jussieu, Tour 44-54, 75252 Paris Cedex 05, France
[2]Université de Lyon, Univ. Lyon 1, CPE Lyon, CNRS UMR 5265, C2P2, Team LCPP Bat 308F, 43 Bd du 11 novembre 1918, 69616 Villeurbanne, France

Water-soluble poly(*N,N*-dimethylacrylamide)s (PDMAAm) with a reactive trithiocarbonate group exhibiting different structures were used as macromolecular RAFT (reversible addition-fragmentation chain transfer) agents in the surfactant-free emulsion polymerization of *n*-butyl acrylate and styrene, in *ab initio*, batch conditions. Independently of the structure of the RAFT group, the polymerizations were fast and controlled with molar masses that matched well the theoretical values and rather low polydispersity indexes. Monomer conversions close to 100% were reached and the polymerizations behaved as controlled systems, even when solids contents up to 40% were targeted. The system thus led to poly(*N,N*-dimethylacrylamide)-*b*-poly(*n*-butyl acrylate) and poly(*N,N*-dimethylacrylamide)-*b*-polystyrene amphiphilic diblock copolymers formed *in situ* and self-assembling upon chain extension. The stability of the aqueous dispersions, measured by the amount of coagulum formed, improved with increasing length of the stabilizing hydrophilic PDMAAm segments.

- *Polymer* DOI : 10.1016/j.polymer.2010.08.043

Incorporation of magnetic nanoparticles into lamellar polystyrene-b-poly(n-butyl methacrylate) diblock copolymer films: influence of the chain end-groups on nanostructuration
Siham Douadi-Masrouki [a, b, c], Bruno Frka-Petesic [a, b, c], Maud Save [d, e], Bernadette Charleux [d, e], Valérie Cabuil [a, b, c], Olivier Sandre[*a, b, c]

[a] UPMC Univ Paris 6, UMR 7195 Physicochimie des Electrolytes, Colloïdes et Sciences Analytiques – 4 place Jussieu, case 51 75005 Paris France
[b] Centre National de la Recherche Scientifique, UMR 7195 PECSA, 75005 Paris France
[c] ESPCI ParisTech, UMR 7195 PECSA, 75005 Paris France
[d] UPMC Univ Paris 6, UMR 7610 Laboratoire de Chimie des Polymères – 4 place Jussieu, case 185 75005 Paris France
[e] Centre National de la Recherche Scientifique, UMR 7610 LCP, 75005 Paris France

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

2. **Articles in press.** * Corresponding author

- *Journal of Materials Chemistry*

About the suitability of the seeded-dispersion polymerization technique for preparing micron-sized silica-polystyrene clusters
D. NGuyen[1], S. Ravaine[2], E. Bourgeat-Lami[3], E. Duguet [1*]

[1]CNRS Université de Bordeaux ICMCB, 33608 Pessac Cedex, France. [2]CNRS, Université de Bordeaux ,CRPP, 33600 Pessac, France. [3]Chimie Catalyse Polymères Procédés - UMR 5265 CNRS/CPE/UCBL, ESCPE, 69616 Villeurbanne Cedex, France.

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

- *The Canadian Journal of Chemical Engineering*

Miniemulsions using static mixers: Part 2. Co-emulsification and composite materials using SMX static mixers.
G. Farzi[1], T. F.L. McKenna [1,2*], E. Bourgeat-Lami[1]

[1]CNRS-LCPP/CPE-LYON, BP 2007, Université Claude Bernard Lyon 1, Villeurbanne, 69616, France. [2]Department of Chemical Engineering, Queen's University, Kingston, Ontario, Canada

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

- *Macromolecular Symposia*

Small strain mechanical properties of latex-based nanocomposite films
C. Plummer[1*], R. Ruggerone[1], N. Negrete-Herrera[2], E. Bourgeat-Lami[2], J-A. Manson[1]

[1]Laboratoire de Technologie des Composites et Polymères (LTC), Ecole Polytechnique Fédérale de Lausanne (EPFL), 1015 Lausanne, Switzerland. [2]Chimie, Catalyse, Polymère, Procédé, C2P2/LCPP, UMR 5265 CNRS/CPE/UCBL, Bât. 308F, BP 2077- 43, Bd. Du 11 Nov. 1918, 69616 Villeurbanne Cedex, France.

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

- *Journal of Applied Polymer Science*

Waterborne polyurethane dispersions obtained by the acetone process: A study of colloidal features.
H. Sardon[1,2], L. Irusta[1], M.J. Fernández-Berridi[1*], J. Luna[1], M. Lansalot[2], E. Bourgeat-Lami[2]

[1]Departamento de Ciencia y Tecnología de Polímeros e Instituto de Materiales Poliméricos (POLYMAT), Facultad de Química UPV/EHU P.O.Box 1072 20018-Donostia. [2]Université de Lyon, Univ. Lyon 1, CPE Lyon, CNRS UMR 5265, Laboratoire de Chimie, Catalyse, Polymères et Procédés (C2P2), LCPP team, 43 Bd du 11 Novembre 1918, F-69616, Villeurbanne, France

> Waterborne polyurethane dispersions were prepared from isophorone diisocyanate (IPDI), 2-bis(hydroxymethyl) propionic acid (DMPA), 1,4-butane diol (BD), poly(propylene glycol) (PPG) and triethylamine (TEA) by means of phase inversion through the acetone process. Changes in DMPA content, initial polyurethane content in acetone, phase inversion temperature, evaporation conditions and solvent nature were found to have a great impact on dispersion properties. Using a DMPA concentration of 0.30 mmol/gpol, stable polyurethane dispersions could only be obtained when the initial polyurethane content in acetone was at least 60 wt% and

phase inversion temperature was lower than 30ºC. However, when increasing the polyurethane content to 75 wt%, stable dispersions were obtained using DMPA concentrations three times lower. Finally, viscosity curves during the water addition step as well as a phase diagram were determined in order to understand the particle formation mechanism.

- *Macromolecules*

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

Jacques-Antoine Raust[1,*], Lisa Houillot[2], Maud Save,[2,3] Bernadette Charleux[2,4], Claudine Moire[5], Céline Farcet[5], Harald Pasch[6]

[1] *Deutsches Kunststoff-Institut (German Institute for Polymers), Schlossgartenstrasse 6, Darmstadt, Germany,*
[2] *UPMC Université Paris 6 and CNRS, UMR 7610, Laboratoire de Chimie des Polymères, 4 place Jussieu, 75252 Paris cedex 05, France*
[3] *IPREM Equipe Physique et Chimie des Polymères, UMR 5254, CNRS- Université de Pau et des Pays de l'Adour, Technopole Hélioparc, 2 Av Président Angot, 64053 PAU cedex 9, France.*
[4] *Université de Lyon, Univ. Lyon 1, CPE Lyon, CNRS UMR 5265, Laboratoire de Chimie Catalyse Polymères et Procédés (C2P2), Equipe LCPP Bat 308F, 43 Bd du 11 novembre 1918, F-69616 Villeurbanne, France.*
[5] *L'Oréal Recherche, 1 avenue Eugène Schueller, 93600 Aulnay sous Bois, France.*
[6] *SASOL Chair of Analytical Polymer Science, Department of Chemistry and Polymer Science, University of Stellenbosch, Private Bag X1, 7602 Matieland, South Africa.*

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

3. Recently submitted papers. * Corresponding author

- *Polymer*

Small strain mechanical properties of latex-based nanocomposite films

C. Plummer[1*], R. Ruggerone[1], E. Bourgeat-Lami[2], J-A. Manson[1]

[1]*Laboratoire de Technologie des Composites et Polymères (LTC), Ecole Polytechnique Fédérale de Lausanne (EPFL), 1015 Lausanne, Switzerland.* [2]*Chimie, Catalyse, Polymère, Procédé, C2P2/LCPP, UMR 5265 CNRS/CPE/UCBL, Bât. 308F, BP 2077- 43, Bd. Du 11 Nov. 1918, 69616 Villeurbanne Cedex, France.*

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

- *Macromolecules*

Facile synthesis of innocuous comb-shaped polymethacrylates with PEG side chains by nitroxide-mediated radical polymerization in hydroalcoholic solutions

Marion Chenal,† Simona Mura,† Cathie Marchal,¥ Didier Gigmes,¥ Bernadette Charleux,‡ Elias Fattal,† Patrick Couvreur,† and Julien Nicolas*,†

† Laboratoire de Physico-Chimie, Pharmacotechnie et Biopharmacie, Université Paris-Sud, UMR CNRS 8612, Faculté de Pharmacie, 5 rue Jean-Baptiste Clément, F-92296 Châtenay-Malabry cedex,France.
¥ Laboratoire Chimie Provence CNRS, CROPS, Université Aix-Marseille, UMR CNRS 6264, Case 542, avenue Escadrille Normandie-Niemen, F-13397 Marseille cedex 20, France.
‡ Laboratoire de Chimie Catalyse Polymères et Procédés (C2P2), LCPP, Université de Lyon 1, CPE Lyon, UMR CNRS 5265, Bat 308F, 43 boulevard du 11 novembre 1918, F-69616 Villeurbanne, France.

The nitroxide-mediated copolymerization of poly(ethylene glycol) methyl ether methacrylate (MePEGMA) with a small amount of acrylonitrile using an SG1-based alkoxyamine initiator was shown to be a very simple and efficient technique to synthesize graft copolymers with poly(ethylene glycol) side chains. The copolymerizations were carried out in ethanol/water solutions as environmentally-friendly media. Following our observation that the rate increased with the proportion of water, a polymerization temperature as low as 71 °C could be used for a water content

of 75 %, which conferred great flexibility to the process. The so-formed copolymers were living, with high crossover efficiency toward block copolymers. Importantly, following a cytotoxicity study over three different cell lines that represent important cell types in mammalian, these polymers were shown to be non-cytotoxic even at very high doses without any other purification step than a simple precipitation. It was concluded that these comb-shaped PEG-based polymers may represent an ideal platform for the synthesis of PEGylating moieties for proteins and nanoparticles intended to be used in the biomedical field.

- *Polymer Chemistry*

Synthesis and use of a new alkene-functionalized SG1-based alkoxyamine
C. Bernhardt, F. Stoffelbach,* B. Charleux*

[a] *UPMC Univ. Paris 6, UMR 7610 Laboratoire de Chimie des Polymères, Place Jussieu, Tour 44-54, 75252 Paris Cedex 05, France.*
[b] *CNRS Univ. Paris 6, UMR 7610 Laboratoire de Chimie des Polymères, Place Jussieu, Tour 44-54, 75252 Paris Cedex 05, France.*
[c] *Université de Lyon, Univ. Lyon 1, CPE Lyon, CNRS UMR 5265, C2P2, Team LCPP Bat 308F, 43 Bd du 11 novembre 1918, 69616 Villeurbanne, France.*

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

4. Ph-D Thesis

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

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

S. Boisse - oct. 2007 –oct. 2010
Synthesis of hairy nanoparticles and polymersomes
B. Charleux, J. Rieger (Paris 6)

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

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

V. Chabrol - oct. 2009 – oct 2012

Grafting from latex particles
B. Charleux, F. D'Agosto

X. Qiao – September 2010 – September 2013
Hybrid latex particles by nitroxide-mediated polymerization in aqueous dispersed media
E. Bourgeat-Lami, M. Lansalot, B. Charleux

C. Chong – Oct. 2010 – Oct. 2013
Multifunctional polymer particles for the preparation of biological samples
E. Bourgeat-Lami, M. Lansalot, F. D'Agosto, B. Charleux

I. Chaduc - September 2010 - September 2013
Design and synthesis of hydrophilic macroRAFT agents derived from renewable sources and their use as precursor of stabilizers in emulsion polymerization
M. Lansalot, F. D'Agosto

Wenjing Zhang – October 2010 – October 2013
In situ synthesis of amphiphilic block copolymer nano-objects
B. Charleux, F. D'Agosto

Emilie Groison - October 2010 – October 2013
Nitroxide-mediated controlled free-radical polymerization in emulsion
B. Charleux, F. D'Agosto

5. Post-docs

Dr. J. Parvole - 2010

Synthesis of controlled assemblies of silica spheres and latex particles through in situ emulsion polymerization.
E. Bourgeat-Lami, M. Lansalot.

Dr. F. Pardal - 2010

High temperature resistant waterborne coatings

E. Bourgeat-Lami

Dr. Xue Wei - 2010

Synthesis of hairy, non-spherical nanoparticles via RAFT in aqueous dispersed systems
B. Charleux, J. Rieger (Paris 6)

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

IPCG Report October, 2010

Published Papers:

Ye, Yuesheng F. Joseph Schork, “Modeling of Sequence Length and Distribution for the Nitroxide-Mediated Controlled Radical Polymerization of Styrene and 4-Methylstyrene in Batch and Semi-batch Reactors,” *Macromolecular Reaction Engineering*, **4(3-4)** 197-209 (2010).

*Grover, Martha, Jonathan A. Rawlston and F. Joseph Schork, "Multiscale Modeling of Branch Length in Butyl Acrylate Solution Polymerization," Macromolecular Theory & Simulations***, 19(6),** *309-322 (2010) .*

Ouyang, Liu, Lianshi Wang and F. Joseph Schork, “Synthesis of Well-Defined Statistical and Diblock Copolymers of Acrylamide and Acrylic Acid by Inverse Miniemulsion RAFT Polymerization,” *Macromolecular Chemistry and Physics* (in press, May 2010).

Papers in Press:

Ouyang, Liu, Lianshi Wang and F. Joseph Schork, “Synthesis of Well-Defined Statistical and Diblock Copolymers of Acrylamide and Acrylic Acid by Inverse Miniemulsion RAFT Polymerization,” *Macromolecular Chemistry and Physics* (in press, May 2010).

Abstract

Well-defined statistical and diblock copolymers with acrylamide and acrylic acid were synthesized by inverse miniemulsion RAFT polymerization. Statistical copolymers with various composition ratios were synthesized. Compositional drift was observed during polymerization. Acrylamide was polymerized with a water soluble initiator (VA-044) at 60 °C to give RAFT-agent containing AM homopolymer (RAFT-PAM) with a narrow molecular weight distribution (MWD<1.3), RAFT-PAM was then chain extended with acrylic acid to obtain the diblock copolymer.

Contribution to the IPCG Newsletter Sept.2010

Gérard RIESS
Ecole Nationale Sup. de Chimie de Mulhouse
3, rue A.Werner, 68093 Mulhouse Cedex France
Email : gerard.riess@uha.fr

PhD thesis submitted by L.I.ATANASE on May 21st 2010

Poly (vinyl acetate-co-vinyl alcohol) copolymers, designated by PVA, are macromolecular surfactants obtained by partial hydrolysis of poly (vinyl acetate) (PVAc). If the surfactant properties of PVA have been correlated with molecular characteristics it is not the same for the colloidal aggregates in aqueous solutions so-called *nanogels*.
The objective of this thesis was to characterize the *nanogels* using techniques such as dynamic light scattering, size exclusion chromatography and viscometry.
9 PVA with degrees of hydrolysis between 73 and 88 mole% and polymerization degrees of 650 to 2500 were studied. It appeared that the *nanogels*, formed by hydrophobic-hydrophobic interactions between acetate sequences, are the size in the range of 20 to 40 nm with volume fractions between 20 and 30%. The disaggregation of *nanogels* by complex formation with anionic surfactants such as SDS and SDBS was further demonstrated. By using the *"cloud point"* fractionation technique it appeared that SDS is complexed by the sequences with high acetate content and in particular those with significant lengths of acetate sequences.
As a model system diblock copolymers PVAc-b-PVOH containing a PVAc hydrophobic sequence and a PVOH hydrophilic sequence were prepared by RAFT polymerization, followed by a click reaction. A preliminary micellization study of these copolymers showed a very strong analogy between PVAc-b-PVOH block copolymer micelles and PVA *nanogels* discussed above.

Keywords: Poly (vinyl acetate-co-vinyl alcohol) copolymers (PVA), nanogels, sodium dodecyl sulfate, complex formation, particle size determination, cloud point, cloud point fractionation, block copolymers, micelles

This thesis was published in part in “*Colloids and Surfaces A: Physicochemical and Engineering Aspects*, 355, **(2010)**, 29-36”

Warren T. Ford
Recent Publications

Qin, D.; Lian, G.; Qin, S.; Ford, W. T.,* Microscopic Composition Maps of Poly(styrene-co-2-hydroxyethyl methacrylate) Colloidal Crystals and Interconnected Colloidal Arrays, *Langmuir* **2010**, *26*, 6256-6261.

Ford, W. T., Polymers Grafted to Single-walled Carbon Nanotubes by Radical Polymerization, *Macromolecular Symposia* **2010**, accepted.

Kaur, B.; McBride, S. P.; Ford, Paul, A.; W. T.,* Hydrolysis of *p*-Nitrophenyl Esters Promoted by Semi-fluorinated Quaternary Ammonium Polymer Latexes and Films, *Langmuir* **2010**, *26*, 00000-00000.

