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IPCG

INTERNATIONAL POLYMER COLLOIDS GROUP

Newsletter
February 2000

IPCG Website

Bob Fitch has set up the IPCG website, on Http:///www.newmex.com/PICCG_Home/ For more information, including input into the site, contact him on bobfitch@newmex.com This is a most timely and economic way for us to communicate, and will eventually replace this hard-copy Newsletter.

Forthcoming Conferences

74th Colloid & Surface Science Symposium -Colloid 2000
Lehigh University, Bethlehem PA June 19th – 21st 2000

UK Polymer Colloids Forum, Surrey 4th – 6th April 2001

International Microsymposium "Preparation of Nonconventional Polymer Dispersions" Slovak Academy of Sciences June 25th –28th 2001

Gordon Conference Polymer Colloids – New Hampshire 1-6th July, 2001

As previously notified to members by email, because of the growing size of this Newsletter, it is necessary to limit contributions to (extended) abstracts of work in progress or in press, titles and sources of papers which have been published, and news items such as conference details. IPCG members who wish to communicate full text of papers can post them on the IPCG website.

VOLUME 31 **February 2000** **NUMBER 1**

TABLE OF CONTENTS

Conferences

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IPCG

INTERNATIONAL POLYMER COLLOIDS GROUP

From Mohamed El-Aasser

The next meeting of the IPCG will be held during the 74th Colloid and Surface Science Symposium {Colloid 2000}. Colloid 2000 will be held at Lehigh University, Bethlehem, PA from June 19-21,2000. If you have not had an opportunity to read about the meeting, please check out the meeting's web site at:

http://www.lehigh.edu/~esd0/Colloid2000/collhome.html

There will be three events held during Colloid 2000 which will be of particular interest to our membership:

1. The John W. Vanderhoff Symposium on Polymer Colloids.
2. The IPCG General Meeting on Wednesday, June 21st from Noon to 2:00.
3. A dinner in memory of John Vanderhoff on Wednesday, June 21st starting at 6:30.

To help with our planning I would appreciate knowing how many of the IPCG membership will be attending these three events. Please e-mail Debra Nyby (dhn0@lehigh.edu) if you will be attending any of the three events.

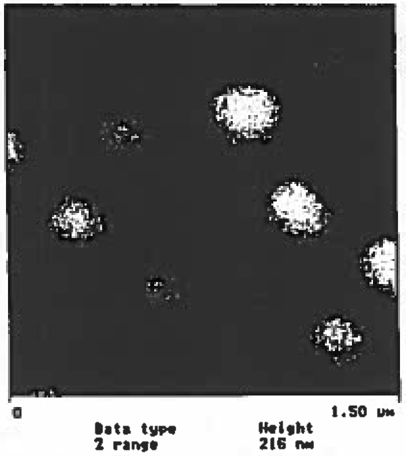
Please note that if you attend the John W. Vanderhoff Symposium you will need to register for the overall meeting.

Best regards.

Mohamed

First Circular and Call for Papers

Frontiers of Polymer Colloids



The 7th Meeting of the

UK Polymer Colloids Forum

4 – 6 April, 2001
University of Surrey
Guildford, Surrey

Introduction

The UK Polymer Colloids Forum was set up under MacroGroupUK in the Autumn of 1993 with expansion of UK academic activity in the field as one objective. Another aim was to bring the UK polymer colloids community together for discussions of topics and issues of both academic and industrial importance, the principal vehicle for which has been the regular meetings of the Forum.

The Technical Programme

The aim of the meeting is to highlight and discuss the developments at the "frontiers" of research in polymer colloids. The three-day programme will consist of plenary lectures, invited lectures, and contributed lectures. Two poster sessions are planned and will be an important part of the programme.

Plenary Speakers

The following notable scientists have agreed to deliver plenary lectures:

Professor M. El-Aasser (Lehigh University)

Professor R. Gilbert (University of Sydney)

Professor W. Russel (Princeton University)

Professor B. Vincent (University of Bristol)

Professor M. Winnik (University of Toronto)

Call for Papers and Posters

Submissions of papers and posters are welcomed in all areas relevant to the science and engineering of polymer colloids. The following topics are of particular interest:

- Applications of Polymer Colloids
- Novel Polymer Particles: Design and Characterisation
- Latest Polymerisation Techniques
- Film Formation and Waterborne Coatings

If you wish to submit a paper for oral or poster presentation, please fill out an electronic **enquiry form** or return the form printed overleaf.

Poster Prize

Students and young researchers are particularly encouraged to attend the meeting. A prize will be given for the best poster presented by a postgraduate student.

Conference Fees

The registration and accommodation fees for the meeting have not been yet determined, but there will be reduced fees for speakers and for students.

The Venue

The conference will be held on the green, parkland campus of the University of Surrey in the historic town of Guildford, Surrey. Guildford has frequent train services to and from London Waterloo, Reading and Portsmouth. It is reached by car on the A3 (Junction 10 of the M25).

Conference Dinner

The conference dinner will take place at Clandon Park, an outstanding Palladian house and a National Trust property. A drinks reception will be held in the magnificent Marble Hall. Transportation will be provided.

Social Programme

Delegates staying on to Saturday, 7 April are invited to on a day-long visit to Hampton Court Palace, which dates from the early 1500s, and is one of the former homes of King Henry VIII of England. Transportation will be provided. On the evenings of 4 and 6 April, the bar will be open after dinner until late into the evening.

Local Conference Organiser

Dr Joe Keddie, Department of Physics, University of Surrey

Request for Information and Pre-Registration

If you are interested in receiving registration information please fill in an electronic enquiry form at www.ph.surrey.ac.uk/polcol/Frontiers.html, or return the form printed overleaf.

Enquiry Form

Frontiers of Polymer Colloids
4-6 April, 2001
Guildford, Surrey UK

Title (Prof., Dr., Ms., Mr.)_______

First Name(s)______________________________

Surname______________________________

Affiliation______________________________

Postal Address______________________________

____

City______________________________

County/State/Province______________________________

Post/Zip Code______________ Country______________

Telephone______________________________

Facsimile______________________________

E-mail:______________________________

Please tick as appropriate:

☐ I would like to submit an oral paper.

☐ I would like to submit a poster.