Langmuir XXXX, XXX(XX), XXX–XXX DOI: 10.1021/la1024982

Hydrolysis of *p*-Nitrophenyl Esters Promoted by Semi-fluorinated Quaternary Ammonium Polymer Latexes and Films

Baljinder Kaur,[+] *Sean P. McBride,*[#] *Abhijit Paul,*[+] *and Warren T. Ford*[+]*
[+]Department of Chemistry, Oklahoma State University, Stillwater, OK 74078 and [#]Department of Physics, Kansas State University, Manhattan, KS 66506

warren.ford@okstate.edu

Semifluorinated polymer latexes were prepared by emulsion polymerization of 2.5-25% of a fluoroalkyl methacrylate, 25% chloromethylstyrene, 1% styrylmethyl(trimethyl)ammonium chloride, and the remainder 2-ethylhexyl methacrylate under surfactant-free conditions. The chloromethylstyrene units were converted to quaternary ammonium ions with trimethylamine. In aqueous dispersions at particle concentrations of less than 1 mg mL$_{-1}$ the quaternary ammonium ion latexes promoted hydrolyses of *p*-nitrophenyl hexanoate (PNPH) in pH 9.4 borate buffer and of diethyl *p*-nitrophenyl phosphate (Paraoxon) in 0.1 M NaOH at 30 $_{o}$C with half-lives of less than 10 minutes. Thin 0.7-2 μm films of the latexes on glass promoted fast hydrolysis of Paraoxon but not of PNPH under the same conditions. Even after annealing the quaternary ammonium ion polymer films at temperatures well above their glass transition temperatures, AFM images of the film surfaces had textures of particles. Contact angle measurements of the annealed films against water and against hexadecane showed that the surfaces were not highly **fluorinated.**

Contribution to The IPCG Newsletter (Fall 2010)

Do Ik Lee, doiklee@aol.com

Western Michigan University and EcoSynthetix Inc., Lansing, Michigan

http://www.wmich.edu/pci/faculty/lee_N.htm
www.ecosynthetix.com

"Development of New Biobased Emulsion Binders"

Do Ik Lee, Adjunct Professor, Western Michigan University and Scientific Advisor to ECOSYNTHETIX INC. and Steven Bloembergen, EVP Technology, John van Leeuwen, CEO, ECOSYNTHETIX INC., presented at TAPPI PaperCon 2010, "Talent, Technology and Transformation", Atlanta, GA, May 2-5, 2010.

ABSTRACT

Biobased emulsion polymers were first adopted by the industry as coating binders in 2008 with the ability to match the performance of synthetic binders with up to 35% replacement. These new binders for paper coating applications have shown to impart unique rheological, coating holdout, coating structure, and optical properties to wet and dry paper coatings, respectively. The mechanisms for these unique behaviors will be discussed based on the fact that these biobased latex binders are made up of deformable, water-swollen crosslinked biopolymer nanoparticles and tend to shrink less upon coating consolidation during drying. Furthermore, recent breakthroughs in technology have allowed us to develop new grades of biobased latex binders with improved binder properties. These new grades address the initial deficiencies of inferior optical properties and certain strength properties, specifically wet pick, that limited their use in certain coated paper and paperboard applications. A new brightness grade made by co-extruding TiO2 particles in the production of biopolymer nanoparticles has shown that the co-extruded TiO2 particles are many times more efficient for both brightness and opacity of paper coatings than those TiO2 particles post-added either into biobased latex binders or coating formulations. The new wet strength grade blended with polymeric curing agents has shown that substitution levels of up to 75% are achievable in basecoat applications and up to 60% in topcoat and single coat paper and paperboard applications. Finally, the reduction in carbon footprint and green house gas emissions that results from the use of biobased latex binders will be discussed.

INTRODUCTION

Biobased latex binders adopted in the paper industry in 2008 were the first use of biopolymer-based microgels and nanogels for large-scale industrial applications [1-7], although they had been explored and used for drug delivery and other bio-medical applications for a long time [8]. Both biobased latex binders and biopolymer-based microgels and nanogels can be broadly defined as a special class of latexes whose particles are made up of water-swollen crosslinked hydrophilic polymers. Since the biobased latex binders currently used in the paper industry are water-swollen crosslinked starch nanoparticles, their wet and dry properties depend mainly on their particle size and crosslink density. The crosslink density of starch molecules forming the nanoparticles is especially important because it controls the extent of water swelling (swell ratio) [3,4], that is, as the crosslink density increases, the swell ratio of crosslinked starch nanoparticles decreases. Varying swell ratios of the water-swollen starch nanoparticles not only set them apart from conventional starches and synthetic latexes in their rheological behavior, but also differentiate themselves in paper coating performance. Their unique rheological behavior and paper coating performance will be discussed based on theoretical considerations as well as some laboratory testing, pilot coater and mill trial results.

The current biobased latex binders are manufactured by a continuous reactive extrusion process comprising of solubilizing starch granules, i.e. converting the very high-solids starch paste into a thermoplastic melt phase, and then crosslinking and sizing the solubilized starch molecules into nanoparticles [9,10]. The resulting product from the extruder is nearly dry agglomerates of crosslinked starch nanoparticles which are subsequently pulverized as a final powder product. This process was thought to be a good way to disperse TiO2 particles uniformly and associate them with starch nanoparticles. This is how we have developed a new brightness grade of biobased latex binders. The performance of this new biobased latex binder grade will be discussed in terms of the brightness and opacity of paper coatings.

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

"Specialty Biobased Monomers and Emulsion Polymers Derived from Starch"

Steven Bloembergen, Executive VP Technology, Ian J. McLennan, Senior Scientist, and John van Leeuwen, CEO ECOSYNTHETIX INC. and Do Ik Lee, Adjunct Professor, Western Michigan University and Scientific Advisor to ECOSYNTHETIX INC. to be presented at T2010 APPI 11th Advanced Coating Fundamentals Symposium, Munich, Germany, October 11-13, 2010.

ABSTRACT

Two biobased technology platforms have been developed that include a biobased sugar macromer technology and a biobased latex polymer technology. The sugar macromer platform provides a means of incorporating renewable monomers that are GRAS (generally recognized as safe) and contain no VOCs (volatile organic compounds). FAB Mass Spec demonstrated the sugar macromer consists of a mixture of different maleated alkyl polyglycosides, containing the monomer and oligomers of glucose with up to three polymerizable vinyl substituents per macromer molecule. The biobased latex platform consists of aqueous biopolymer nanoparticle latex dispersions which provide a direct substitute for petrochemical-based latex binders. A proposed model describes the nanoparticles (average size ~100 nm) as individual crosslinked macromolecular units. The product shipped dry for on-site dispersion consists of larger agglomerates (average size ~300 μm), from which nanoparticles are released when they are dispersed in water. In dispersed form the water-swollen crosslinked nanoparticles possess an effective solids that is higher than their actual solids. As a result, paper coating colors containing biobased latex binders are closer to their immobilization solids, exhibiting higher coating holdout, enhanced fiber coverage and coating smoothness. Proper dispersion is critical, as illustrated by controlled agglomeration studies in the presence of different molecular weight dextrins.

1. INTRODUCTION

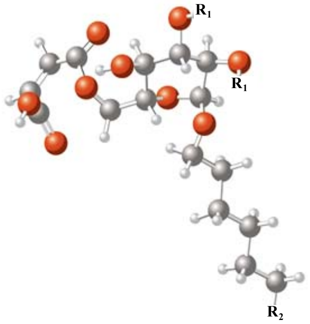
Using biobased raw materials and scalable production techniques, two biobased technology platforms have been developed: a biobased sugar macromer technology and a biobased latex polymer technology.

1.1 Biobased Sugar Macromer Technology

The first technology platform utilizes the monosaccharide glucose (dextrose) derived from corn starch and provides a means of incorporating biodegradable sugar based macromonomers. These sugar macromers, referred to as ECOMER®, impart new performance attributes by incorporating into the main copolymer backbone structure, for the production of novel hybrid vinyl copolymers including vinyl acetate, acrylic, styrene butadiene (SB) and styrene acrylate (SA) sugar copolymer latexes. Few renewable monomers or macromers exist. One example that has been explored for paper coating applications includes the synthesis of alkyd/acrylic hybrid latexes using vegetable oil macromonomers, in an effort to provide for lower VOCs, renewable content and new performance attributes.[1]

Similarly, the intent of the sugar macromer platform was to develop a family of renewable macromonomers suitable for copolymerization with conventional vinyl monomers. To this end, glucose was converted to alkyl polyglycoside (APG), wherein the alkyl group (referred to as the "hydrophobe") was designed to impart solubility in vinyl monomers, as well as chemical and thermal stability of the sugar as it converts glucose (a reducing sugar) to a more stable non-reducing sugar moiety.[2-4] A simplified structure is illustrated in Figure 1.

Maleic anhydride (MAn) is used as the source of double bonds. MAn is highly reactive towards the glucose hydroxyls, and the resulting vinyl ester substituents readily copolymerize with other vinyl monomers. Given the macromer does not homopolymerize with itself, this has provided a safe manufacturing process that is free from the potential of run-away polymerization conditions. The sugar macromer is a resinous solid in 100% active form that flows at temperatures of 45-55 °C, and it can be dissolved in other vinyl comonomers such as butyl acrylate or methyl methacrylate to provide a low-viscosity fluid with a Brookfield viscosity substantially below 1000 cps (Pa.s). Sugar macromers in 100% active form are GRAS (generally recognized as safe) and contains no volatile organic compounds (VOCs).



Where R_1 = unsaturated ester or H;
R_2 = alkyl or other functional group

Figure 1. Simplified ball & stick schematic illustrating some of the essential features of the chemical structure of the biobased macromer technology.

Maleic anhydride (MAn) is used as the source of double bonds. MAn is highly reactive towards the glucose hydroxyls, and the resulting vinyl ester substituents readily copolymerize with other vinyl monomers. Given the macromer does not homopolymerize with itself, this has provided a safe manufacturing process that is free from the potential of run-away polymerization conditions. The sugar macromer is a resinous solid in 100% active form that flows at temperatures of 45-55 °C, and it can be dissolved in other vinyl comonomers such as butyl acrylate or methyl methacrylate to provide a low-viscosity fluid with a Brookfield viscosity substantially below 1000 cps (Pa.s). Sugar macromers in 100% active form are GRAS (generally recognized as safe) and contains no volatile organic compounds (VOCs).

The sugar macromers are copolymerized with vinyl comonomers in an aqueous starve-fed emulsion copolymerization process to produce close to random copolymers that contain the biobased sugar moiety within the backbone of the copolymer network (Figure 2).

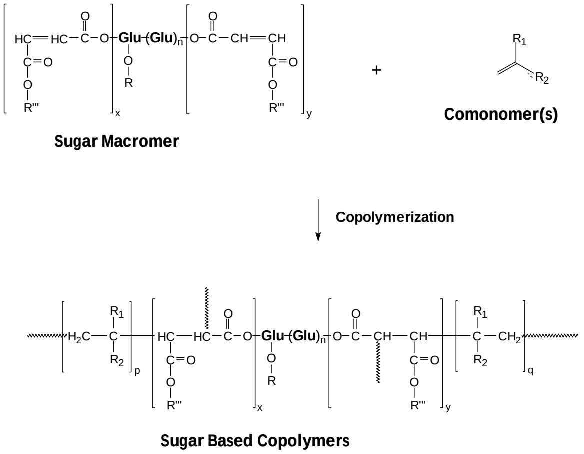


Figure 2. Schematic illustrating the chemical structure of the sugar macromer and resultant sugar-vinyl copolymers, wherein the corn based sugar is built into the main polymer network structure.

Applications of this technology include pressure sensitive adhesive (PSA) labels, thermosets for wood and plastics, biocomposites for structural materials, circuit boards, ink resins, bioplastics and biopolyesters.[2-5] Given the greening of the paper industry, the use of these sugar macromers as renewable functional comonomers for replacement of more toxic comonomers such as acrylonitrile is being explored in the development of novel hybrid SB and SA latex binders.

1.2 Biobased latex Polymer Technology

The second technology platform utilizes starch derived from crops including corn, tapioca, potato, wheat, etc., and provides a direct replacement for petro-based binders such as SB and SA latex. The biobased latex binders, referred to as biolatex® binders, provide performance that is comparable to SB and SA latex systems for important paper properties.[6-8]

As illustrated in Figure 3, the biobased latex nanoparticles are manufactured from starch derived from corn, potato, tapioca, etc. via a proprietary twin screw extrusion process, and then shipped as a dry powder product to the coated paper and board manufacturer, which eliminates the need to ship the binder as an aqueous 50% solids latex dispersion typical of SB and SA latex emulsions.

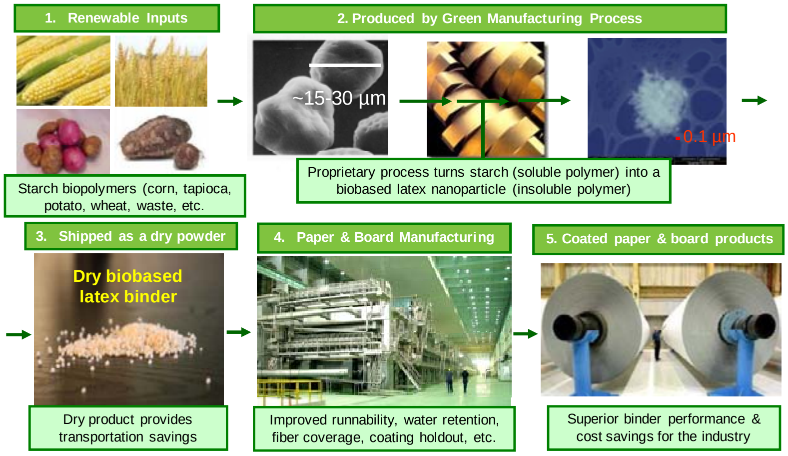


Figure 3. Schematic illustrating raw material inputs (starch from corn, tapioca, potato, wheat, etc.), biobased latex manufacturing and coated paper manufacturing.

Crosslinked biopolymer nanoparticles have unique properties when dispersed as a latex in water. First, their swelling under conditions of extreme dilution with water achieves the maximum swelling value that is balanced between their elastic constraint due to their crosslinked network and the osmotic pressure.[9] By measuring the relative viscosity at low concentrations for a polymer colloid, one can gather relevant information about the viscosity and swelling behavior of that colloid. The effective volume factor (the maximum volume swell ratio) of the biobased latex with different crosslink densities has been reported to range from 6.7 to 9.3 to 16.0 for relatively high, medium and low crosslink densities, respectively.[9] Biobased latex nanoparticles de-swell by addition of water-miscible solvents such as alcohols and many other water-soluble species such as electrolytes, and they de-swell with increasing solids.[9]

Since the biobased nanoparticles in dispersions exist in the form of water-swollen crosslinked nanoparticles, their % effective solids and volume solids are higher than their % actual solids and volume solids. Figure 4 shows the % effective volume solids as a function of the % actual solids of a biobased latex nanoparticle dispersion with a volume swell ratio, SR(V), of 2.5 as a parameter, along with the % volume solids of a conventional cooked starch solution and a synthetic latex for comparison, where the densities of starch, biobased latex and SB latex were taken to be 1.6 g/cm^3 and 1.0 g/cm^3, respectively.[9] As can be seen in Figure 4, the water-swelling of biobased latex nanoparticles significantly increases % effective volume solids over their % actual solids as compared to typical cooked starch solutions and synthetic latexes.