☐ Please send me further details and registration information.

☐ I am a postgraduate student.

Please return to:
Dr Joseph Keddie, Department of Physics, University of Surrey
Guildford, Surrey GU2 5XH United Kingdom
e-mail: j.keddie@surrey.ac.uk
Or fill out the on-line enquiry form at: **www.ph.surrey.ac.uk/polcol/Frontiers.ht**

Announcement

International Microsymposium entitled,

“ Preparation of Nonconventional Polymer Dispersions “ ,

organized by Department of Polymerization Reactions, Polymer Institute, Slovak Academy of Sciences, in the year 2001, from June 25th through June 28th, will be held in Congress Centre of the Slovak Academy of Sciences in Smolenice Castle (70 km northeast from Bratislava).

Information :
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Tatiana Aslamazova

CATIONIC AMINO-CONTAINING POLYMERIC PARTICLES: APPLICATION OF THE DLVO THEORY TO CHARACTERIZATING THEIR COLLOIDAL STABILITY

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The stability of cationic amino-containing polymeric particles has been studied in view of the Theory of DLVO by estimating potential barrier of particles interaction.

The positive charge of latex particles was achieved by using of 2,2'-azo-bis(isoamidinopropane) as an initiator of polymerization. The fragments of the decomposed initiator located on the particles surface, providing positive charge of surface, are responsible for the electrostatic stabilization of particles.

The hydrophobic-hydrophilic balance and zeta-potential of surfaces of latex particles of polystyrene, poly-N-isopropylacrylamide (NIPAM) and "core-shell" copolymer of styrene and N-isopropylacrylamide were compared.

The correlation between zeta-potential and hydrophilicity of polymeric surface, from one side, and from the other, colloidal stability of particles was shown. The stability correlates to value of potential barrier of particles interaction. The maximum stability of latexes was observed in case of "core-shell" copolymer of styrene and N-isopropylacrylamide which cationic groups are mainly located in particles "shell".

1) Experimental study.

Under equal concentration of initiator and temperature of polymerization of styrene and NIPAM, the value of zeta-potential and radius of particles are significantly differed. It indicates at the different mechanism of particle formation due to the difference in monomeric solubility in water phase (correlated with polymeric hydrophobity of polystyrene and polyNIPAM). From values of zeta-potential and hydrophobicity of polystyrene and polyNIPAM followed, the higher hydrophobicity of polymer the higher value of zeta-potential. It means that the stabilization of hydrophobic polymeric surface requires the higher concentration of ionic groups. In the turn, the smaller concentration of ionic groups on surface promotes increasing the particles size due to decreasing their repulsion. The radius of polyNIPAM particles is rather higher than polystyrene which surface is characterized by the greater value of zeta-potential.

The other situation was in the case of "core-shell" polymer. The value of zeta-potential and radius of particles are not correlated with polymeric hydrophobicity as it was in case of the gomopolymer of styrene or NIPAM. The close radius of the particles of gomopolymer styrene and "core-shell" copolymer was connected with the small concentration of NIPAM in the particle "shell" equal only to 1/10 of the total polymeric content. The slight increase of "core-shell" particles radius in comparison with polystyrene particles can be explained by the polymer concentration.

The "core-shell" particles are characterized by the greater value of zeta-potential than the gomopolymer styrene and by rather greater than polyNIPAM that was explained by the higher content of ionic polymer in particles "shell".

The significant increase of zeta-potential of "core-shell" particles covered by polyNIPAM "shell" in comparison with polyNIPAM particles could be explained by an effect of polystyrene bulk on the preferencial location of ionic groups on the particles surface. Herewith the final hydrophilicity of "shell" surface of "core-shell"polymer is close to polyNIPAM as it was followed from the value of contact angle of polymers in water.

As followed from the value of contact angle, the of polymeric particles surface can be considered as hydrophobic one because the hydrophilic surface is characterized by the contact angle of water smaller than ten grades as mentioned in [1]. The polymeric hydrophobicity increases from polyNIPAM to "core-shell" copolymer and then to the gomopolystyrene. The dissolution of NIPAM in water and consequently high hydrophilic property of polyNIPAM surface, from one side, and from the other, small value of zeta-potential of polyNIPAM particles in comparison with polystyrene and "core-shell"polymer - all these facts should be taken into account for describing polymeric surface in view of its forces of interaction.

2) Theoretical study.

With the purpose of estimating the forces of particles interaction, the polymeric surface is considered in view of its electrostatic, molecular and hydrophobic forces of interactions. The total surface charge is characterized by the value of zeta-potential. The higher zeta-potential is observed for "core-shell" particles. Molecular factor of stabilization of EFL is connected with potential energy of attraction which promotes the particles coalescence. As a result of the intermolecular (van der Waals) forces of attraction this factor depends on polarity, polarisability, etc. These forces are characterized by Hamaker constant (A) estimated from refractive index or other data. According to literature [2,3] it can be taken as 10-20 J for styrene (or alkylmethacrylates) while as 2.4 x10-21 J for NIPAM [4].

Taking into account the data on latexes of polystyrene, polyNIPAM and their copolymer, the electrostatic and molecular component of interaction were estimated. The electrostatic component correlates to the value of zeta-potential of the particles surfaces, whereas the molecular component increases with increasing the content of hydrophilic component in the polymer molecule. The higher forces of intermolecular attraction was observed in case of polyNIPAM.

The potential barrier responsible for stability increases with increasing the electrostatic forces of particles repulsion and with decreasing the molecular forces of their attraction. The maximum barrier was observed for "core-shell"copolymer. The greater coalescence of polymeric particles was observed in case of polyNIPAM that connected with the smaller forces of electrostatic repulsion and the higher forces of molecular attraction.

The adequate representation of character of particles surface would not be complete without considering structural component of interaction. Its particular importance could be in case of polyNIPAM hydrogel layer below the low critical solution temperature when suggested [5] that particles stabilization occurs by the hairy layer of hydrophilic "shell". Structural factor of stabilization of emulsifier-free latexes is connected with hydrophilicity of polymeric surface and water structure near by it [1]. In case of the hydrophobic polymer the particles interaction is considered in view of surface forces of their attraction, whereas in case of the hydrophilic polymer - in view of the forces of particles repulsion. As mentioned in [1] the hydrophilic surfaces are characterized with contact angle smaller ten grades. Therefore the structural component of hydrophobic polymeric surface of polystyrene, polyNIPAM and their "core-shell" polymer should be considered as hydrophobic force!

s of attraction. The potential

As followed from potential barrier of interation particles, the maximum of potential energy equals to 4.95.10-12, 0.85.10-12 and 0.2.10-12 erg respectively for "core-shell"copolymer of styrene and NIPAM, polystyrene and polyNIPAM.

3) Conclusions.

By taking into account colloidal, electrokinetic and hydrophilic-hydrophobic properties of the polymeric surface of cationic amino-containing emulsifier-free latexes particles, the electrostatic, molecular and structural surface forces of their interaction were studied. The colloidal stability of particles of poly- styrene, its traditional copolymer and "core-shell"copolymer with poly-N-isopropylacrylamide was estimated by estimating potential barrier of their interaction. The greater colloidal stability of cationic "core-shell"copolymeric latex was explained by combining the higher forces of electrostatic repulsion and the smaller forces of particles attraction. The greater forces of electrostatic repulsion are caused by the value of zeta-potential of "core-shell"particles surface created by ionic groups located in their "shell". The smaller forces of particles attraction are a result of hydrophilic properties of highly hydrophilic poly-N-isopropylacrylamide located in the "!

shell"layer of "core-shell" pol

4) References

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3. M.L.Snowden,Boardman W.W., J.Chem.Phys., 9, 798 (1941).

4.W.B.Russel, D.A.Saille, W.R.Schowalter, Colloidal Dispersions; Cambridge University Press: Cambridge, 1989.

INTERNATIONAL POLYMER COLLOIDS GROUP NEWSLETTER

Contribution from the Institute for Polymer Materials "POLYMAT" and Grupo de Ingeniería Química, Facultad de Ciencias Químicas, Universidad del País Vasco, Apdo. 1072, 20080 San Sebastián, Spain.

Reported by José M. Asua
January 2000

MWD IN COMPOSITION CONTROLLED EMULSION COPOLYMERIZATION

Claudia Sayer, Enrique L. Lima, Jose Carlos Pinto, Gurutze Arzamendi and José M. Asua

J. Polym. Sci. Part A: Polym. Chem. (to appear).

The effect of different strategies for copolymer composition control on MWD and gel fraction in the emulsion copolymerization of methyl methacrylate and butyl acrylate was investigated. Both starved and semistarved processes for copolymer composition control were considered. It was found that for gel-forming systems, the starved process give more gel and lower molecular weights than the semistarved process. The feasibility of simultaneous control of the copolymer composition and the MWD was assessed.

USING MULTIPLICITY TO IMPROVE REACTOR PERFORMANCE AND PRODUCT QUALITY IN EMULSION POLYMERIZATION IN CONTINUOUS LOOP REACTORS

Pedro H. H. Araújo, Carlos Abad, José C. de la Cal, José C. Pinto, José M. Asua.

Polym. React. Eng. J. (to appear).

The emulsion copolymerization of vinyl acetate and Veova 10 in a continuous loop reactor was investigated finding that the system presents steady state multiplicity. It is shown how to take advantage of the reactor dynamics to conduct the process in such a way that a pseudo steady state is reached in which high polymerization rates at low temperatures and/or low initiator concentrations are obtained. These conditions allow to achieve high production rate of a high molecular weight polymer which yields high wet scrub resistance. If these conditions were implemented from the beginning of the process, low conversions, and in some cases coagulation, would be obtained.

MAXIMIZING PRODUCTION RATE AND SCRUB RESISTENCE OF VINYL ACETATE-VEOVA 10 LATEXES

María J. Unzué, Agustín Urretabizkaia, José M. Asua

J. Appl. Poly. Sci. (to appear).

Optimal strategies for the emulsion copolymerization of vinyl acetate and VeoVa 10 were developed. The strategies are based on a hybrid mathematical model for the process which includes rigorous material and energy balances and empirical equations for uncertain terms. The strategies were implemented in a lab-scale calorimetric reactor.

COPOLYMERIZATION BEHAVIOR OF AN ISOBUTENYL-BASED SURFMER

Santanu Roy , Philippe Favresse, André Laschewsky, José C. de la Cal, José M. Asua

Macromolecules 32, 5967 (1999)

The copolymerization behavior of an isobutenyl-based surfmer during the emulsion copolymerization of methyl methacrylate-butyl acrylate-acrylic acid was investigated. The surfmer was chosen because its reactivity ratios were in the adequate range to avoid early polymerization of the surfmer, which would otherwise result in burying of the surfmer, and to achieve a high degree of incorporation at the end of the process. It was found that the localization of the surfmer polymerization in the outer shell of the polymer particles, as well as the partitioning of the surfmer between the particles and the aqueous phase, have a critical influence on the surfmer incorporation.

INFLUENCE OF THE POLYMERIC HYDROPHOBE ON THE KINETICS OF VINYL ACETATE MINIEMULSION POLYMERIZATION

Imanol Aizpurua, Javier I. Amalvy, María J. Barandiaran

Colloids &Surfaces A: (to appear).

The influence of polymeric hydrophobes on the stabilization and kinetics of the vinyl acetate miniemulsion polymerization was investigated by conducting reactions in batch mode of miniemulsions prepared with poly(vinyl acetate) or polystyrene as cosurfactants. The results were compared with a miniemulsion stabilized with hexadecane and with the conventional emulsion. The shelf life stability analysis showed that miniemulsions prepared with polymer as the unique cosurfactant were not stable. However, the appearance of the separated phases was not similar to the conventional emulsion, which was interpreted as the formation of small monomer swollen particles in the case of the miniemulsion. The kinetic analysis confirmed the different nucleation mechanism of these unstable miniemulsions compared with the conventional emulsion.