Interfacial Layers of stimuli-responsive Poly-(N-isopropylacrylamide-co-methacrylicacid (PNIPAM-co-MAA) microgels characterized by interfacial rheology and compression isotherms

B. Brugger, J. Vermant, W. Richtering
Phys. Chem. Chem. Phys., DOI:10.1039/C0CP01022G

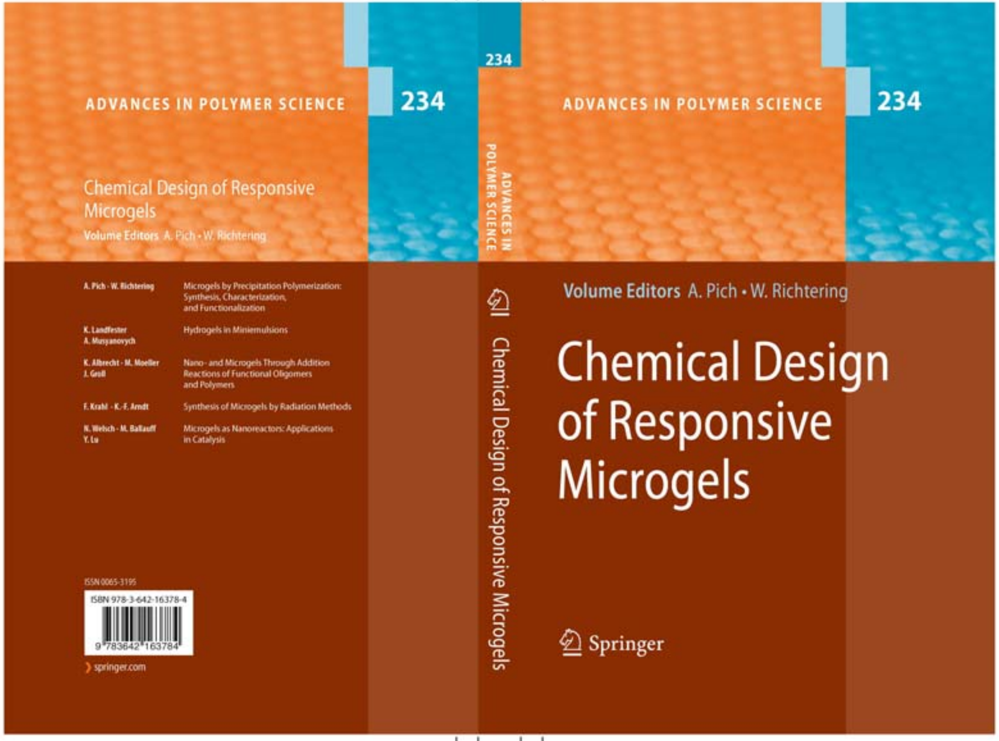
Microgels by Precipitation Polymerization: Synthesis, Characterization, and Functionalization
A. Pich, W. Richtering
Advances in Polymer Science (2010), online first

Cononsolvency of Poly(*N,N*-diethylacrylamide) (PDEAAM) and Poly(*N*-isopropylacrylamide) (PNIPAM) Based Microgels in Water/Methanol Mixtures: Copolymer vs Core-Shell Microgel
C. Scherzinger, P. Lindner, M. Keerl, W. Richtering
Macromolecules, 43(16), 6829–6833 (2010)

Influence of pressure on the state of poly(N-isopropylacrylamide) and poly(N,N-diethylacrylamide) derived polymers in aqueous solution as probed by FTIR-spectroscopy
M. Pühse, M. Keerl, C. Scherzinger, W. Richtering, R. Winter
Polymer, 51(16). 3653-3659 (2010)

Polyampholyte Microgels with Anionic Core and Cationic Shell
S. Schachschal, A. Balaceanu, C. Melian, D. E. Demco, T. Eckert, W. Richtering, A.Pich
Macromolecules, 43, 4331–4339 (2010)

Influence of Architecture on the Interaction of Negatively Charged Multisensitive Poly(-isopropylacrylamide)- co-Methacrylic Acid Microgels with Oppositely Charged Polyelectrolyte: Absorption vs Adsorption
J. Kleinen, A. Klee, W. Richtering
Langmuir, 26(13), 11258–11265 (2010)



ADVANCES IN POLYMER SCIENCE 234

Chemical Design of Responsive Microgels

Volume Editors A. Pich · W. Richtering

A. Pich · W. Richtering	Microgels by Precipitation Polymerization: Synthesis, Characterization, and Functionalization
K. Landfester **A. Musyanovych**	Hydrogels in Miniemulsions
K. Albrecht · M. Moeller **J. Groll**	Nano- and Microgels Through Addition Reactions of Functional Oligomers and Polymers
F. Krahl · K.-F. Arndt	Synthesis of Microgels by Radiation Methods
N. Welsch · M. Ballauff **Y. Lu**	Microgels as Nanoreactors: Applications in Catalysis

ISSN 0065-3195
ISBN 978-3-642-16378-4
springer.com

234
ADVANCES IN POLYMER SCIENCE
Chemical Design of Responsive Microgels

ADVANCES IN POLYMER SCIENCE 234

Volume Editors A. Pich · W. Richtering

Chemical Design of Responsive Microgels

Springer

Oct 2010

Per B. Zetterlund

A/ Professor
Centre for Advanced Macromolecular Design (CAMD)
School of Chemical Sciences and Engineering
University of New South Wales
High Street Gate 2 - Chemical Science Building F10
Phone: +61-2- 9385 4331
Fax: +61-2-9385 6250
Email: p.zetterlund@unsw.edu.au
http://www.camd.unsw.edu.au

Recently published papers

- Nitroxide-Mediated Radical Polymerization in Nanoreactors: Can Dilution or Increased Nitroxide Concentration Provide Benefits Similar to Compartmentalization?, P. B. Zetterlund, *Aust. J. Chem.* **2010**, *63*, 1195-1200.

- Nitroxide-Mediated Radical Polymerization in Miniemulsion on the Basis of in situ Surfactant Formation without use of Homogenization Device, Y. Guo, J. Liu, P. B. Zetterlund, *Macromolecules* **2010**, *43*, 5914-5916.

- Controlled/Living ab Initio Emulsion Polymerization via a Glucose RAFTstab: Degradable Crosslinked Glyco-Particles for Concanavalin A/FimH Conjugations, S. R. S. Ting, E. H. Min, P. B. Zetterlund, M. H. Stenzel, *Macromolecules* **2010**, *43*, 5211–5221.

- Compartmentalization in Atom Transfer Radical Polymerization to High Conversion in Dispersed Systems: Effects of Diffusion-Controlled Reactions, P. B. Zetterlund, *Macromolecules* **2010**, 43, 1387-1395.

- Nitroxide-Mediated Radical Polymerization in Dispersed Systems: Compartmentalization and Nitroxide Partitioning, P. B. Zetterlund, *Macromol. Theory Simul.* **2010**, *19*, 11–23.

- Effect of Monomer Loading and Pressure on Particle Formation in Nitroxide-Mediated Precipitation Polymerization in Supercritical Carbon Dioxide, P. O'Connor, P. B. Zetterlund, F. Aldabbagh, *Macromolecules* **2010**, *43*, 914-919.

- Effects of the Oil-Water Interface on Network Formation in Nanogel Synthesis using Nitroxide-Mediated Radical Copolymerization of Styrene/Divinylbenzene in Miniemulsion, P. B. Zetterlund, Md. N. Alam, M. Okubo, *Polymer* **2009**, *50*, 5661–5667.

- Nitroxide-Mediated Radical Polymerization of Styrene in Aqueous Microemulsion: Initiator Efficiency, Compartmentalization and Nitroxide Phase Transfer, P. B. Zetterlund, J. Wakamatsu, M. Okubo, *Macromolecules* **2009**, 42, 6944–6952.

Unpublished papers

- Controlled/Living Radical Polymerization in Nanoreactors: Compartmentalization Effects, Per B. Zetterlund, *Polymer Chemistry*, **in press**.

  ABSTRACT: Compartmentalization in nanoreactors, i.e. the confinement of reactants to monomer droplets or polymer particles with diameters in the approximate range 20 - 200 nm, may have a marked beneficial effect on the progression of a controlled/living radical polymerization based on the persistent radical effect such as nitroxide-mediated radical polymerization and atom transfer radical polymerization. Compartmentalization effects comprise the confined space effect, which acts as to improve the control over the molecular weight distribution (narrower), and the segregation effect which results in increased livingness (end-functionality). Exploitation of nanoreactors thus offers novel means of improving the performance of controlled/living radical polymerizations.

- Miniemulsion Polymerization Based on Low Energy Emulsification with Preservation of Initial Droplet Identity, S. Cheng, Y. Guo, P. B. Zetterlund, *Macromolecules*, **in press.**

  ABSTRACT: A low energy emulsification technique involving dilution of a microemulsion precursor has been successfully applied to synthesis of polystyrene nanoparticles by miniemulsion polymerization, featuring an exceptionally high degree of preservation of the initial droplet identity, thus offering superior particle size control to conventional high-energy methods. Investigations are currently underway directed at the miniemulsion formation mechanism, as well as application of the technique to other systems (e.g. CLRP).

- Nitroxide-Mediated Radical Polymerization of Carbon Dioxide-Expanded Methyl Methacrylate, D. W. Pu, F. P. Lucien, P. B. Zetterlund, *J. Polym. Sci.: Part A: Polym. Chem.*, **in press**.

  ABSTRACT: NMP based on the nitroxide TEMPO has been performed for MMA under conditions of CO_2-expanded monomer at 7 MPa and 90 °C. Based on 1H NMR and GPC analysis, the fraction of propagating radicals that irreversibly lost their activity due to the disproportionation reaction with nitroxide decreased somewhat in the presence of CO_2. This finding is consistent with the deactivation reaction between propagating radical and nitroxide proceeding more rapidly in the lower viscosity induced by the presence of CO_2. However, similarly to what has been previously observed in bulk NMP of MMA with TEMPO and other nitroxides, the polymerization ceased at relatively low conversions of approximately 19% both with and without CO_2, indicating that disproportionation between propagating radical and nitroxide is a major problem also in CO_2-expanded MMA. Modeling and simulations allowed estimation of the rate coefficient for the disproportionation reaction to be of the order of 5 x 104 $M^{-1}s^{-1}$ (with or without CO_2).

- Nitroxide-Mediated Radical Polymerization of Butyl Acrylate Using TEMPO: Improvement of Control Exploiting Nanoreactors?, P. B. Zetterlund, *Macromol. React. Eng.*, **in press**.

ABSTRACT: Compartmentalization effects in the nitroxide-mediated radical polymerization of butyl acrylate in a dispersed system using the nitroxide 2,2,6,6-tetramethylpiperidine-N-oxyl (TEMPO) at 130 ºC have been examined by means of modelling and simulations employing modified Smith-Ewart equations that account for compartmentalization effects on both propagating radicals and free nitroxide species. TEMPO-mediated acrylate polymerization is known to be problematic, speculated to be mainly related to excessive accumulation of free TEMPO with increasing conversion. The present theoretical results indicate that it may be possible to at least partially overcome this difficulty by careful exploitation of compartmentalization effects in nanoreactors.

Polymer Colloids Publications W.-D. Hergeth

“Influence of polyvinyl alcohol on phase development during the hydration of Portland cement“
D. Jansen, F. Goetz-Neunhoeffer, J. Neubauer, W.-D. Hergeth, R. Härzschel
ZKG International / Cement Lime Gypsum **63** (2010) 100-107

Poly(vinyl alcohols) (PVOH) affect the aluminate reaction during the hydration of Portland cement. PVOH retards the dissolution of both the sulphate carrier and the C_3A*, and accelerates ettringite formation after about 16 hours of hydration.*

“Online Reaktionsverfolgung bei der Polymerisation”
(„Online Reaction Monitoring of Polymerizations“)
E. Frauendorfer, W.-D. Hergeth
Chem. Ing. Tech. **82** (2010) 503 – 507

Klassische Messgrößen wie Temperatur oder Druck, die den physikalischen Zustand eines Reaktors beschreiben, werden kombiniert mit instrumentell analytischen Techniken, um den Reaktionsfortschritt zu verfolgen. Am Beispiel industrieller Polymerisationen wird der Einsatz von NIR- und Raman-Spektroskopie, Kalorimetrie und Softsensoren zur Rohstoffeingangskontrolle, Reaktionsverfolgung und Vorhersage von Produkteigenschaften beschrieben.

“Polymerization Online Monitoring – A Review“
E. Frauendorfer, A. Wolf, W.-D. Hergeth
Chem. Eng. Technol. **33** (2010) in press

Online monitoring of polymerization reactions is not only important due to the high exothermic nature of most polymerization systems, data gained also provides information on product composition and quality and control possibilities thereof. Many in-line and on-line methods are still in development and are better suited for application in laboratory or pilot-plant scale. Industrial polymerization plant environments pose additional technical and financial challenges and constraints for the use of such systems. Available methods and current developments are reviewed concerning their practicability and usefulness under these aspects.

“Industrial Polymerization Monitoring“
E. Frauendorfer, W.-D. Hergeth
Macromol. Symp. (2010) in press

Monitoring and control of polymerization reactions is essential for high process safety, high product quality and competitive production costs. Ideally the entire process chain is regarded, starting with raw material analysis and the polymerization reaction up to the measurement of polymer- and application- properties. Process data like temperatures and pressures can be used to monitor reaction trajectories in a cost effective way, e.g. using calorimetric evaluations. Additional sensors can provide chemical or morphological information but must be robust and inexpensive for commercial applications (e.g. NIR- or Raman spectroscopy). Data from these different sources can be used for multivariate data analysis, delivering additional insights that might not be obtained by direct measurement.

Contribution of Eindhoven Group (Van Herk/Heuts)

* Publication of reviews

- Emulsion Polymerization. *Encyclopedia of Polymer Science and Technology*. (pp. 1-38) Hoboken, N.J.: Wiley. Herk, A.M. van,
Heuts, J.P.A (2009)

-Modeling of Emulsion Polymerization, will it ever be possible? Part-2: determination of basic kinetic data over the last ten years, van
Herk, Alexander M. *Macromolecular -Symposia* (2009), 275-276 (Microstructural Control in Free-Radical Polymerization), 120-132.

-Historic Account of the Development in the Understanding of the Propagation Kinetics of Acrylate Radical Polymerizations , van
Herk, Alex M. *Macromolecular Rapid Communications* (2009), 30(23), 1964-1968.

-Chapter 3 in Royal Society of Chemistry book on Nanotechnology ;*Polymer–Clay Nanocomposite Particles by Direct and Inverse*
*Emulsion Polymerization ,*W. Ming, D.-J. Voorn A. M. Van Herk, **in Print**

-Historical Overview of (Mini)emulsion Polymerizations and Preparation of Hybrid Latex Particles in special issue of *Advances in*
Polymer Science (also editing this special issue on hybrid particles together with Katharina Landfester) **in Print**

* Publication of some older work

-Determination of Propagation Rate Coefficients ofa Family of Acrylates with PLP-MALDI-ToF-MS Willemse, R. X. E.; van Herk, A. M.
Macromolecular Chemistry and Physics (2010), 211(5), 539-545.

-Determination of propagation rate coefficients of fast polymerizing heterocyclic side-chain acrylates with pulsed laser polymerization
and MALDI-ToF MS: Tetrahydrofurfuryl acrylate and (R)-a-Acryloyloxy-b,b-dimethyl-g-butyrolactone C. Boukaftane' A.M. van Herk *Macromol. Chem. Phys*. **In Print**

* Publication of new results

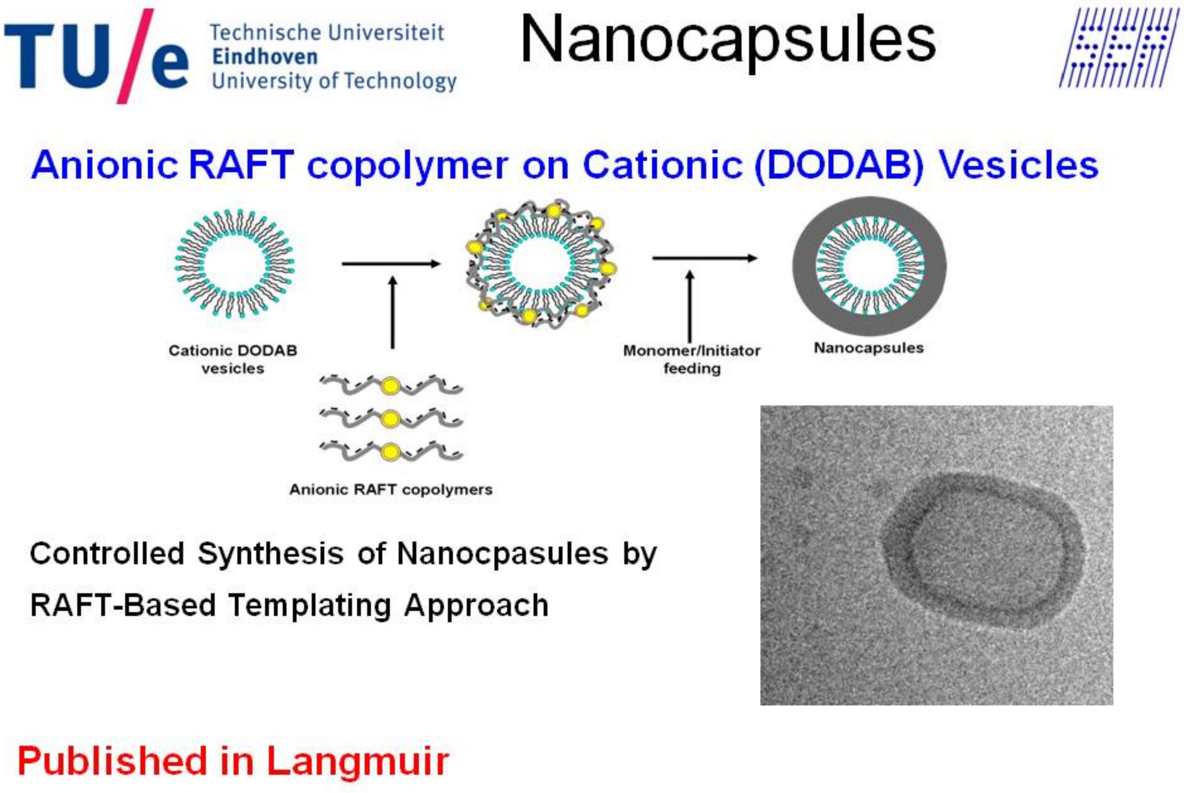
-S.I. Ali, J.P.A. Heuts, A.M. van Herk, Controlled Synthesis of Polymeric Nanocapsules by RAFT-Based Vesicle Templating. Langmuir, 26, 7848-7858 2010

-L. Zhaparova , Y. Tazhbayev , M. Burkeev , Syed I. Ali , A.M. van Herk E.A. Buketov Synthesis and Characterization of Hollow Polyethylcyanoacrylate Nanocapsules *The Herald of Karaganda State university.* 3, 2010. **in Print**

- Monique A. Mballa Mballa, Ulrich S. Schubert, Johan P. A. Heuts, Alex M. van Herk, Automated Batch Emulsion Copolymerization of Styrene and Butyl Acrylate, Accepted in *J. Polym. Sci. Part A: Polymer Chemistry*

Future activities:

*** Organizing Jubilee symposium 25 years SEP (early 2013)**
*** Writing a book**; invited by World Scientific (Singapore)
Controlled Release Systems: Advances in Nanobottles and Active Nanoparticles
Jacqueline Forcada (Uni San Sebastian), Alex van Herk , Yi-Yan Yang (IBN Singapore)
*** Preparing a Second edition of Chemistry and Technology of Emulsion Polymerization, Wiley**



Nanocapsules

Anionic RAFT copolymer on Cationic (DODAB) Vesicles

Controlled Synthesis of Nanocpasules by RAFT-Based Templating Approach

Published in Langmuir

Contribution: Dr. Norio Ise
norioise@sea.plala.or.jp

Recent publications:

(1) **Like Likes Like: Counterion-mediated Attraction in Macroionic and Colloidal Interaction (Perspective)** by Norio Ise

Phys.Chem.Chem.Phys. ,**12**, 10279-10287 (2010).

Abstract: The colloidal and macroionic interaction is discussed within the mean-field approach. Bound pairs of latex particles are photographed at a low particle volume fraction of 10^{-4}. The effective pair-potential obtained therefrom has an attractive tail for highly charged samples, while no attraction is detected for a low-charge sample. This attraction also manifests itself in the reversible aggregation of polystyrene sulfonate or DNA double strands by multivalent counterions. It is furthermore found in intra-macroionic interaction, affecting the conformation of flexible macroions. The reason why the DLVO theory predicts only repulsion is discussed. The Fowler-Guggenheim-McQaurrie analysis of the Debye–Hückel theory indicates that electrostatic Helmholtz free energy F^{el} is generally not equal to Gibbs free energy G^{el}. The difference $(G^{el} - F^{el})/V$ (V: system volume) corresponds to the electrostatic osmotic pressure p^{el}, which increases with increasing charge number. This consideration *hints* that $(G^{el} - F^{el})$ might not be negligible for highly charged macroions and colloidal particles. On the other hand, the DLVO approach is based on the assumption of $G^{el} = F^{el}$. It means that the role of small ions is not correctly taken into consideration in the DLVO approach. Using a mean-field approach, Sogami showed that the pair-potential is purely repulsive at the level of F^{el}, in conformity with the DLVO theory, whereas it contains a short-range repulsion and a long-range attraction at the level of G^{el}. The prevailing view, that the interparticle interaction is purely repulsive in the mean-field approach, is not justified: it originates from the assumption that $G^{el} = F^{el}$. The DLVO theory is practically correct for low charge samples, but is not generally valid, while the like-likes-like attraction appears for highly charged ones.

(2) **Comment on "On the Theory of Electrostatic Interactions in Suspensions of Charged Colloids" by Willem H. Mulder**

by Norio Ise and I. S. Sogami.

Soil Science Society of America Journal, **74,** 1-2 (2010)

The criticism of the Sogami theory on colloidal interaction presented by Mulder (Soil Sci. Soc. Am. J. **74**, 1, 2010) has been refuted. While the DLVO theory is constructed on the assumption that the electrostatic Helmholtz (F^{el}) and Gibbs free energies (G^{el}) are indistinguishable, the Sogami theory shows that this assumption is not generally valid. Mulder questions Sogami's treatment. However, Mulder's argument (and also the DLVO assumption as well) can be readily seen to be wrong when the Debye-Hückel (D-H) theory is carefully analyzed. McQuarrie demonstrates that $F^{el}$and G^{el} are not equal in this theory. Thermodynamics requires that $(G^{el}- F^{el})/V$ (V: system volume) is equal to the electrostatic osmotic pressure p^{el}, which turns out to be $-\kappa^3 k_B T/24\pi$ in the D-H theory.

It is reminded that the $G^{el}=F^{el}$ relation was claimed to correct in the DLVO theory on the basis of solvent being incompressible during charging-up process. However, if this argument is correct, the equality relation must hold also for the D-H theory because these two theories can be commonly used for water as solvent. As shown above, the relation does not hold for the D-H theory, however. It is important to recall that $(G^{el}- F^{el})/V$ in the D-H theory has nothing to do with the incompressibility but is determined solely by κ^3 (interionic interaction).

In contradiction to Mulder's claim, the $G^{el}=F^{el}$ assumption is thus not always valid and represents, at the best, the specific situation corresponding to $p^{el} = 0$. Evidently, the Sogami approach corresponds to a much more general case. Practically, the DLVO theory would give seemingly good agreements with observation only when the particle charge number is low (See N. Ise and I. S. Sogami, *Structure Formation in Solutions: Ionic Polymers and Colloidal Particles*, Springer, Berlin, 2005).

It is furthermore pointed out that the relation $G^{el}= F^{el}$ was erroneously derived by an improper mathematical treatment of the free energies in Overbeek's criticism of Sogami theory (J. Chem. Phys.**87,** 4406, 1987).

Contribution: **Dr. M. S. El-Aasser** **and** **Dr. H. D. Ou-Yang**
E-mail: mse0@lehigh.edu hdo0@lehigh.edu

International Polymer Colloids Group
Newsletter
October 2010

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

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

Invited Presentations

Asia Pacific Center for Theoretical Physics Workshop on Chemi- Thermo- EM Phoresis in Complex Fluids, Pohang, South Korea; August 25 – 28, 2010
Organizers:
Mahn Won Kim (KAIST, Korea)
Daniel Ou-Yang (Lehigh University, USA)
Hyuk Kyu Pak (Pusan University, Korea)
Phillip A. Pincus (University of California, Santa Barbara, USA)

2-D Mapping of Frequency Dependent AC Electro-osmosis Flow Velocities in a Microfluidic Chamber, Daniel Ou-Yang, Workshop on Chemi-Thermo-EM Phoresis in Complex Fluids (Invited talk), Asia Pacific Center for Theoretical Physics Workshop on Chemi- Thermo- EM Phoresis in Complex Fluids, Pohang, South Korea; August 25 – 28, 2010

Presentations at Conferences

Thermal and Non-thermal Intracellular Mechanical Fluctuations of Living Cells, Ming-Tzo Wei and H. Daniel Ou-Yang; SPIE Optics and Photonics 2010, August 1-5, 2010, San Diego, California, USA

Fluorescence Correlation Spectroscopy in an Optical Trap, Yi Hu, Xuanhong Cheng, and H. Daniel Ou-Yang, SPIE Optics and Photonics 2010, August 1-5, 2010, San Diego, California, USA

Optical Tweezers as a Force Sensor for Separating Dielectrophoresis and AC Electroosmosis Forces, Jingyu Wang and H. Daniel Ou-Yang, SPIE Optics and Photonics 2010, August 1-5, 2010, San Diego, California, USA

Measurements of Charged Colloidal Bulk Moduli using Optical Bottles, Joseph Junio and H. D. Ou-Yang, SPIE Optics and Photonics 2010, August 1-5, 2010, San Diego, California, USA

A Method to Separate Dielectrophoresis and AC Electroosmosis, Jingyu Wang and H. Daniel Ou-Yang, ITP 2010: 17th International Symposium on Capillary Electroseparation Techniques, August 29 to September 1, 2010, Baltimore, Maryland, USA

Redox-initiated 'Adiabatic' Emulsion Polymerization, Shi Wang, Andrew Klein, and Eric S. Daniels, To Be Presented at the AIChE's 2010 Annual Meeting taking place November 7-12, 2010 in Salt Lake City, UT

(Please note: detailed information on the information presented at the conferences listed above is available upon request)

Recent Publications

Synthesis and Characterization of PNIPAM/PS Core/Shell Particles, L. Zhang, E. S. Daniels, V. L. Dimonie, and A. Klein, *J. Appl. Polym. Sci.*, **118**, 2502 (2010)

Submitted Publications

Encapsulation of Colloidal Silica Particles by Emulsion Polymerization, Andrés F. Vargas, E. David Sudol, Andrew Klein, Eric S. Daniels, and Betty L. López, Submitted to J. *Appl. Polym. Sci.*, August 2010.

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

Mechanism of Seeded Dispersion Polymerization of Methyl Methacrylate using Submicron Polystyrene Seed Latexes, Zhipeng Song, Eric S. Daniels, E. David Sudol, Mohamed S. El-Aasser, and Andrew Klein, Submitted to *J. Appl. Polym. Sci.*, September 2010.

Submicron polystyrene (PS) latex particles were used as seed in seeded dispersion polymerization of methyl methacrylate (MMA). Particle growth and number evolution during the reaction were studied. The PS seed particles were located and tracked during the reaction using a refractive index matching technique. The distribution of the number of PS seed particles in the poly(methyl methacrylate) (PMMA) particles was investigated in detail throughout the reaction. Two significant transition points could be detected under the reaction conditions studied. One occurred at less than 1% polymerization conversion and the other at 8.7% conversion. From the beginning of the reaction to the first transition point, the number of particles containing one seed decreased from 100% to about 75%; the number of particles containing no seed increased from zero to about 9%; and the number of particles containing two seed particles increased from zero to about 15%. Between the first and second transition point, the number of particles containing one seed continued to decrease to 60%, the number of particles containing two seed particles continued to increase to 23%, and the number of particles containing no seed started to level off. From the second transition point to the end of the reaction, the numbers of these three populations of particles remained constant. There were some particles containing more than two seed particles, but these comprised only a small population. These results are interpreted with respect to the mechanism of seeded dispersion polymerization where particle nucleation and aggregation are processes competing during the reaction.

Completed PhD Dissertations

Role of Reactive Surfactants in Miniemulsion Polymerization

Samantha N. Braganza-Pugh (Faculty Advisors: Andrew Klein and Mohamed S. El-Aasser)

Reactive surfactants which contain a polymerizable group that can be irreversibly bound to polymer particles are used to reduce the negative effects of conventional surfactants in latex films, greatly increasing both the latex stability and the water resistance of the film. Miniemulsion polymerization is proposed as an alternative to conventional emulsion polymerization to increase the amount of surfactant incorporated on the particle surfaces and to minimize the amount of buried surfactant. Two reactive surfactants, HITENOL BC-20 (polyoxyethylene alkylphenyl ether ammonium sulfate) (anionic) and HITENOL KH-10 (polyoxyethylene-1-(allyloxy methyl alkylether sulfate) (anionic), have been studied. The critical micelle concentrations (cmc), and their partitioning behavior were determined. The stability of miniemulsions prepared using reactive surfactants HITENOL BC-20 and HITENOL KH-10 was studied and compared with miniemulsions prepared using a conventional surfactant (SLS).

Results indicate that Ostwald ripening is occurring for all three surfactants, but it is more prominent in styrene miniemulsions prepared with a conventional surfactant (SLS).

The kinetics of conventional emulsion polymerizations of styrene using reactive surfactants HITENOL BC-20 and HITENOL KH-10 were found to be similar to the conventional surfactant. However, a decrease was observed in the reaction rate when HITENOL KH-10 was used in comparison with HITENOL BC-20 due to the retardation effect caused by the resonance stability of the allylic radical. In the kinetics of the miniemulsion polymerization of styrene using the reactive surfactants HITENOL BC-20 and HITENOL KH-10, similar kinetics were found for the two reactive surfactants. Further latex characterization by TEM showed that the number of particles increased with increasing monomer conversion up to 10 % and then remained constant until the end of the reaction for both reactions indicating a short nucleation period.

To characterize the surfactant incorporation in the latexes prepared by miniemulsion and conventional emulsion polymerization, ion exchange/conductometric titration combined with UV analysis was applied. The results show that for miniemulsion polymerization carried out with 5 mM HITENOL BC-20 (20 % solids), 82 % of the BC-20 was chemically bound to the polymer particles out of which 68 % was bound on the surface while 14 % was buried. In a parallel study using conventional emulsion polymerization, of the 77 % that was chemically bound, 55 % was on the surface and 22 % was buried inside the particles. In styrene miniemulsion and conventional emulsion polymerizations using HITENOL KH-10, the amounts incorporated on the surface of the particles were found to be higher than in the BC-20 reactions. Results from control experiments and molecular weight studies show that major incorporation of HITENOL BC-20 is through copolymerization, and chain transfer occurs mainly during nucleation period. For HITENOL KH-10, chain transfer combined with copolymerization resulting in intermolecular branching acts as a primary mode for incorporation. AFM studies of latex morphology showed that reactive surfactants can only be partially removed from latexes. Freeze-thaw cycles and contact angle studies show that latexes prepared with reactive surfactants by miniemulsion polymerization showed improved stability and little surfactant migration.

Seeded Dispersion Polymerization

Zhipeng Song (Faculty Advisors: Mohamed S. El-Aasser and Andrew Klein)

Particle formation, aggregation, and growth behavior were investigated in seeded dispersion polymerization of methyl methacrylate (MMA) using sub-micron size polymer particles as seed.

The relationship between the final particle number (*N*(final)) and the initial seed number (*N*(initial)) was studied under various reaction conditions. It was found that there is a critical point for *N*(initial) to control *N*(final). The critical point is located at *N*(*ab initio*), which is the number of final particles obtained from the *ab initio* (non-seeded) dispersion polymerization using the same recipe. *N*(final) is equal to *N*(*ab initio*) when *N*(initial) is less than *N*(*ab initio*). A linear relationship between *N*(final) and *N*(initial) was found when *N*(initial) is greater than *N*(*ab initio*). The slope of the straight line, which indicates the ratio of *N*(final) over *N*(initial) is a function of reaction conditions (initial seed size, number, and material; initiator concentration). The slope decreases with the initiator concentration. It was found that when a high initiator concentration (0.52 wt% and 1 wt% AIBN) was used, the slope is typically less than 1 and increases with the seed size. In the cases of low initiator concentration (0.23 wt% and 0.3 wt% AIBN), the slope can be greater than 1. When the same size particles were used in seeded dispersion polymerizations of MMA, poly(methyl methacrylate) (PMMA) seed gave the largest slope, polystyrene (PS) gave a medium one, and crosslinked PMMA seed gave the smallest one (nearly zero).

Seed particles were traced in seeded dispersion polymerization of MMA using sub-micron size crosslinked fluorescent PMMA particles as seed. All of the seed particles ended up inside the final particles. Final particles containing more than one seed indicate that aggregation occurred during the reaction.

Seed particles were located and tracked in the seeded dispersion polymerization of MMA using sub-micron PS latex particles as seed by means of a refractive index matching technique. The populations of particles containing different number of seeds were analyzed during the reaction. It was found that there are two transition points for the population change. The number of PMMA particles containing no seed particle increased from zero to 9% at the first transition point, which occurred at a quite low conversion (<1%), and remained constant after that. The number of PMMA particles with one seed decreased from 100% to 75% at the first transition point and continued to decrease to 60% at the second transition point, which occurred at 8.7% conversion. After this point, its number remained constant towards the end of the reaction. The number of PMMA particles with two seeds increased from zero to 15% at the first transition point and continued to increase to 23% at the second transition point. It then remained constant. There were some PMMA particles containing more than two seed particles, but their population was less than 10% of the total.

A model was developed to describe the whole dispersion polymerization process, including: (1) polymerization in both particle and continuous phases; and (2) particle nucleation, aggregation, stabilization, and growth. Two particle populations were detected during the simulation using this model. The first population of particles are small, but have a number that is one to three orders of magnitude greater than that of the second population of particles. They are unstable and are considered as transient species. They are continuously generated and captured. They serve as a volume reservoir to the second population of particles. The second population of particles is large in size, but small in number, compared to the first population. They are stable and capture all the first population particles. The model prediction for the seeded dispersion polymerization agrees well with the experimental data on the *N*(final) and *N*(initial) relationship.

Fundamental Study and Applications of Convective Deposition of Microsphere Monolayers

Pisist Kumnnorkaew (Faculty Advisor: James F. Gilchrist)

We examine the fundamental nature of the rapid convective deposition of micro- and nanoscale particles. This process uses a blade to draw a suspension droplet across a substrate thus advancing thin film where particles assemble due to capillary force and create monolayer close-packed structures. The optimal operating ranges to form 2D close-packed microsphere arrays are obtained by varying deposition rate and blade angle. Previous deposition models do not fully describe various aspects of this deposition process. For instance, blade angle and hydrophobicity affect the rapid 2D crystal formation by varying shape and flow within the thin film. High speed confocal laser scanning microscopy reveals the dynamic self-assembly of colloidal particles under convective evaporation. Image analysis of deposited layer quantifies crystal quality through radial distribution function, the fraction of the number of nearest neighbors, and local bond order. Lubrication theory describes flow inside the extended meniscus and explains accelerated and reversal flow phenomena during monolayer deposition.

Building on this foundation, we investigate the coupling between suspension properties and the deposition process during the convective deposition of aqueous binary suspensions of 1 μm silica microspheres and 100 nm polystyrene nanoparticles. At optimal conditions, this binary colloidal suspension creates higher-quality and longer-range monolayer of microsphere with nanoparticle-filled interstitial region. A model is developed to predict the optimum ratio of micro to nanoparticle fluxes during the deposition for creating long-range 2D crystal of microspheres. With unmatched flux, instabilities arise that result in the formation of stripes perpendicular to the direction of deposition.