INVERSE MICROMULSION POLYMERIZATION OF MADQUAT INITIATED WITH SODIUM METABISULFITE

Alberto Sáenz de Buruaga, José C. de la Cal, José M. Asua

Polymer, 41, 1269 (2000)

The kinetics of the inverse microemulsion polymerization of MADQUAT initiated with sodium metabisulfite in both batch and semi-continuous reactors was studied using reaction calorimetry. It was found that the metabisulfite was able to initiate the polymerization at low temperature (20°C) and that in batch reactor the polymerization stopped well before the complete conversion of the monomer due to complete consumption of the initiator, which disappeared according a first-order kinetics. High conversions were reached in short periods of time when the initiator was continuously fed during the process. In the semi-continuous process, the transport of metabisulfite from the droplets of the initiator solution to the particles seemed to be diffusionally limited and was accelerated by the availability of the emulsifier. The polymerization rate showed a complex evolution during the process. This was the result of the interplay between transport phenomena, polymerization and initiation rates, and nucleation rate.

KINETICS OF THE SEEDED SEMICONTINUOUS EMULSION COPOLYMERIZATION OF METHYL METHACRYLATE AND BUTYL ACRYLATE

C. Sayer, E.L. Lima, J.C. Pinto, G. Arzamendi and J.M. Asua

J. Polym. Sci. Part A: Polym. Chem. (to appear).

The effect of chain transfer agent (CTA) on the kinetics and molecular weight distribution of the MMA/BuA semicontinuous emulsion polymerization was investigated. It was observed that the dodecanethiol had a slight effect on reaction rate whereas significantly affects secondary nucleation. The effect of the CTA concentration on gel formation and the effect of reaction conditions on the mass transfer limitations of the CTA were discussed.

DIFFUSIONAL LIMITATIONS IN EMULSION POLYMERIZATION

M. Zubitur, J. Mendoza, J.C. de la Cal, J.M. Asua

Macromol. Symposia (to appear).

The effect of diffusional limitations on the kinetics of the process and the molecular weights of the polymer produced by both batch and semicontinuous emulsion polymerization was investigated. A mathematical model that accounts for the main effects observed experimentally was developed.

AGITATION EFFECTS IN THE SEMICONTINUOUS EMULSION POLYMERIZATION OF STYRENE AND BUTYL ACRYLATE

M. Zubitur, J.M. Asua

Journal of Applied Polymer Science (to appear).

The effect of agitation on the semicontinuous emulsion copolymerization of styrene and butyl acrylate was investigated. Both neat monomer addition and preemulsified feed were used. Experiments with and without chain transfer agent were carried out. For neat monomers addition a mild degree of agitation (0.1 kW/m3) was required to avoid monomer mass transfer limitations, but even a moderate degree of agitation (0.3 kW/m3) was not enough to overcome the CTA mass transfer limitations. Agitation was much less critical when preemulsified feeds were used.

CONTROL OF EMULSION POLYMERIZATION REACTORS USING A HIERARCHICAL FUZZY LOGIC / MODEL-BASED CONTROLLER

José M. Asua

Polym. React. Eng. J. (to appear)

A common problem in emulsion polymerization reactors is to maximize the production under safe conditions of copolymers of the desired composition. This is a difficult task because of the lack of accurate models for the process. In this work this problem is solved by using a hierarchical fuzzy-logic model-based controller. The fuzzy system was used for planning and its role was to determine the optimal trajectory. A model-based controller was used to track this trajectory. The controller performance was checked by simulation of the emulsion polymerization of styrene and butyl acrylate carried out in a 15 m^3 reactor.

ACETAL -FUNCTIONALIZED POLYMER PARTICLES USEFUL FOR IMMUNOASSAYS. II. SURFACE AND COLLOIDAL CHARACTERIZATION

Rosa María Santos and Jacqueline Forcada

J. Polym. Sci., Part A: Polym. Chem., 37, 501 (1999).

Monodisperse polymer colloids with dimethyl and diethyl acetal functionalities were synthesized by a two-step emulsion polymerization process. The first step consisted of a batch emulsion homopolymerization of styrene (St). The dimethyl and diethyl acetal functionalities were obtained by batch emulsion terpolymerization of St, methacrylic acid (MAA) and methacrylamidoacetaldehyde dimethyl acetal (MAAMA), or methacrylamidoacetaldehyde diethyl acetal (MAADA) in the second step, onto the previously formed polystyrene latex particles. The latexes were characterized by TEM and conductimetric titration, in order to obtain the particle size distribution and the amount of carboxyl and acetal groups on the surface, respectively. The chemical stability of the functionalized surface groups during the storage time was analyzed. The hydrophilic character of the surface of the polymer particles was determined by means of non-ionic emulsifier titration. The colloidal stability of the synthesized latexes was studied by measuring the critical coagulation concentration (CCC) against KBr electrolyte, and the existence of a hairy layer on the surface of the latex particles was analyzed by measuring the hydrodynamic particle diameter at several electrolyte concentrations. The surface functionalized groups remained stable for two years. The relative hydrophilic character and the colloidal stability were affected by the pH of the medium. On the other hand, the higher the surface charge, the larger the thickness of the hairy layer.

ACETAL-FUNCTIONALIZED POLYMER PARTICLES USEFUL FOR IMMUNOASSAYS. III. PREPARATION OF LATEX-PROTEIN COMPLEXES AND THEIR APPLICATIONS

Rosa María Santos and Jacqueline Forcada

J. Material Sci., Materials in Medicine (to appear)

Monodisperse polymer colloids with dimethyl and diethyl acetal functionalities synthesized by a two-step emulsion polymerization process were chosen as the polymeric support to carry out the covalent coupling with the antibody IgG anti C-reactive protein, and to test the utility of the latex-protein complexes formed in immunoassays with the specific CRP antigen. More than the 80% of the initially linked protein was covalently coupled in all of the latexes. The agglutination reaction was followed by turbidimetry. With the aim of analyzing the effect of some of the variables of the immunological reaction, the reaction time, the particle concentration and the coverage degree of protein in the complexes were varied.