We successfully utilize 2D crystal formation in various applications. Microlens arrays convectively assembled on the GaN surface improve the efficiency of LEDs by increasing photon extraction efficiency. Our process increased LEDs efficiency by as much as 262%. Furthermore, potential application of this periodic structure on cell capture devices, biological membranes, and photoelectrode of dye sensitized solar cells are discussed.

Optical Bottles: A Quantitative Analysis of Optically Confined Nanoparticle Ensembles in Suspension

Joseph Junio (Faculty Advisor: H. Daniel Ou-Yang)

We present a novel method, the optical bottle that uses a focused laser beam to trap and analyze the optically confined multiple nanoparticles. A theoretical framework based on the mechanical equilibrium of the optical radiation pressure produced by the focused laser beam, and the osmotic pressure produced by the enriched particle concentration in the optical trap is developed for analyzing the ensemble behavior of the optically confined nanoparticles. Experiments were conducted for fluorescently labeled polystyrene nanospheres to determine the optical trapping energy of individual particles as well as the osmotic compressibility of the colloids. The new method has the advantage over conventional methods because it is not limited by the particle concentration, and is relatively easy to implement in situ.

Professor Jung-Hyun Kim

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

Recently Published Papers

Poly(thiophene) Nanoparticles Prepared by Fe3+-Catalyzed Oxidative Polymerization: A Size-Dependent Effect on Photoluminescence Property
Sun Jong Lee, Jung Min Lee, Hak-Ze Cho, Won Gun Koh, In Woo Cheong, and Jung Hyun Kim
Macromolecules, 43 (5), 2484-2489 (2010)

Poly(thiophene) (PTh) nanoparticles with various sizes were directly prepared by Fe3+-catalyzed oxidative emulsion polymerization of thiophene with varying hydrogen peroxide (H_2O_2) concentrations. In the polymerization, $FeCl_3/H_2O_2$ (catalyst/oxidant) combination system was used as an initiator couple. At the optimized reaction condition, percentage monomer conversions were above 90%. With increasing H_2O_2 molar concentration from 2.35 M to 5.88 M, the average sizes of the PTh nanoparticles decreased from 51 nm to 12 nm, and their photo-emission wavelengths shifted from red to blue color at the maximum excitation wavelength (λ_{UVmax} = 400 nm). However, the molecular weights of all PTh nanoparticles were about 3500 g/mol. As a result, we could tune the emitting colors which resulted from variations of the effective conjugation chain length by manipulating the size of PTh nanoparticles.

Self-Doped Conducting Core-Shell Poly(styrene/pyrrole) Nanoparticles via Two-Stage Shot-Growth
Dong Gyu Lee, Jung Min Lee, Yeon Hwa Jo, Sun Jong Lee, Jung Hyun Kim, and In Woo Cheong
Journal of Nanoscience and Nanotechnology, 10 (10), 6912-6915(4) (2010)

Self-doped conducting core-shell poly(styrene/pyrrole) (poly(St/Py)) nanoparticles were successfully prepared by a one-pot synthetic route in both Fe^{3+}-catalyzed oxidative polymerization and emulsifier-free emulsion polymerization. Modified two-stage shot-growth method was introduced to obtain higher doping level of the self-doped conducting core-shell poly(St/Py) nanoparticles. The particle size and core-shell morphology of the resulting particles before and after two-stage shot-growth were investigated by SEM and TEM analyses. Surface charge density of the particles highly increased after two-stage shot-growth and was measured by potential analysis. The self-doped core-shell nanoparticles showed a high conductivity after two-stage shot-growth.

PSS Resin-Fortified Polythiophene Nanoparticles for Highly Transparent Conducting Films
Sun Jong Lee, Ki Nam Oh, Jung Min Lee, Jung Hyun Kim, and In Woo Cheong
Journal of Nanoscience and Nanotechnology, 10 (10), 6944-6947(4) (2010)

Polythiophene/poly(sodium 4-styrene sulfonate) (PT/PSS) composite nanoparticles having different particle size were prepared by Fe3+-catalyzed oxidative polymerization in aqueous medium. This facile method includes a $FeCl_3/H_2O_2$ (catalyst/oxidant) combination system, which guarantees a high conversion (more than 95%) of thiophene monomers in various concentration of poly(styrene sulfonate) (PSS) with only a trace of $FeCl_3$. Particle size of PT/PSS composite nanoparticles decreased from 134 nm to 26 nm as the concentration of PSS and H_2O_2 increased, and which was confirmed by SEM and CHDF analyses.

The poly(ethylene terephthalate) (PET) film coated with PT/PSS was transparent and showed a high conductivity in a dried state. The sheet resistivity decreased as the ratio of PT to PSS increased. Photoluminescence property of the PT/PSS composite nanoparticles was also investigated.

Coming Papers

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

Yeon Jae Jung, Patakamuri Govindaiah, Tae-Joon Park, Sun Jong Lee, Du Yeol Ryu, In Woo Cheong , and Jung Hyun Kim

Journal of Materials Chemistry, Online published (2010)

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

Luminescent Iron Oxide Nanoparticles Prepared by One-pot Aphen-functionalization

Patakamuri Govindaiah, Tae-Joon Park, Yeon Jae Jung, Sun Jong Lee, Du Yeol Ryu, Jung Hyun Kim, and In Woo Cheong

Macromolecular Research, In Press (2010)

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

Effect of Deproteinized Methods on the Proteins and Properties of Natural Rubber Latex during Storage

1. Kanjanee Nawamawat[1],
2. Jitladda T. Sakdapipanich[1,2,*],
3. Chee C. Ho[3]

Macromolecular Symposia

Special Issue: Advanced Particles

Volume 288, Issue 1, pages 95–103, February 2010

DOI: 10.1002/masy.201050212

Keywords:
deproteinization;
gel formation;
natural rubber latex particle;
proteins

Abstract

Summary: Three different methods of deproteinization, i.e. saponification, surfactant washing and enzymatic treatment were employed to unravel the effect of deproteinized on the properties of natural rubber (NR) latex. The cleavage of proteins in NR latex was found to proceed with concomitant formation of low molecular weight polypeptides. This results in a lowering in gel formation of the enzyme-treated latex, indicating modification of the remaining proteins at the rubber chain-end. Washing NR latex with surfactant would efficiently reduce and remove proteins from NR latex particles through denaturation and transferring them to the serum phase. The relatively stable gel formed during storage of surfactant-washed NR latex is an indication of the absence of branch formation of proteins at the rubber molecule terminal. Saponification by strong alkali would hydrolyze the proteins and phospholipids adsorbed on the latex particle surface. The reason of the significantly higher gel formed in saponified NR latex is still not clear. The present study shows that deproteinization treatments result in modification of the proteins at the surface of NR latex particles and also those freely-suspended in the serum. The cleavage or the denaturation of the rubber proteins during purification by washing has a profound effect on the properties of the deproteinized NR latex upon storage, in particular the thermal oxidative aging properties of the rubber obtained.

Professor Joe Keddie

University of Surrey, Guildford, UK

New Book Published This Year

J.L. Keddie and A.F. Routh, *Fundamentals of Latex Film Formation: Processes and Properties* (2010) Springer

This book introduces the reader to latex, which is a colloidal dispersion of polymer particles in water, and explains how useful products are made from it.

The primary focus is the process by which wet latex can be transformed into coatings, adhesives, and composites in the process known as film formation. The book reviews the main experimental techniques used to study the film formation process. It then presents the fundamental concepts for each of the three main stages of the process: evaporation of water, particle deformation, and polymer diffusion. The latest experimental observations are presented along with theoretical descriptions and models. Later chapters consider the effects of surfactant on film properties and describe films made from nanocomposite particles and from blends of latex with nanoparticles, such as clays or carbon nanotubes. The book concludes with a chapter considering the remaining technical challenges and highlighting a few exciting future directions. Throughout the presentation, fundamental concepts are emphasised. Relevant models are explained in an accessible way that does not assume prior knowledge.

This book will serve as a state-of-the art reference for scientists working in industrial R&D and also for researchers in diverse academic subjects, including chemistry, physics, engineering, and materials science.

Recently Accepted Papers

Dan Liu, Che Azurahanim Che Abdullah, Richard P. Sear and Joseph L. Keddie, "Cell adhesion on nanopatterned fibronectin substrates." accepted in *Soft Matter* (available on-line)

Patnarin Worajittiphon, Izabela Jurewicz, Alice A.K. King, Joseph L. Keddie and Alan B. Dalton, "Enhanced Thermal Actuation in Thin Polymer Films through Particle Nano-Squeezing by Carbon Nanotube Belts," accepted in *Adv. Mater.* (available on-line)

Papers Published Since my Last Report

Colloidal Nanocomposites

Tao Wang, Carolina de las Heras Alarcón, Monika Goikoetxea, Itxaso Beristain, Maria Paulis, Maria J. Barandiaran, José M. Asua, and Joseph L. Keddie, "Crosslinked network development in compatibilized alkyd/acrylic hybrid latex films for the creation of hard coatings," *Langmuir* (2010) *26*, 14323–14333.

I. Jurewicz, A.A.K King, P. Worajittiphon, P. Asanithi, E. Brunner, R.P. Sear, T.J.C. Hosea, J.L. Keddie, and A.B. Dalton, "Colloid-Assisted Self-Assembly of Robust, Three-Dimensional Networks of Carbon Nanotubes Over Large Areas," *Macromolecular Rapid Communications* (2010) 31, 609-615. **(Cover article)**

Amaia Agirre, Carolina de las Heras Alarcón, Tao Wang, Joseph L. Keddie, and José M. Asua, "Semicrystalline waterborne pressure-sensitive adhesives," *ACS Applied Materials* *and Interfaces* (2010) **2**: 443-451.

T. Wang, P. J. Colver, S. A. F. Bon, and J. L. Keddie, "Synergistic Effects between Clay and a Soft Polymer in a Supracolloidal Structure Leading to Increased Tack Energy in Pressure-Sensitive Adhesives," *Soft Matter* (2009) **5**, 3842 (**Cover Article**)

E. Canetta, J. Marchal, C.H. Lei, F. Deplace, A. König, C. Creton, K. Ouzineb, and J.L. Keddie, "A Comparison of Tackified, Miniemulsion Core-Shell Acrylic Latex Films with Corresponding Particle-Blend Films: Structure-Property Relationships," *Langmuir* (2009) **25**, 11021-11031

F. Deplace, M.A. Rabjohns, T. Yamaguchi, A.B. Foster, C. Carelli, C.-H. Lei, K. Ouzineb, J.L. Keddie, P.A. Lovell and C. Creton, "Deformation and adhesion of a soft-soft nanocomposite designed with structured polymer colloid particles," *Soft Matter* (2009) **5**, 1440 – 1447.

T. Wang and J.L. Keddie, "Design and fabrication of colloidal polymer nanocomposites," *Adv. Coll. Interf. Sci.* **147-148** (2009) 319-332. (**Review Article**)

Film Formation

T. Wang, E. Canetta, T. G. Weerakkody, J. L. Keddie, "pH-dependence of the properties of waterborne pressure-sensitive adhesives containing acrylic acid," *ACS Applied Materials and Interfaces* (2009) **1**, 631–639.

P. Ekanayake, P.J. McDonald and J.L. Keddie, "An Experimental Test of the Scaling Prediction for the Spatial Distribution of Water during the Drying of Colloidal Films," *European Physical Journal – Special Topics* (2009) **166**, 21-27.

Polymer Films and Surfaces

Akarin Intaniwet, Christopher A. Mills, Paul J. Sellin, Maxim Shkunov and Joseph L. Keddie, "Achieving a Stable Time Response in Polymeric Radiation Sensors under Charge Injection by X-rays," *ACS Applied Materials and Interfaces* (2010) 2, 1692-1699.

I.A. Bushnak, F.H. Labeed, R.P. Sear and J.L. Keddie, "Adhesion of micro-organisms to bovine submaxillary mucin coatings: Effect of coating deposition conditions," *Biofouling* (2010) **26**: 387-397.

A. Intaniwet, C. A. Mills, M. Shkunov, H. Thiem, J. L. Keddie, and P. J. Sellin, "Characterization of thick film poly(triarylamine) semiconductor diodes for direct X-ray detection," *J. Appl. Phys.* (2009) **106**, 064513 (7 pages)

N. A. Nikonenko, I. A. Bushnak, and J. L. Keddie, "Spectroscopic Ellipsometry of Mucin Layers on an Amphiphilic Diblock Copolymer Surface," *Applied Spectroscopy* (2009) **63**, 889-898.

Melanie Bradley, Dan Liu, Joseph L. Keddie, Brian Vincent, and Gary Burnett, "The Uptake and Release of Cationic Surfactant from Polyampholyte Microgel Particles in Dispersion and as an Adsorbed Monolayer," *Langmuir* (2009) **25,** 9677–9683

D. Liu, T. Wang, J.L. Keddie, "Protein nanopatterning on self-organized PS-b-PI thin film templates," *Langmuir* (2009) **25**, 4526–4534.

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

Publication in print

Imino diacetic acid-modified magnetic poly(2-hydroxyethyl methacrylate)-based polymer microspheres for phosphopeptide enrichment. Novotná L., Emmerová T., Horák D., Kučerová Z., Tichá M., *J. Chromatogr. A*

Abstract. Magnetic non-porous hydrophilic poly(2-hydroxyethyl methacrylate-*co*-glycidyl methacrylate) microspheres prepared by the dispersion polymerization and modified with iminodiacetic acid (IDA) were employed for the IMAC separation of phosphopeptides. Fe^{3+} and Ga^{3+} ions immobilized on IDA-modified magnetic microspheres were used for the enrichment of phosphopeptides from the proteolytic digests of two model proteins differing in their physico-chemical properties and phosphate group content: porcine pepsin A and bovine α-casein. The optimum conditions for phosphopeptide adsorption and desorption in both cases were investigated and compared. The phosphopeptides separated from the proteolytic digests were analyzed by matrix-assisted laser desorption/ionization time-of-flight mass spectrometry.

Keywords: IMAC phosphopeptide separation, IDA-modified magnetic microspheres, porcine pepsin A, bovine α-casein

Recent publications

The use of superporous Ac-CGGASIKVAVS-OH modified PHEMA scaffolds to promote cell adhesion and the differentiation of human fetal neural precursors. Kubinová Š., Horák D., Kozubenko N., Vaněček V., Proks V., Price J., Cocks G., Syková E., *Biomaterials* 31, 5966-5975 (2010).

Abstract. Modifications of poly(2-hydroxyethyl methacrylate) (PHEMA) with laminin-derived Ac-CGGASIKVAVS-OH peptide sequences have been developed to construct scaffolds that promote cell adhesion and neural differentiation. Radical copolymerization of 2-hydroxyethyl methacrylate with 2-aminoethyl methacrylate (AEMA) and ethylene dimethacrylate in the presence of ammonium oxalate crystals resulted in the formation of superporous P(HEMA-

AEMA) hydrogels. They were reacted with γ-thiobutyrolactone to yield 2-(4-sulfanylbutanamido)ethyl methacrylate (P(HEMA-AEMA)-SH) unit. The Ac-CGGASIKVAVS-OH peptide was immobilized to the sulfhydryl groups of P(HEMA-AEMA)-SH by 2,2′-dithiodipyridine linking reagent via 2-[4-(2-pyridyldisulfanyl)butanamido]ethyl methacrylate (P(HEMA-AEMA)-TPy). The adhesion and morphology of rat mesenchymal stem cells were investigated on the Ac-CGGASIKVAVS-OH-modified P(HEMA-AEMA) as well as on PHEMA, P(HEMA-AEMA)-SH and P(HEMA-AEMA)-TPy hydrogels. Superporous Ac-CGGASIKVAVS-OH modified PHEMA scaffolds significantly increased the number of attached cells and their growth area on the hydrogel surface in the absence and in the presence of serum in the culture medium. Additionally, the Ac-CGGASIKVAVS-OH peptide supported the attachment, proliferation, differentiation and process spreading of human fetal neural stem cells during the first two weeks of expansion and contributed to the formation of a high percentage of more mature neural cells after four weeks of expansion. The Ac-CGGASIKVAVS-OH modification of superporous P(HEMA-AEMA) hydrogels improves cell adhesive properties and promotes neural stem cell differentiation.

Keywords: cell adhesion, laminin, mesenchymal stem cell, neural cell, polyHEMA

Semisynthesis of C17:0 isoforms of sulphatide and glucosylceramide using immobilised sphingolipid ceramide N-deacylase for application in analytical mass spektrometry. Kuchař L., Rotková J., Asfaw B., Lenfeld J., Horák D., Korecká L., Bílková Z., Ledvinová J., *Rapid Commun. Mass Spectrom*. 24, 2393-2399 (2010).

Abstract. Sphingolipid ceramide N-deacylase (SCDase, EC 3.5.1.69) is a hydrolytic enzyme isolated from Pseudomonas sp. TK 4. In addition to its primary deacylation function, this enzyme is able to reacylate lyso-sphingolipids under specific conditions. We immobilised this enzyme on magnetic macroporous cellulose and used it to semisynthesise C17:0 glucosylceramide and C17:0 sulphatide, which are required internal standards for quantification of the corresponding glycosphingolipids (GSL) by tandem mass spectrometry. A high rate of conversion was achieved for both lipids (80% for C17:0 sulphatide and 90% for C17:0 glucosylceramide). In contrast to synthesis with a soluble form of the enzyme, use of immobilised SCDase significantly reduced the contamination of the sphingolipid products with other isoforms, so further purification was not necessary. Our method can be effectively used for the simple preparation of specifically labelled sphingolipids of high isoform purity for application in mass spectrometry.

Keywords: mass spectrometry, magnetic, cellulose

Contribution to the September 2010 IPCG Newsletter from:
Prof. Donald Sundberg and Prof. John Tsavalas
Nanostructured Polymers Research Center
University of New Hampshire, Durham, NH 03824
Don.sundberg@unh.edu: John.Tsavalas@unh.edu

Carboxylic Acid Functional Monomers in Emulsion Polymerization

Amit Tripathi and Donald Sundberg

Acrylic acid (AA) and methacrylic acid (MAA) represent a very important class of functional monomers. These monomers are much more water soluble than other monomers commonly used in emulsion polymerization and due to the presence of carboxylic acid group, they are responsive to pH changes. Incorporation of AA or MAA in emulsion polymerization provides better colloidal stability when the acid groups are ionized by changing the pH. In order to understand the effect of these functional monomers on polymer reaction kinetics and particle morphology, it is important to understand the distribution of these monomers between all phases present during the reaction. Carboxylic acid monomers have both hydrogen bond donor and acceptor groups and can form hydrogen bonded structures like dimers or multimers. Also, possible ionization brings yet another complexity.

Scientists in the food and petroleum industries have extensively studied carboxylic acid containing compounds (e.g. acetic acid) and in general the distribution of organic acids between water and organic phases is treated by equation (1) ([1])

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

where, D = partition coefficient for the acid i.e. (total measureable concentration of acid in organic phase / total measureable concentration of acid in aqueous phase)

K_d: Equilibrium constant between the monomer form of the acid in the organic phase and the undissociated monomer form of the acid in the aqueous phase

$K_{dim,o}$ = Equilibrium constant for dimerization in the organic phase

[HA] = concentration of the undissociated monomer form of acid in the aqueous phase

K_a = acid dissociation constant

We studied the effect of factors like pH, ionic strength, temperature and non-acid monomer(s) (organic phase) on acid distribution. We learned that in presence of monomers having groups with H-bond acceptors, as in the case of acrylates, dimerization of the acid is limited due to the competition between *acid group to acid group H-bonding* and *acid group to H-bond acceptor group*. On the other hand, in case of styrene the acid dimerization is very high. As a result of these experimental studies, we can now predict the partitioning behavior of AA and MAA between water and mixtures of many different acrylic and styrene monomers. We have also studied the influence of isomeric structures of monomers (e.g. *n*-BMA and *t*-BMA) on the acid monomer distribution and augmented our results with molecular modeling (Spartan).

Along with studies on partitioning between water and monomer phases, we have also studied the partitioning of acid comonomers between water and polymer particles. We used the Noël approach [2] to describe partitioning equilibria. This uses the Flory-Huggins equation to describe partial molar free energy in polymer particle while the partial molar free energy in water phase is described as $\Delta F_{ai} = RT\ln\left({[M_i]_a}/{[M_i]_{a,sat}(h)}\right)$ where $[M_i]_a$ and $[M_i]_{a,sat(h)}$ are the monomer concentration in the water phase and the saturated monomer concentration in the water phase, respectively. With this approach, we obtained Flory-Huggins interaction parameters (χ) for acid monomer and polymer pairs. This gives satisfactory results but the energy contribution from H-bonding is included in the interaction parameter. We are currently using the method demonstrated by Coleman and Painter [3] to describe the partitioning of acid monomers by separating the free energy contributions due to dispersive and dipole forces from those due to H-bonding. We think that this approach holds great promise.

References

1. Al-Modhaf, H. F., Hegazi, M. F., Amer, S. A., & Abu-Shady, A. I., "Partition data of propionic and butyric acids between aqueous NaCl solutions and cyclohexane", *Separation and Purification Technology*, *24*, 329-335, (2001).
2. Noël, L. F. J., Maxwell, I. A. and German, A. L., "Partial swelling of latex particles by two monomers." *Macromolecules* 26(11): 2911-2918, (1993).
3. Coleman, M. M., and Painter., P. C., "Hydrogen bonded polymer blends." *Progress in Polymer Science* 20(1): 1-59, (1995).

Water Whitening of Polymer Films

Bo Jiang, John Tsavalas and Donald Sundberg

It is well known that polymer films, especially those derived from emulsion polymers, blush or whiten when exposed to water in either the liquid or vapor form (the latter happens more slowly, of course). There are many reasons for this and there have been quite a number of papers written on this topic, many of them concentrating on the role of surfactants from the latex in water borne films. However this same whitening can happen in solvent borne films and many people over the years have written about such phenomena in the food packaging industries. Lately we have become interested in differentiating between absorbed ("bound") water that plasticizes the polymer from the "free" water that appears to be responsible for whitening of the polymer. To do this we turned to the DSC so as to first measure the plasticizing effect of water on polymers [1,2], especially in the latex form where the polymer particles are completely saturated with water at all times. This is quite easy to do in an accurate manner. Second, we used the DSC to measure the amount of "free" water in polymer samples that had whitened to various degrees

Figure 1 shows modulated temperature DSC results (plotted as the derivative of the Rev. Cp data) for a poly(methyl acrylate), PMA, film prepared from a simple latex . As indicated in the figure insert, the simple, dry film (optically clear) displayed a Tg peak at ~ 19 C. Placing other pieces of the same film in water for various periods of time resulted in hydroplasticized films with lower and lower Tg's as shown in the figure. At 100 minutes the effective Tg decreased to 9 C and at 230 minutes that dropped to ~7 C. A close look at the latter curve shows another transition occurring ~ 0 C, that being the onset of a melting peak for simple water. When the film was left in the water for 20 hours (it was quite white by then), the DSC results in Figure 1 show a major water melting peak in addition to a hydroplasticized Tg of ~ 3 C. The water content in the polymer for all of the transitions can be quantified to obtain the water in each transition, and can be summed to measure the total water in the sample. The latter can also be measured gravimetrically and compared to the DSC results. In this manner we can separate the bound water responsible for hydroplasticization from that associated with the whitening, or blushing, phenomenon. For the PMA shown in Figure 1 as an example, we calculate that for the 100 minute sample all of the water is "bound" and responsible for lowering the Tg from 19 to 9 C. For the 230 minute sample, most of the water in the polymer (4.8%) is bound, but the film has just started to whiten. Obviously the sample at 20 hours has whitened dramatically and most of the water in the film (10.6%) is free water. Thus we conclude that the DSC can be a simple and accurate instrument with which to study the phenomenon of water whitening of polymer films, whether they are water borne, solvent borne and applied in the melt form.

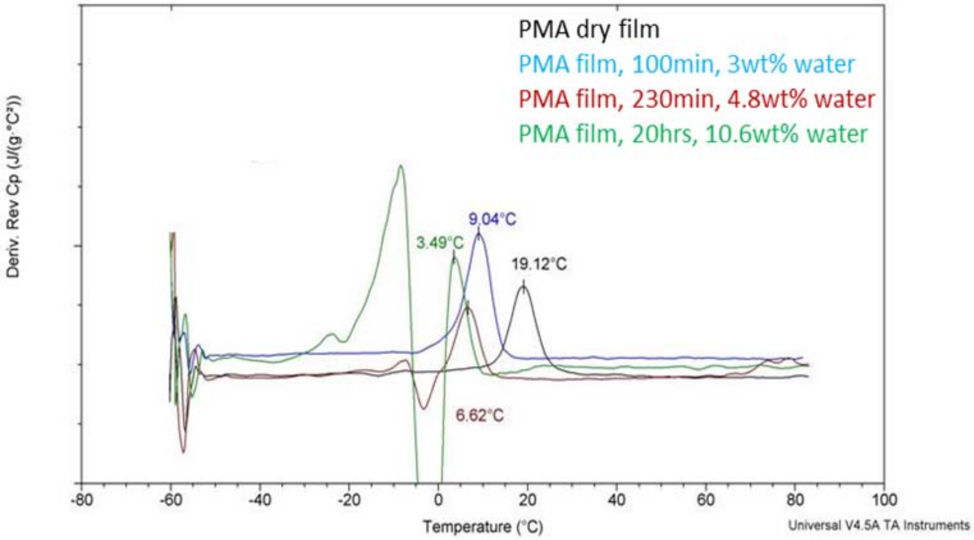


Figure 1. DSC results for PMA films in contact with water

References

1. "Measuring the Glass Transition of Latex Based Polymers in the Hydroplasticized State via Differential Scanning Calorimetry", Bo Jiang, John Tsavalas and Donald Sundberg, Langmuir, *26*, 9408-9415 (2010).
2. "Hydroplasticization of Polymers – Model Predictions and Application to Emulsion Polymers", John Tsavalas and Donald Sundberg, Langmuir, *26*, 6960-6966 (2010).

ICG Montpellier | Institut Charles Gerhardt IAM

Dr. Patrick LACROIX-DESMAZES

Submitted articles:

- *"Solubility and self-assembly of amphiphilic gradient and block copolymers in supercritical CO_2"* T. Ribaut, J. Oberdisse, B. Annighofer, B. Fournel, S. Sarrade, H. Haller, P. Lacroix-Desmazes ***J. Phys. Chem. B***, submitted.

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

Recently published articles:

- *"Synthesis of cationic amphiphilic diblock copolymers of poly(vinylbenzyl triethylammonium chloride) and polystyrene by reverse iodine transfer polymerization (RITP)"* B.N. Patra, D. Rayeroux, P. Lacroix-Desmazes ***Reactive & Functional Polymers*** **2010**, *7*, 408-413. http://dx.doi.org/10.1016/j.reactfunctpolym.2010.03.006
- *"Well architectured PDMS-containing copolymers obtained by radical chemistry: synthesis and properties"* E. Pouget, J. Tonnar, P. Lucas, P. Lacroix-Desmazes, F. Ganachaud, B. Boutevin ***Chemical Reviews*** **2010**, *110*, 1233-1277. http://dx.doi.org/10.1021/cr8001998. *This review contains a small section on silicone containing core-shell particles.*
- *"SANS study of the self-organization of gradient copolymers with ligand groups in supercritical CO_2"* T. Ribaut, J. Oberdisse, B. Annighofer, I. Stoychev, B. Fournel, S. Sarrade, P. Lacroix-Desmazes ***Soft Matter*** **2009**, *5*, 4962-4970. http://dx.doi.org/10.1039/B912268K

Work in progress:

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

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

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

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

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

Dr. François GANACHAUD

All information gathered below concerns exclusively colloidal topics. Productions relating on silicones are available on demand.

Papers (to be) submitted

"Nanoprecipitation of PMMA by solvent shifting 2. Stabilizers"
J. AUBRY, K. ROGER, B. CABANE, F. GANACHAUD
Langmuir, to be submitted (2010)
The influence of various additives on PMMA nanoparticles prepared by solvent shifting emulsification ("Ouzo effect") was investigated. To do so, the variations in particle size right after emulsification and on the long term (typically one month) were studied in the presence of hydroxide anions (obtained via increasing pH aqueous solutions) or non-ionic surfactants. The influence of pH was found striking, with smaller particles generated at high pH values (above 11) and an Ouzo limit shifted towards larger final solute concentrations. On the other hand, surfactants brought on little effects on immediate particle size, even at large concentrations, but increased in some extent the long term colloidal stability. It was demonstrated that the fast adsorption of hydroxide anions onto nuclei surface slows down aggregation, whereas surfactants diffuse too slowly to act similarly. Another general conclusion from this study is that the DLVO theory does not apply to Ouzo-made colloids, whatever the polymer solute considered.

"Cationic Polymerization of Styrene Derivatives and Cyclopentadiene Catalyzed by $B(C_6F_5)_3$ in Aqueous Media: Comparison of Suspension, Emulsion and Dispersion Processes"
S. V. KOSTJUK, F. GANACHAUD, A. V. RADCHENKO, I. V. VASILENKO
Macromol. Symp., submitted (2010).
The cationic polymerization of styrene derivatives [p-methoxystyrene (pMOS), p-hydroxystyrene (pHS), styrene (St)] and cyclopentadiene (CPD) using $B(C_6F_5)_3$-based initiating systems in aqueous media is reported, focusing specifically on the influence of various additives (surfactant, solvent) on the control of the polymerization rate and molar masses. 1-(4-Methoxyphenyl)ethanol (1)/$B(C_6F_5)_3$ system induced living dispersion (in solvent/water mixture, without surfactant) cationic polymerization of pMOS and pHS, affording polymers which M_ns increased in direct proportion to monomer conversion ($Mn \leq 4500$ g mol^{-1}) and which exhibited rather narrow molecular weight distributions ($Mw/Mn \leq 1.5$). Polymerization of St and CPD in suspension (in water without surfactant) proceeded uniquely through activation of the initiator followed by irreversible termination by water giving oligomers with $Mn \leq 2000$ g mol^{-1} and $Mw/Mn \leq 2.0$. Besides, pHSalso polymerized in a living fashion under emulsion (in micellar aqueous solutions) conditions ($Mn \leq 4500$ g mol^{-1}; $Mw/Mn \leq 1.5$) using either BRIJ®97 or hexadecyltrimethylammonium bromide (CTAB) as surfactants, whereas conventional non-living cationic polymerization occurred with pMOS (using BRIJ®97 or CTAB as surfactants) and CPD (using dodecylbenzenesulfonic acid, DBSA).

"Cationic Polymerization of Isoprene Catalyzed by $B(C_6F_5)_3$ Lewis Acid: A Different Route Towards Natural Rubber Polymer Analogues"
S. V. KOSTJUK, S. OUARDAD, F. PERUCH, A. DEFFIEUX, F. GANACHAUD
Macromolecules, to be submitted (2010).

The cationic polymerization of isoprene using 1-(4-methoxyphenyl)ethanol (**1**)/$B(C_6F_5)_3$ initiating system in solution (dichloromethane or α,α,α-trifluorotoluene) and in aqueous media (suspension, dispersion or emulsion) is reported. In organic solvents, reaction proceeded through a controlled initiation via **1** followed by irreversible termination, affording polymers with a number average molar mass $M_n \leq 5{,}000$ g mol^{-1}, relatively narrow molar mass distribution or MMD ($M_w/M_n \leq 2.5$) and rather high content of intact double bonds (≥70%) in polymer backbone. In particular, using α,α,α-trifluorotoluene as polymerization solvent in place of dichloromethane promoted the synthesis of poly(isoprene) chains with quite narrow MMD ($M_w/M_n \sim 1.4$) and larger content of intact double bonds (up to 88%). Meanwhile, polymers with fairly high molar mass (M_n up to 18,000 g mol^{-1}) and reasonable MMD ($M_{w/}M_n<2.4$) were synthesized in absence of **1** through adventitious water/$B(C_6F_5)_3$-initiated cationic polymerization of isoprene. In aqueous media, the cationic polymerization of isoprene with **1**/$B(C_6F_5)_3$ proceeded without any side reactions (cyclization, branching). Nevertheless, polymerization with large contents of surrounding water afforded only moderate yield (up to 60% monomer conversion) and polyisoprene chains of low M_n (≤1,200 g mol^{-1}) and relatively broad MMD ($M_w/M_n \leq 1.7$). By crossing different characterization data (NMR, mass spectrometry), it was demonstrated that under appropriate conditions (in organic solvents at −30 °C or in aqueous media), 1,4-poly(isoprene)s carrying a specific initiator fragment at the α-end and an olefinic terminal group can be produced almost exclusively in a *trans*-1,4 configuration (92–96.5%).

Work in progress on emulsions:

Sergei KOSTJUK (Post-Doc, 2 years): *Cationic polymerization of dienes in aqueous-based processes: towards the generation of synthetic Natural Rubber?*
Julien AUBRY (Third year PhD student): *Application of Ouzo effect in encapsulation of active ingredients.*

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

Papers or patent recently published:

"New Synthetic Strategies for Structured Silicones Using $B(C_6F_5)_3$"
M. A. BROOK, J. B. GRANDE, F. GANACHAUD
Advances in Polymer Science, published in advance (2010).
DOI: 10.1007/12_2009_47

"Nanocomposite materials and fabrication process by nanoprecipitation"
P. LUCAS, F. GANACHAUD, J. AUBRY, M. VAYSSE
World Patent WO2010040218, assigned to Nanoledge Inc. (2010).

Contribution: Dr. A. Yu. Menshıkova
E-mails: asya@hq.macro.ru ; mensh_asya@yahoo.com

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

Recently published papers

Mitrokhin, V. P.; Ivanov, A. A.; Men'shikova, A. Yu.; Yakimanskii, A. V.; Alfimov M. V.; Zheltikov, A. M.
Highly refractive three-dimensional photonic crystals for optical sensing systems
Nanotechnologies in Russia, 2010, 5(7–8), 538–542.

Abstract

We investigate optical properties of three-dimensional photonic-crystal systems consisting of spherical nanoparticles of styrene copolymer with methacrylic acid closely packed into a face-centered cubic lattice. The effective refractive index of such structures is shown to be much higher than effective refractive indices typical of synthetic-opal-type photonic crystals. Highly refractive photonic-crystal systems combined with diffuse light scattering components radically improve the sensitivity of optical sensing elements within a broad frequency range.