A DECREASE IN EFFECTIVE ACRYLATE PROPAGATION RATE CONSTANTS CAUSED BY INTRAMOLECULAR CHAIN TRANSFER

C. Plessis, G. Arzamendi, J.R. Leiza, H.A.S. Schoonbrood, D. Charmot and J.M. Asua

Macromolecules <u>37</u>, 4 (2000)

The seeded semibatch emulsion polymerization of n-BA was investigated using potassium persulfate as initiator at 75°C. The kinetics (conversion and number of radicals per particle), the fraction of gel, the weight-average molecular weight and the level of branches were determined. It was observed that the fraction of gel was not affected by varying the initiator concentration whereas the instantaneous conversion, the weight average molecular weights and the level of branches were. A mathematical model was employed to gain a deeper understanding of the mechanisms occurring in the emulsion polymerization of butyl acrylate. It was showed that backbiting is the predominant mechanism of transfer to polymer in the polymerization of butyl acrylate. Because the resulting tertiary radicals are much less reactive than the secondary radicals, the effective propagation rate constant decreases when monomer concentration decreases. This means that the propagation rate coefficients determined from pulsed laser polymerization (PLP) are effective constants that cannot be safely applied outside the range of monomer concentrations used in the determination.

REACTIVE SURFACTANTS IN HETEROPHASE POLYMERIZATION

José M. Asua, Harold A.S. Schoonbrood

Acta Polymerica, <u>49</u>, 671 (1999).

This work reviews the publications concerning the use of polymerizable surfactants (surfmers) in heterophase polymerization in terms of the mechanisms relevant during the process. The goal was to gain some insight about these mechanisms and to help the reader on the way in trying to find a suitable surfmer and to apply it in an appropriate way for a specific polymerization system.

SEEDED SEMIBATCH EMULSION POLYMERIZATION OF n-BUTYL ACRYLATE. I. KINETICS AND STRUCTURAL PROPERTIES.

C. Plessis, G. Arzamendi, J.R. Leiza, H.A.S. Schoonbrood, D. Charmot and J.M. Asua

The seeded semibatch emulsion polymerization of n-BA was investigated using potassium persulfate as initiator at 75°C. The effect of initiator concentration and monomer feeding time (feed flow rate) on the kinetics, fraction of gel, molecular weight distributions and level of branches were studied. It was found that the amount of gel formed was independent of initiator concentration and monomer feed flow rate if the process proceeded under starved conditions. On the other hand, the higher the initiator concentration and the feeding times, the higher the level of branches but the lower the molecular weights. A high level of branches was found, which was attributed to intramolecular transfer to polymer or backbiting.

SEEDED SEMIBATCH EMULSION POLYMERIZATION OF n-BUTYL ACRYLATE. II. MODELING KINETICS, BRANCHING FRECUENCY, SOL MWD AND GEL FRACTION

C. Plessis, G. Arzamendi, J.R. Leiza, H.A.S. Schoonbrood, D. Charmot[3] and J.M. Asua

A mathematical model for the computation of kinetics, branching frequency, sol molecular weight distribution, and gel fraction for the seeded semicontinuous emulsion polymerization of n-BA is presented. The model incorporates mechanistic features that have been found to play an important role in the polymerization of n-BA, such as backbiting and the low reactivity of the tertiary radicals obtained in such reaction. Model parameters for which values are not available in the literature were obtained by fitting the model predictions to the kinetic data and structural properties such as fraction of gel, sol molecular weight distribution and level of branches gathered in seeded semicontinuous emulsion polymerizations of n-BA. The model fits all these experimental data quite well.

MODEL-BASED CONTROL OF EMULSION TERPOLYMERS BASED ON CALORIMETRIC MEASUREMENTS

Isabel Sáenz de Buruaga, José R. Leiza and José M. Asua

Polym. React. Eng. J. (to appear)

The feasibility of the on-line control of emulsion terpolymers based on calorimetric measurements was assessed. First the inference of the terpolymer composition from calorimetric measurements was studied and experimentally validated. Two control strategies were used to maximize the production of BuA/MMA/Sty latexes under safe conditions, maintaining simultaneously the terpolymer composition of the polymer at predefined values. The application of these strategies to systems affected by a severe gel effect is discussed.

Contribution to IPCG newsletter

from

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Titles and Abstracts of unpublished papers

Synthesis and characterization of core-shell colloids with fluoro-carbon cores

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SUMMARY:The synthesis of core-shell particles with polycrystalline fluorocarbon (MFA) cores (derived from preformed seeds) and highly crosslinked polystyrene (PS) shells via essentially surfactant-free emulsion polymerization is reported. The composite latexes in aqueous dispersion and in THF solution were characterized by light scattering, asymmetric field flow fractionation and TEM. The results indicate that while in aqueous dispersion one obtains core-shell particles with a narrow size distribution and a sharp fluorocarbon/ polystyrene interface, the dissolution of the latexes in THF leads to hollow sphere structures of crosslinked polystyrene.

Macromol. Symp., in press

Film-forming Colloidal Dispersions Studied by Tracer Methods

Tobias Baumgart[1], Sibylle Cramer[2], Thilo Jahr[3], Andrei Veniaminov[3], Jörg Adams[1], Jürgen Fuhrmann[1], Gunnar Jeschke[2], Uli Wiesner[2], Hans W. Spiess[2], Eckhard Bartsch*[,3], Hans Sillescu[3]

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SUMMARY: We have studied the dynamics of small probe molecules in film forming latex dispersions by non-radiative energy transfer, forced Rayleigh scattering and electron paramagnetic resonance. First results indicate that on drying the dynamics of the different probes expose characteristic changes at comparable water contents. This could be used for correlating dispersion and film properties in subsequent experiments.

Macromol. Symp., in press

Crystallizing Polystyrene-Microgel-Colloids

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Abstract: Spherical microgel particles of sufficiently high degree of internal crosslinking and swollen in a good solvent in many respects behave similar to hard sphere colloids. Due to solvent uptake the can be refractive index and density matched in suitable organic solvents. We here present preliminary measurements of the crystallization kinetics of 1:10 crosslinked polystyrene microgel particles. We measured Bragg and small angle light scattering of the solidifying shear melt. Two different scattering patterns, a set of Debye-Scherrer rings and a second ring pattern at small angles could be observed. We check for similarities and differences as compared to previously investigated colloidal systems.

Prog. Coll. Polym. Sci., submitted

Synthesis and Characterization of Highly Crosslinked, monodisperse Core-Shell and Inverted Core-Shell Colloidal Particles. The Poly(*t*-butyl acrylate) Seeds.

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Abstract

Poly(t-butyl acrylate) microgel latices to be used as seeds for the preparation of core-shell particles have been synthesized by surfactant-free emulsion polymerization and standard emulsion polymerization. The latices were internally crosslinked by using ethylenegylcol-di-acrylate, a bifunctional crosslinker. Special emphasis was given to the influence of different reaction parameters (e.g. the ratio of crosslinker to monomer = crosslink density, the reaction temperature, the amount of initiator or surfactant as well as the oil to water phase ratio) on the

particle formation. The effect of these parameters on the final particle size and particle size polydispersity has been investigated and a model for the microgel particle formation is suggested.

#Present address: BASF Aktiengesellschaft, ZKD-B1, D-67056 Ludwigshafen, Germany

Macromolecules, submitted

Work in progress

- Glass transition dynamics of highly crosslinked polystyrene microgel colloids (Ph.D. thesis)
- Phase behaviour and short-range order of polystyrene microgel colloids of varying crosslink density (Ph.D. thesis)
- On the crosslink density distribution in polstyrene microgel particles - A SANS study
- Particle coalescence in film forming colloidal dispersions studied b forced Rayleigh scattering (Ph.D. thesis)
- Long-time self-diffusion and rheology of microgel particles (Ph.D. thesis)
- Synthesis and characterization of core-shell colloids with fluorocarbon cores (Ph.D. thesis)
- Phase behaviour, short-range order and dynamics of mixtures of polystyrene microgel colloids and linear polstyrene (Ph.D. thesis)

Recent publications

S. Kirsch, V. Frenz, W. Schärtl, E. Bartsch, H. Sillescu
Multi-Speckle Autocorrelation Spectroscopy and its Application to the Investigation of Ultra-Slow Dynamical Processes
J. Chem. Phys. **104**, 1758 (1996)

F. Renth, E. Bartsch, A. Kasper, S. Kirsch, S. Stölken, H. Sillescu, W. Köhler, R. Schäfer
The Effect of the Internal Architecture of Polymer Micronetwork Colloids on the Dynamics in Highly Concentrated Dispersions
Prog. Colloid Polymer Sci. **100**, 127 (1996)

A. Kasper, S. Kirsch, F. Renth, E. Bartsch, H.Sillescu
Development of Core-Shell Colloids to Study Self Diffusion in Highly Concentrated Dispersions
Prog. Colloid Polymer Sci. **100**, 151 (1996)

E. Bartsch, V. Frenz, J. Baschnagel, W. Schärtl, H. Sillescu
The Glass Transition Dynamics of Polymer Micronetwork Colloids - A Mode Coupling Analysis
J. Chem. Phys. **106**, 3743 (1997)

E. Bartsch, V. Frenz, S. Kirsch, W. Schärtl, H. Sillescu
Multi-Speckle Autocorrelation Spectroscopy - A New Strategy to Monitor Ultraslow Dynamics in Dense and Nonergodic Media
Progr. Colloid Polym. Sci. **104**, 40 (1997)

W. Köhler, R. Schäfer, E. Bartsch, S. Stölken
Collective and self diffusion of PS microgels in solution as observed by thermal diffusion forced Rayleigh scattering
Progr. Colloid Polym. Sci. **104**, 132 (1997)

A. Kasper, E. Bartsch, H. Sillescu
Self-Diffusion in Concentrated Colloid Suspensions Studied by Digital Video Microscopy of Core-Shell Tracer Particles
Langmuir **14**, 5004 (1998)

E. Bartsch
Diffusion in concentrated colloidal suspensions and glasses
Current Opinions in Colloid&Interface Science **3**, 577 (1998)

E. Bartsch, S. Kirsch, P. Lindner, S. Stölken, T. Scherer
Spherical Microgels - Hard Spheres from Soft Matter
Ber. Bunsenges. Phys. Chem. **102**, 1597 (1998)

S. Kirsch, A. Dörk, E. Bartsch, H. Sillescu, K. Landfester, H.-W. Spiess, W. Mächtle
Synthesis and Characterization of Highly Crosslinked, Monodisperse Core-Shelland Inverted Core-Shell Particles. Polystyrene/Poly-t-Butylacrylate Core-Shell and Inverse Core-Shell Particles.
Macromolecules **32**, 4508 (1999)

A link to the PDF-Files of recent and submitted papers will be soon available at:

http://www.uni-mainz.de/FB/Chemie/AK-Sillescu/embart.htm

Contribution from the Department of Polymerization Reactions, Polymer Institute,Slovak Academy of Sciences, 842 36 Bratislava, Slovak Republic

Reported by **Jaro Barton**
(November 1999)

Work in progress :

Acrylamide and Butyl Acrylate Polymerization in Winsor IV (w/o) and Winsor I (o/w) Microemulsions .

The preparation of Winsor IV (w/o) toluene-based inverse microemulsions containing the (co)monomer couple acrylamide(AAm)/butyl acrylate (BA), their transformation to Winsor I (o/w) direct microemulsions and homo-and (co)polymerization of (co)monomers in both types of microemulsions were studied. It was found that for obtaining the high values of volume fractions of aqueous phase, Φ_{aw2} , at which the transition of Winsor IV→Winsor I occurred, the best was the three-component titration system composed from water, AAm and SDS. Thus for inverse microemulsion characterized by molar ratio ([T] / [AOT] = 19.4 and/or 11.6 the values of Φ_{aw2} 0.39 and/or 0.50 were obtained. It was found that the APS initiated homopolymerization of AAm in Winsor IV w/o inverse microemulsion proceeded with the highest rate in comparison to (co)polymerization of AAm/BA couple or BA homopolymerization.This is the result of the kinetic behaviour of AAm and BA monomers in free-radical polymerization (different values of $k_p/k_t^{0.5}$), different monomer partition coefficients between water- and oil-phases of the dispersion system and capability of monomer radical and oligomer radical formation in individual phases and of transfer of these radicals between individual phases of the w/o and/or o/w microemulsions. Maximum rate of (co)polymerization of AAm/BA couple in Winsor IV w/o inverse microemulsion is only 1.5 times greater than that in Winsor I o/w microemulsion phase. Maximum homopolymerization rate of BA in toluene-based Winsor IV inverse w/o microemulsion in comparison to BA-based Winsor IV inverse w/o inverse microemulsion is only 1/75 of the maximum rate of BA homopolymerization in the latter system. The proposed reaction mechanism for initiation of homo- and (co)polymerization reactions underlines the role of the monomer and of the monomer radical partitioning between water- and oil phase of the dispersion system.
(Contact : Jaroslav Barton, e-mail : upolbart@savba.sk)

Polymerization of Butyl Acrylate in the Presence of Polyacrylamide Nanoparticles.