Moskalenko, Yu.; Shevchenko, N.; Mokeev, M.; Men'shikova, A.; Yakimanskii, A.; Gribanov, A.
Solid-state ^{13}C NMR spectroscopic examination of lower alcohol vapor sorption by cross-linked poly(methyl methacrylate) particles
Russian J Appl Chem, 2010 83(3), 400-405

Abstract

The sensitivity and selectivity of methyl methacrylate-ethylene glycol dimethacrylate copolymers with respect to lower alcohol (methanol, ethanol, and propanol-2) vapors were examined by solid-state ^{13}C NMR spectroscopy. A comparative analysis was carried out for the capabilities of various spectral techniques for studying sorption processes in cross-linked polymer particles.

INTERNATIONAL POLYMER COLLOIDS GROUP - NEWS LETTER

Haruma Kawaguchi, Ph.D.
Professor, Kanagawa University
Professor Emeritus, Keio University
haruma@kanagawa-u.ac.jp

Publication

"Advanced Particles" - - - Macromolecular Symposia, 288 (published in March, 2010**)**

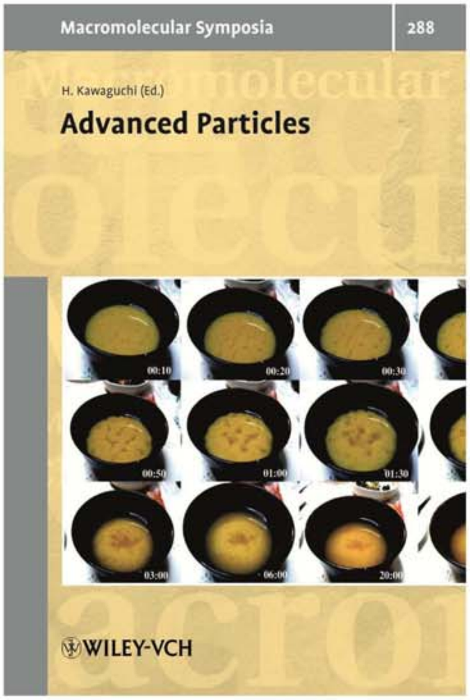
This is a special issue of Macromolecular Symposia for the conference "2nd International Symposium on Advance Particles (ISAP2009) / 19th IKETANI Conference" (held on April 26-29, 2009 at Keio University, Yokohama, JAPAN).

The issue was edited by myself and included 16 articles which were presented at ISAP 2009.

List of articles in the special issue:

1. Mechanism and modeling of emulsion polymerization: New ideas and concepts
   1.Particle Nucleation., K. Tauer, P. Nazaran
2. Mechanism and modeling of emulsion polymerization: New ideas and concepts
   2.Modeling strategies., K. Tauer, H. Hernandez.
3. Fundamentals of RAFT miniemulsion polymerization kinetics. H. Tobita
4. Emulsifier-free, organ tellurium-mediated living radical emulsion polymerization of styrene.
   Y. Kitayama, A. Chaiyasat, M. Okubo
5. Formation of nonspherical parties with uneven surface in emulsion copolymerization of styrene and methacrylic acid with nonionic emulsification process.
   L. Haipu, T. Suzuki, M. Okubo.
6. Preparation of uniform microspheres and microcapsules by modified emulsification process.
   G..H. Ma, J. Yang, P. P. Lv, L. Y. Wang, W. Wei, R. Tian, J. Wu, Z. Z. Su.
7. Preparation of Nylon-6 particles in ionic liquids.
   H. Minami, H. Minami, . W. Tarutami, K. Yoshida, M. Okubo,
8. Effect of polymer end group on the morphology of polystyrene/ poly(methyl methacrylate) composite particles prepared by the solvent evaporation method,
   T. Tanaka, M. Okayama, M. Okubo.
9. Dissipative structure in the course of drying suspensions and solutions. T. Okubo
10. Shear thinning behavior of concentrated latex dispersions.
    K. Takamura, Theo G. M. van de Ven
11. Photon trapping and the enhancement of electronic excitation energy transfer efficiency caused by colloidal crystals. A. Tsuchida, Y. Ohi, S. Takahashi. H. Kimura, T. Okubo.

12. Effect of deproteinized methods on the proteins and properties of natural rubber latex during storage. K. Nawamawat, Jitladda, T. Sakdapipanich, c. C. Ho.
13. Metal nanoparticle/polymer hybrid particles. The catalytic activity of metal nanoparticles formed on the surface of polymer particles by UV irradiation.
    M. Tamai, M. Watanabe, T. Teramura, N.NIshioka, K..Matsukawa.
14. Encapsulation of Hemoglobin using condensation reaction of butylcyanoacetate with formaldehyde. H. Shimizu, M. tomozawa, R. Wada, M. Okabe.
15. Reactive and highly submicron magnetic latexes for bionanotechnology applications.
    A. Elaissari, H. Fessi
16. Functionalized biodegradable nano- and micro-spheres for medical applications.
    S. Slomkowski.



Macromolecular Symposia 288

H. Kawaguchi (Ed.)

Advanced Particles

WILEY-VCH

Cover of the special issue of Macromolecular Symposia

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

Papers submitted or in press

Preparation and optical properties of novel bioactive, photonic crystals obtained from core-shell poly(styrene/α-tert-butoxy-ω-vinylbenzyl-polyglycidol) microspheres

Monika Dybkowska[1], Nebewia Griffete[2], Claire Mangeney[2], Teresa Basinska[1], Mohamed M. Chehimi[2], Stanislaw Slomkowski[2]

Center of Molecular and Macromolecular Studies, Polish Academy of Sciences,
Sienkiewicza 112, 90-363 Lodz, Poland
2Interfaces, Traitements, Organisation & Dynamique des Systèmes (ITODYS), Université
Paris Diderot-CNRS (UMR 7086), 15 rue Jean de Baïf, 75013 Paris, France

Abstract

Optical properties of polymer microspheres with polystyrene cores and polyglycidol enriched shells (P(S/PGL)), in the 225-819 nm size range, were studied before and after immobilization of ovalbumin. The P(S/PGL) particles were synthesized by emulsifier free emulsion copolymerization of styrene and polyglycidol macromonomer (poly(styrene/α-tertbutoxy-ω-vinylbenzyl-polyglycidol)) initiated with potassium persulfate. Particles with various diameters and polyglycidol fractions in interfacial regions (from 24.5 to 42.3 mol%) were obtained, depending on the initial concentration of macromonomer in the polymerization mixture. Colloidal crystals from the abovementioned particles were obtained by deposition of particles suspensions in water on the glass slides and subsequent water evaporation. All particles were found to be suitable for formation of colloidal crystals with fcc type arrangement. The first maximum in the Bragg scattering spectrum of colloidal crystals from P(S/PGL) particles did vary from 548 nm (for particles with Dn = 225 nm) to 648 nm (for particles with Dn = 271 nm). It has been found that properties of colloidal crystals from P(S/PGL) microspheres strongly depend on modification of their interfacial layer. In the case of colloidal crystal from the primary P(S/PGL) particles (Dn = 271 nm) the Bragg scattering maximum was at 570 nm, whereas for crystals from the same particles modified by covalent attachment of ovalbumin the maximum Bragg signal was at 560 nm. It is concluded that PGL-based colloidal particles combine interesting optical and bioactive properties potentially useful for the development of new optical biosensors.

Submitted to Colloids and Surfaces B-Biointerfaces

Recently published papers

1. Stanislaw Slomkowski
   Polymer nano- and microparticle based systems for medical diagnostics
   Macromolecular Symposia, 288,121-129 (2010)

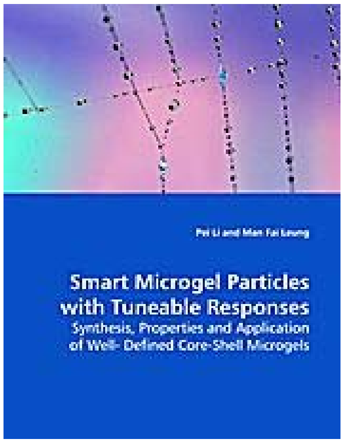
2. Nebewia Griffete, Monika Dybkowska, Bartosz Glebocki, Teresa Basinska, Carole Connan, Agnès Maître, Mohamed M. Chehimi, Stanislaw Slomkowski, Claire Mangeney
   Thermoresponsive colloidal crystals built from coreshell poly(styrene/α-tert-butoxy-ω-vinylbenzylpolyglycidol)microspheres
   Langmuir, 26, 11550-11557 (2010)

Contribution from Prof. Pauline Pei Li, E-mail: bcpeili@polyu.edu.hk

Department of Applied Biology and Chemical Technology
The Hong Kong Polytechnic University, Hong Kong

Recent Publications

1. Pei Li and Man Fai Leung, A monograph entitled *"Smart Microgel Particles with Tunable Responses: Synthesis, Properties and Application of Well-Defined Core–Shell Microgels"* Based on a Ph.D. thesis published by VDM Verlag, Germany (http://www.vdm-publishing.com, ISBN-10: 3639002970), **2009**

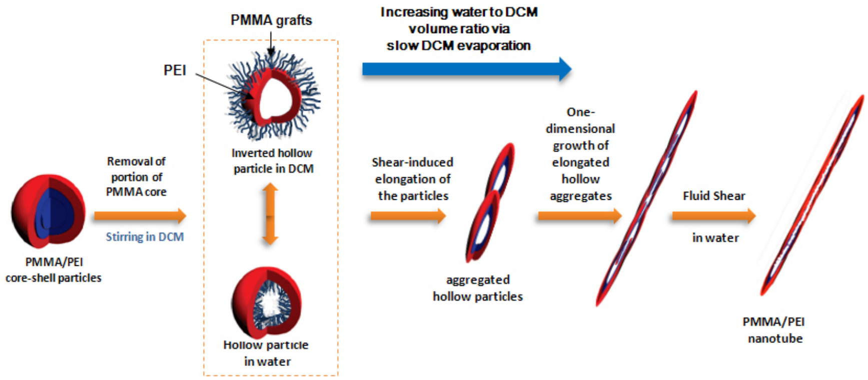

Pei Li and Man Fai Leung

Smart Microgel Particles with Tuneable Responses
Synthesis, Properties and Application of Well- Defined Core-Shell Microgels

Abstract: Colloidal microgels that are able to alter their volume and properties in response to environmental stimuli are attractive materials for various applications. However, current methods to prepare microgels that possess both pH- and temperature-sensitive properties still suffer from two major drawbacks: 1) Limit to the use of pH-sensitive vinylic monomer. Thus, many pH-sensitive polymers like bio- and synthetic polymers cannot be used. 2) Phase transition temperature of the polymer is influenced by protonation degree of the pH-sensitive polymer. In this book, a novel method to prepare smart microgels that consist of well-defined temperature-sensitive cores with pH-sensitive shells is described in details. The microgels are synthesized directly from aqueous graft copolymerization of *N*-isopropylacrylamide or *N*-vinylcaprolactam with a crosslinker, from water-soluble polymer of poly(ethylenimine) or chitosan. The well-defined core–shell nanostructure exhibits tunable responses to pH, temperature and electrolyte changes. Thus, this new type of smart materials should be extremely useful in drug delivery, biosensing, separation technology, etc.

2. Cheng Hao Lee, Kin Man Ho, Frank W. Harris, Stephen Z. D. Cheng and Pei Li "Formation of Nanostructured Materials using Inexpensive Hollow Particles of Amphiphilic Graft Copolymers as Building Blocks: 1. Insight into the Mechanism of Nanotube Formation". *Soft Matter* **2009**, *5*, 4914.

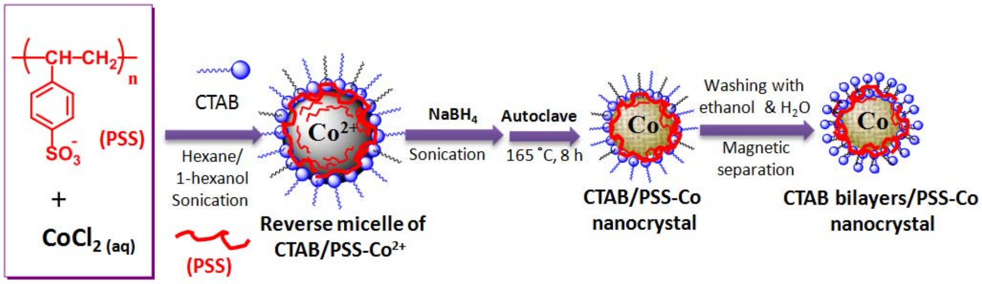
Abstract: The aim of this research is to elucidate the mechanism for the formation of nanotubes from hollow particles of amphiphilic graft copolymers, such as poly(ethyleneimine)-*graft*-poly(methyl methacrylate) (PEI-*g*-PMMA), under non-equilibrium conditions. The study was performed at either 15 or 17 °C with fluid shear in a mixture of dichloromethane (DCM)–water using the amphiphilic hollow particle as a building block. Effects of stirring rate and DCM to water ratio on the hollow particle assembly were systematically investigated. Surface properties and morphology of the hollow particles and the resulting assemblies in both DCM and water were characterized by X-ray photoelectron spectroscopy, scanning electron microscopy, transmission electron microscopy and atomic force microscopy. Results from these studies suggest four key features of this assembly process: (1) morphology of the amphiphilic hollow particle can be inverted in organic solvent and water. (2) The assembly process can only occur with appropriate fluid shear and DCM : water ratio. (3) The hollow particles can undergo deformation to ellipsoidal shapes with stirring rate at 350 rpm in an appropriate DCM : water (*e.g.* 3:7 v/v) mixture. (4) The elongated hollow particles then assemble to form linear aggregates *via* tip-to-tip connection, followed by coalescence and fusion to generate nanotubes with diameters less than 150 nm. The lengths of the nanotubes can be up to micron-scale, and they can be easily aligned *via* a simple dip-coating method. This simple and inexpensive assembly process using amphiphilic hollow particles as a building block is dramatically different from the well-known self-assembly of block copolymers into different nanostructures under equilibrium conditions.



3. Xian-Hua Zhang, Kin Man Ho, Ai-Hua Wu, Kin Hung Wong, Pei Li, "Hydrothermal Microemulsion Synthesis of Oxidatively Stable Cobalt Nanocrystals Encapsulated in Surfactant/Polymer Complex Shells" *Langmuir* **2010**, *26(8)*, 6009.

Abstract: Air-stable magnetic cobalt nanocrystals have been conveniently prepared via a reverse micellar synthesis, followed by a hydrothermal treatment. The synthesis was carried out by first mixing an aqueous solution containing cobalt chloride and poly(sodium 4-styrenesulfonate) (PSS) with an organic mixture containing cetyltrimethylammonium bromide (CTAB) to form reverse micelles, followed by reducing cobalt ions with sodium borohydride. The resultant nanoparticles were then undergone a hydrothermal treatment at 165 °C for 8 h to generate well-dispersed CTAB/PSS-encapsulated cobalt nanocrystals with an average diameter of 3.5 ± 0.5 nm. The nanoparticles were highly crystalline with a hexagonal close-packed crystal phase. The

presence of CTAB/PSS complex coatings was identified by FT-IR and UV-Vis spectroscopes as well as thermogravimetry analyses. The nanocrystals exhibited superparamagnetic property at room temperature with a saturation magnetization (M_S) of 95 emu/g. The magnetization could be largely preserved after storage at room temperature for 4 months as the Ms value only slightly decreased to 88 emu/g (measured at 300 K). Thus, the polymer encapsulation could not only improve thermal stability of the micelles for the growth and nucleation of Co atoms but also protect the resulting cobalt nanocrystals from oxidation through forming an oxygen impermeable sheath.

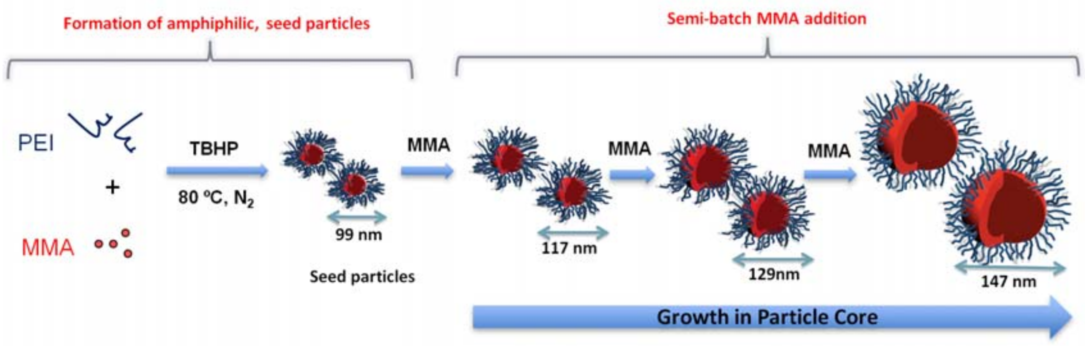


4. Kin Man Ho, Wei Ying Li, Chun Him Wong and Pei Li, A review article entitled "Amphiphilic Polymeric Particles with Core–Shell Nanostructures: Emulsion-Based Syntheses and Potential Applications" *Colloid & Polymer Science* **2010**, DOI: 10.1007/s00396-010-2276-9.