A new method for preparation of modified polymer particles in two steps was proposed. Free radical polymerization of oil soluble vinyl monomer like butyl acrylate in inverse microemulsion containing polyacrylamide particles led to formation of partly hydrophobized, polyacrylamide particles. The method enables the preparation of modified polyacrylamide particles in mixtures of polyacrylamide containing inverse mi-

croemulsions with butyl acrylate containing non-polymerized inverse microemulsions or toluene solutions. For the first step of the process (preparation of polyacrylamide particles) is typical has very high polymerization rate while for the second step (polymerization of butyl acrylate in the presence of polyacrylamide particles) the reverse is true. The second stage of the process is characterized by nearly constant number of polymer particles in the reaction system, close to the number of polyacrylamide particles of parent inverse microemulsion.
(Contact : Jaroslav Barton, e-mail : upolbart@savba.sk)

Water Phase Titration Studies of Winsor IV Inverse Microemulsions.

Classical toluene-based inverse microemulsions containing besides acrylamide (AAm) also oil-soluble vinyl monomer (styrene,butyl acrylate (BA), ethyl acrylate) of various solubility in the water phase of inverse microemulsions were titrated by water, water solutions of acrylamide and/or acrylamide/emulsifier mixture.The amount of water phase absorbed by inverse microemulsion (i.e. before formation of two-phase Winsor II or Winsor I systems containing besides w/o or o/w microemulsions also excluded water or oil phase) depended only slightly on the nature of oil soluble vinyl monomer. It was found,however, that the ratios of intra-phase and inter-phases concentrational parameters such as [toluene]/[AOT], water/AAm, water/emulsifier mixture, [water]/[AOT], BA/AAm and AOT/emulsifier mixture considerably affect the value of the dispersed volume fraction of the aqueous phase necessary for the formation of a two-phase dispersion system.
(Contact : Jaroslav Barton, e-mail : upolbart@savba.sk)

Papers submitted to publication :

I.Capek, Photopolymerization of alkyl (meth)acrylates and polyoxyethylene macromonomers in fine emulsions. Eur. Polym. J.
I.Capek, Microemulsion polymerization of styrene in the presence of anionic emulsifier. Adv. Colloid Interface Sci.
I.Capek, Phtopolymerization of alkyl (meth)acrylates in fine emulsions. Polym. J.
I.Capek, S.Y.Lin, T.J.Hsu, C.S.Chern, Effect of temperature on styrene emulsion polymerization in the presence of sodium dodecyl sulfate. 2. J.Polym.Sci.
I, S.Y.Lin, I.Capek , T.J.Hsu, C.S.Chern, On the emulsion polymerization of styrene in the presence of nonionic emulsifier. J.Polym.Sci.
A.Matsumoto, N,.Murakami, H.Aota, I.Capek, Emulsion polymerization of lauryl methacrylate and its copolymerization with trimethylolpropane trimethacrylate. Polymer.
S.H.Nguyen, D.Berek, I.Capek, O.Chiantore, Polystyrene-graft-polyethyleneoxide copolymers prepared by macromonomer technique: 1. Liquid chromatographic separation of product mixtures. ACS Polym. Preprints.
J.Barton,S.Kawamoto,K.Fujimoto,H.Kawaguchi,I.Capek,Preparation of partly hydrophobized,crosslinked polyacrylamide particles by terpolymerization of acrylamide/N,N'-methylenebisacrylamide/styrene in inverse microemulsion. Polymer International.
J.Barton,V.Juranicova, Polymerization of acrylamide in styrene containing inverse microemulsions. Polymerization kinetics and polymer product composition studies. Polymer International.

Published papers :

I. Capek, On the dispersion radical polymerization of macromonomers in disperse systems. Adv. Polym. Sci. 145, 1-55 (1999)

I. Capek, On the dispersion radical polymerization of hydrophilic macromonomers. J. Disp. Sci. & Technol. 20, 945-992 (1999)

I.Capek, Radical polymerization of unsaturated monomers in direct microemulsion systems. Adv. Colloid Interface Sci. 80, 85-149 (1999)

I.Capek, V.Juranicova, J.Barton, Effect of stable radicals on the radical microemulsion copolymerization of butyl acrylate and acrylonitrile. Eur. Polym. J. 35, 691-698 (1999)

I.Capek, R.Murgasova, D.Lath, E.Lathova, V.Juranicová, J.Barton, Dispersion copolymerization of polyoxyethylene macromonomer and styrene. 4. Solution properties of polystyrene-graft-polyoxyethylene copolymers J.Polym.Sci.A, Polym.Chem. 37, 3087-3097 (1999)

A.Matsumoto,K.Kodama, H.Aota, I.Capek, Kinetics of emulsion crosslinking polymerization and copolymerization of allyl methacrylate. Eur. Polym. J. 35, 1509-1517 (1999)

A.Guyot, J.Chudej, Small particle size in emulsion polymerization using nonionic surfactants. Polymer 40, 5233-5237 (1999)

POLYMER COLLOID GROUP NEWSLETTER

Contribution from the Institut Charles Sadron (CRM)
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reported by **Françoise CANDAU**

Summaries of progress in several research areas of our group are presented below

Viscoelastic Behavior of Semi-Dilute Solutions of Multisticker Polymer Chains

(E. Jiménez-Regalado, J. Selb, F. Candau) [*Macromolecules*, in press]

Multisticker polymer chains consisting of water-soluble polyacrylamides hydrophobically modified with low amounts of *N,N*-dihexylacrylamide have been prepared by a free radical micellar polymerization technique. This process gives multiblock copolymers in which the number and length of the hydrophobic blocks can be tuned by varying the surfactant over hydrophobe molar ratio. The viscoelastic behavior of semi-dilute solutions of various series of copolymers with variable molecular weights ($M_w \approx 4.2 \times 10^4$ to 2.7×10^6), hydrophobe contents ($[H]$ = 0.5 to 2 mol %) and hydrophobic block lengths (N_H = 1 to 7 units per block) has been investigated as a function of polymer concentration, C, using steady-flow and oscillatory experiments.