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

5. Kin Man Ho, Wei Ying Li, Cheng Hao Lee, Chun Ho Yam, Robert G. Gilbert, Pei Li, "Mechanistic study of the formation of amphiphilic core–shell particles by grafting methyl methacrylate from polyethylenimine through emulsion polymerization" *Polymer* **2010**, *51*, 3512.

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



Contribution from J.C. Pinto

Unpublished papers

Evaluation of Water in Crude Oil Emulsion Stability Using Critical Electrical Field: Effect of Emulsion Preparation Procedure and Crude Oil Properties

Raquel C. C. Coutinho, José Carlos Pinto, Marcio Nele, Andreas Hannisdal, Johan Sjöblom

Critical electrical field has been used as a tool to probe water in crude emulsion stability in the presence of electrical fields in previous studies. Given the increasing importance of this technique for characterization of emulsion stability, this study investigates the factors that control the reproducibility of the electrical field measurement and the effect of emulsion preparation variables on critical electrical field. It was observed that the emulsion preparation procedure has a strong effect on the measured critical values due to droplet size effects. Furthermore, the effect of crude oil properties on the critical electrical field was investigated using emulsions from different oils but with the same average droplet diameter. It was found that the electrical field variations were controlled by the crude oil viscosity.

Real-Time Monitoring and Parameter Estimation of the Emulsion Polymerization of Carboxylated Styrene/Butadiene Latexes

Matheus Soares, Fabricio Machado, Alessandro Guimarães, Marcelo M. Amaral, José Carlos Pinto

This work presents a first-principles mathematical model for semibatch carboxylated styrene/butadiene (XSBR) emulsion polymerizations, intended for the online and real-time data reconciliation and monitoring of polymerization reactors. The proposed procedure assumes that some parameters must be estimated in real time, for accommodation of the unavoidable fluctuation of operation conditions, as observed at plant site. A direct search complex algorithm was employed for estimation of model parameters based on available pressure, temperature and feed flow rate profiles, allowing for prediction of important properties of XSBR latexes in real-time, such as the monomer conversion, the solids content and the copolymer composition. The proposed model and monitoring strategy were validated with actual data obtained in a pilot plant reactor and in a full-scale industrial process.

Data Reconciliation and Control in Styrene-Butadiene Emulsion Polymerizations

Paula Naomi Souza, Matheus Soares, Marcelo M. Amaral, Enrique Luis Lima, José Carlos Pinto

A nonlinear model-based predictive control (NLMPC) method was developed using a First Principles model of an emulsion copolymerization of carboxylated styrene butadiene rubber (XSBR). Copolymer composition, conversion and average molecular weights of the copolymer were chosen as the controlled variables due to their influence on the final product properties and quality. These properties, however, are rarely measured in-line due to the operational difficulties associated with their measurement. For this reason a soft-sensor using reaction calorimetry techniques was developed and used to infer reaction conditions, rates, species concentrations and polymer properties in a industrial scale emulsion polymerization reactor.

Work in progress

Barbara Lorca, PhD Thesis, Analysis of kinetic and physical effects during the preparation of nanocapsules and nanospheres that contain sunscreens.

Caio Melo, PhD Thesis, Modeling and control of miniemulsion polymerization reactors.

Laís Fonseca, PhD Thesis, Nanoencapsulation of praziquantel for development of alternative treatments of esquistosomosis.

Marina Besteti, PhD Thesis, Preparation of core-shell polymer particles for use as supports of enzymatic catalysts.

Recently published papers

Magnetic Field Sensor Based on a Maghemite / Polyaniline Hybrid Material, F.G. Souza Jr., J.A. Marins, J.C. Pinto, G.E. Oliveira, C.M. Rodrigues and L.M.T.R. Lima, *J. Mat. Sci*., **45**, 18, 5012-5021, 2010.

A Magnetic Biocomposite for Cleaning of Oil Spills on Water, J.A. Marins, C.H.M. Rodrigues, J.C. Pinto and F.G. Souza Jr, *Macromol. Mat. Eng.*, **295**, 10, 942-948, 2010.

October 2010

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

Manuscripts in Preparation

Thomson, Mary E., Ness, Jason S., Schmidt, Scott C., Cunningham' Michael F. "High solids nitroxide mediated microemulsion polymerization of MMA with a small amount of styrene, and the synthesis of (MMA-co-St)-block-(BMA-co-St) polymers."

Abstract

We report the first nitroxide mediated microemulsion polymerization of methyl methacrylate-co-styrene as well as the synthesis of (MMA-co-St)-block-(n-BMA-co-St) polymers using a one-pot, two-stage differential monomer addition technique. These microemulsion polymerizations were conducted with commercially available materials and do not require a preliminary synthesis step. The latexes are optically translucent with monomodal particle size distributions, particle sizes ranging from 20-30 nm, polymer contents up to 40%, high initiator efficiencies, and low surfactant to monomer ratios (0.28-0.13 wt/wt). The polymerizations exhibited fast reaction rates resulting in well-controlled reactions yielding high molecular weight polymer (>100,000 g·mol^{-1}). The styrene content and duration of the 1st stage were particularly important for obtaining narrow molecular weight distributions, with 30 mol% styrene in the 1st stage (~8-10 mol% styrene overall in the polymer) resulting in the best controlled polymerizations. The overall styrene content in the latexes can be as low as 8 mol% while maintaining excellent control. These MMA-co-St microemulsion latexes can readily be chain extended with n-BMA-co-St while preserving monomodal particle size distributions.

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

Abstract

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

Fowler, Candace I., Muchemu, Christina, Miller, Ricarda E., Phan, Lam, Cunningham, Michael F., Jessop, Philip G. "Emulsion Polymerization of Styrene and Methyl Methacrylate using Cationic Switchable Surfactants"

Abstract

Colloidal latexes of polystyrene and poly(methyl methacrylate) have been prepared using cationic amidine-based switchable surfactants. Particles with sizes ranging from 50 nm to 350 nm have been prepared and the effect of factors such as initiator type, initiator amount, surfactant amount and solid content on the particle size and zeta potential of the resulting latexes have been examined. Destabilization of the latexes requires only air and heat (rather than the conventional salts or acids) which destabilize the latex by removing CO_2 from the system and switching the active amidinium bicarbonate surfactant to a neutral, non-surface active amidine compound. The resulting micron sized particles can be easily filtered to yield a dry polymer powder and a clear aqueous phase.

Recent Publications

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

Abstract

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

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

Abstract

Nitroxide-mediated emulsion polymerization of n-butyl methacrylate (BMA) can produce highly living and well controlled polymer chains when polymerized in the presence of 10 mol% styrene (St) using a one-pot, differential monomer addition technique. When n-BMA-co-St is polymerized in the presence of a surfactant above the critical micelle concentration, bimodal particle size distributions are obtained, likely as a result of combined micellar and aggregative nucleation mechanisms. This phenomenon is not observed for the more hydrophilic monomer system of methyl methacrylate and styrene. In the absence of surfactant, however, it is possible to prepare stable, monomodal latexes.

Using *N-tert*-butyl-*N*-(1-diethylphosphono-2,2-dimethylpropyl) nitroxide (SG1), we report the first nitroxide-mediated polymerization of n-butyl methacrylate with a small amount of styrene in a facile surfactant-free emulsion polymerization system. The surfactant-free system requires no separate macroinitiator synthesis step and produces highly living polymers with monomodal particle size distributions. The initiator efficiency can be increased by the addition of methyl acrylate, or by the addition of surfactant at concentrations below the critical micelle concentration in the absence of methyl acrylate.

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

Abstract

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

Thomson, Mary E.; Cunningham, Michael F.. "Compartmentalization Effects on the Rate of Polymerization and the Degree of Control in ATRP Aqueous Dispersed Phase Polymerization". Macromolecules (2010), 43(6), 2772-2779.

Abstract

Compartmentalization in atom transfer radical polymerization (ATRP) in an aqueous dispersed phase system has been investigated theoretically to understand the effects of particle size on the rate of polymerization and the degree of control on the livingness and polydispersity index (PDI) for the system n-butyl methacrylate/CuBr/EHA$_6$TREN. The simulations indicate there exists a defined range of particle sizes where the rate of polymerization is higher than that of a bulk system, and where PDI and frequency of termination remain below that of bulk polymerization. For this highly active catalyst system, the livingness of the chains is a function only of the particle size and is independent of the rate of reaction. Simulations conducted with very low catalyst concentrations suggest the rate of polymerization decreases and the PDI increases with diminishing catalyst concentration, while the chain livingness is improved.

Thomas E. Enright, Michael F. Cunningham, and Barkev Keoshkerian. Nitroxide-Mediated Bulk and Miniemulsion (Co)Polymerization in a Continuous Tubular Reactor. Macromolecular Reaction Engineering (2010), 4(3-4), 186-196.

Abstract

In previous work, a modified miniemulsion polymerization was demonstrated in a continuous tubular reactor to prepare a latex of polystyrene homopolymer dispersed in water. In that work, some reaction steps were done in a batch reactor and others were done in a continuous tubular reactor. This paper describes an extension of the previous work in which all reaction steps have been done in the continuous tubular reactor and copolymerization has also been attempted. The synthesis of polystyrene homopolymer and poly(styrene-block-*n*-butyl acrylate) copolymers and terpolymers by miniemulsion polymerization in the tubular reactor is described.

Chan, Nicky; Cunningham, Michael F.; Hutchinson, Robin A.. "Reducing ATRP Catalyst Concentration in Batch, Semibatch and Continuous Reactors". Macromolecular Reaction Engineering (2010), 4(6-7), 369-380.

Abstract

An overview of solution ATRPs carried out in batch, semibatch and continuous tubular and stirred-tank reactor systems is presented. Initial work using a heterogeneous catalyst system with copper to polymer chain ratios of close to unity demonstrated the versatility of ATRP in producing homopolymer and copolymer at reasonable rates with good MW control and narrow polydispersity. The significant drawbacks of low catalyst solubility and high copper levels are now being addressed through use of the ARGET ATRP chemistry. Nearly colorless acrylate and methacrylate polymers have been produced with copper catalyst levels below 50 ppm (relative to monomer), with excellent control of MW obtained both in batch and continuous systems.

El-Jaby, U.; Cunningham, Michael F.; McKenna, Timothy F.. "The Advantages of in situ Surfactant Generation for Miniemulsions." Macromolecular Rapid Communications (2010), 31(6), 558-562.

Abstract

The stabilisation of miniemulsions using an in situ generated surfactant is presented. This surfactant, prepared from of a water-soluble base and an oil-soluble long chain acid was successfully used to create stable miniemulsions with up to 60 vol.-% organic phase. It is shown that the creation of a surface active species at the oil-water interface allowed stable miniemulsions to be generated more rapidly than when using conventional surfactant. In addition, polymerised miniemulsions exhibited less secondary nucleation when in situ surfactants were used.

El-Jaby, U.; Cunningham, Michael F.; McKenna, Timothy F.. "Miniemulsions via in situ Surfactant Generation." Macromolecular Chemistry and Physics (2010), 211(12), 1377-1386.

Abstract

The preparation and stabilisation of miniemulsions using in situ generated surfactants is described. Neutralising a water-soluble base with an oil-soluble long-chain acid instantaneously generates in situ surfactants at the oil/water interface, resulting in a rapid homogenisation/polymerisation process. It was found that droplet sizes decreased with surfactant concentration and solid content and that in situ generated potassium stearate is not capable of simultaneously serving as a surfactant and costabiliser. However, the presence of stearic acid delays the rate of ripening. A number of in situ surfactants were prepared with different acids and bases. It was found that the droplet size decreased with the hydrated radius of the counterions.

Smeets, Niels M.B.; Heuts, Johan P.A.; Meuldijk, Jan; Cunningham, Michael F.; van Herk , Alex M.. "The Effect of Co(II) Mediated Catalytic Chain Transfer on the Emulsion Polymerization Kinetics of Methyl Methacrylate Journal of Polymer Science Part A: Polymer Chemistry. (2009) 47, 5078-5089.

Abstract

The effect of the addition of bis[(difluoroboryl) dimethylglyoximato] cobalt(II) (COBF) in the catalytic chain transfer mediated *ab initio* emulsion polymerization of methyl methacrylate was investigated. The emulsion polymerization kinetics have been studied with varying surfactant, initiator and COBF concentrations. The experimentally determined average number of radicals per particle is a strong function of the concentration of COBF and proves to be in good agreement with the theoretical ones. The apparent chain transfer constant, determined up to high conversion, is in excellent agreement with the predicted value based on a mathematical model based on partitioning and the Mayo equation. The results of this work enhance the fundamental understanding of the effects the addition of a catalytic chain transfer agent has on the emulsion polymerization kinetics and the control of the molecular weight distribution.

El-Jaby, Ula; Farzi, Ghomali; Bourgeat-Lami, Elodie; Cunningham, Michael; McKenna, Timothy F.L.. "Emulsification for Latex Production using Static Mixers". Macromolecular Symposia (2009), 281, 77-84.

Abstract

Miniemulsion polymerisation introduces a fresh new outlook on latex production due to its functional versatility to incorporate organic and inorganic compounds. This allows us to create novel latices using the same basic materials used in emulsion technology[i]. Miniemulsion droplets with diameters typically on the order of 50 – 500 nm are created by mechanically dispersing an organic phase in an aqueous medium using a mechanical homogenizer coupled with a well-adapted stabilization system. The organic phase consists of monomer and a hydrophobic costabiliser that reduces the rate of Ostwald ripening[ii]. The aqueous phase typically contains an anionic, cationic or non-ionic surfactant or a blend thereof. In the case of a free radical polymerization, the initiator can be either water[iii] or oil – soluble[iv]. The polymerisation proceeds in such a manner that the monomer droplets are converted directly to polymer particles. In an 'ideal' miniemulsion, each monomer droplet is converted to a polymer particle.

Smeets, Niels M.B.; Heuts, Johan P.A.; Meuldijk, Jan; Cunningham, Michael F.; van Herk , Alex M.. "Mass Transport Limitations and their Effect on the Control of the Molecular Weight Distribution in Catalytic Chain Transfer Mediated Emulsion Polymerization". Macromolecules. (2009) 42, 6422–6428.

Abstract

The existence of mass transport limitations in catalytic chain transfer mediated emulsion polymerization using bis[(difluoroboryl) dimethylglyoximato] cobalt(II) (COBF) was investigated. The rate of mass transport of COBF from the aqueous phase towards the polymer particles proved to depend strongly on the viscosity inside the polymer particles, i.e. the instantaneous conversion. At high instantaneous conversion the partitioning of COBF is severely limited, resulting in accumulation of COBF which severely affects the aqueous phase polymerization kinetics and limits the control of the molecular weight distribution. At low instantaneous conversion COBF readily partitions between the aqueous phase and polymer particles resulting in immediate molecular weight control. The concentration of COBF inside the polymer particles during the polymerization, which can be used as a measure for the rate of COBF mass transport, was successfully quantified using the chain length distribution method.The results of this work clearly show that the presence of a catalytic chain transfer agent can severely affect the emulsion polymerization kinetics. Molecular weight control during the final stages of an emulsion polymerization can be limited by the increasing viscosity inside the polymer particles, which limits the mass transport of COBF from the aqueous phase towards the polymer particles.

Smeets, Niels M.B.; Heuts, Johan P.A.; Meuldijk, Jan; Cunningham, Michael F.; van Herk, Alex M.. "Evidence of Compartmentalization in Catalytic Chain Transfer Mediated Emulsion Polymerization of Methyl Methacrylate". Macromolecules. (2009) 42, 7332-7341.

Abstract

Evidence of compartmentalization of the catalytic chain transfer agent in seeded emulsion polymerization is shown experimentally. The addition of bis[(difluoroboryl) dimethylglyoximato] cobalt(II) (COBF) to seed particles swollen below their maximum saturation concentration, exhibited multimodal molecular weight distributions (MWD) which are contributed to a statistical distribution of COBF molecules over the polymer particles. The experimental observations suggest that there are two limits for catalytic chain transfer in emulsion polymerization: (*i*) at the earlier stages of the polymerization where a global COBF concentration governs the MWD and (*ii*) at the latter stages of the polymerization where a statistical distribution of COBF molecules governs the MWD. To the best of our knowledge, these results are the first to suggest evidence of compartmentalization in catalytic chain transfer mediated emulsion polymerization.

El-Jaby, Ula; Cunningham, Michael; McKenna, Timothy F.L.. "Investigation of the Production of Miniemulsions using an SMX Static Mixer". Industrial and Engineering Chemistry Research (2009), 48, 10147-10151.

Abstract

Ultrasonication, rotor-stator and static mixers were investigated as means of generating miniemulsion droplets in terms of energy consumption and droplet size distributions. It was observed that energy costs per mass of latex produced were of similar orders of magnitude for the devices in question. However, it was found that the absolute widths of the distributions for droplets generated with the sonicator and rotor-stator were larger than those generated with the static mixers and during polymerisation underwent secondary nucleation. This, coupled with the relatively low shear imposed on the fluid by the static mixers makes them an ideal choice for the generation of miniemulsion droplets.

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

Abstract

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

.