The main conclusion that can be drawn from the measurements of the linear viscoelasticity is the existence of three distinct regimes, as in the case of unmodified polymers. The schematic diagram of Figure 1 illustrates these different regimes:

- A dilute regime, $C < C_\eta$, where the chains are isolated and the viscosity is essentially controlled by intramolecular interactions. This regime does not significantly differ from that of unmodified polymers.
- A semi-dilute unentangled regime, $C_\eta < C < C_T$. The break between the first and second regimes is rather sharp with C_η depending on the molar mass but independent of N_H and/or $[H]$. Note that C_η lies in the vicinity of the overlap concentration of the unmodified polymer analogs C^*. At C_η, one observes for a given molar mass a set of diverging straight lines whose slopes increase with N_H and/or $[H]$. This regime is dominated by intermolecular hydrophobic associations and the chains are likely to obey Rouse dynamics.
- A semi-dilute entangled regime, $C > C_T$. The break C_T occurs at a concentration close to the critical concentration C_e where the unmodified polymer chains are entangled. The asymptotic behavior is described by parallel straight lines with an exponent of about 4 in the log-log variations of $\eta_0 = f(C)$ whatever N_H or $[H]$. Here the hydrophobic associations might be fully intermolecular but the number of entanglements increases strongly with C.

Linear viscoelastic measurements show that the relaxation mechanism can be described by a slow process more or less separated from faster modes. In the entangled regime, the plateau modulus associated with the slow process only depends on the polymer concentration within the experimental accuracy. On the other hand, the terminal time rises drastically with either N_H, $[H]$ or M_w. The results obtained, in particular those related to the zero-shear viscosity, which is the parameter determined with the best accuracy, are consistent with the theoretical predictions of the sticky reptation model of Leibler et al., (*Macromolecules* 1991, 24, 4701) as far as the spacing between two consecutive stickers is kept constant. However, a stronger dependence of η_0 with $[H]$ is found which might reflect changes in the aggregation number of the associating clusters as $[H]$ increases. The huge increase of η_0 and T_R with N_H is likely correlated to an increase of the lifetime of a cross-link.

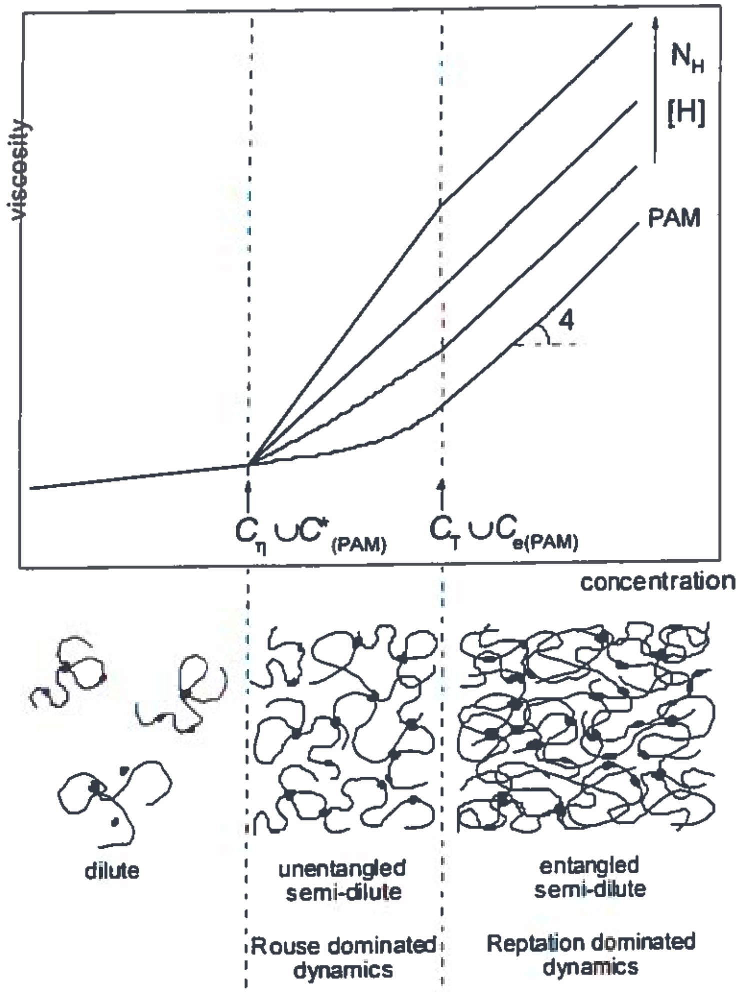

Figure 1. Schematic diagram of the various concentration regimes for multisticker associating polymers.

Multicompartment Polymeric Micelles based on Hydrocarbon and Fluorocarbon Polymerizable Surfactants

(K. Stähler, J. Selb, F. Candau) [*Langmuir*, in press]

The synthesis of multicompartment polymeric micelles (MCPMs) has been achieved by aqueous radical terpolymerization of a water-soluble monomer (acrylamide) with both hydrocarbon (H) and fluorocarbon (F) surfactants (surfmers) in the micellar state. The selected H- and F-surfmers are $CH_2{=}CH\text{-}CON(C_2H_5)\text{-}CH_2\text{-}CH_2\text{-}N(CH_3)_2\text{-}CH_2COOC_{16}H_{33}/Br/Cl$ and $CH_2{=}CH\text{-}CONH\text{-}CH_2\text{-}CH_2\text{-}N(CH_3)_2\text{-}CH_2COOCH_2CH_2\text{-}C_8F_{17}/Br$, respectively. Their mutual incompatibility in aqueous solution has been checked by conductivity and surface tension experiments. Two cmc values are found, in favor of the coexistence of two distinct types of micelles at surfactant concentrations above 1 mmol/L (second cmc) over a broad composition range. The solubilization properties of the pure and mixed surfactant systems have been studied for different hydrophobic probes. Significant differences in the solubilization capacity occur due to the nature of the dye, of the surfactant and of the micelle shape and composition. A kinetic study on the incorporation behavior of the H- and F-surfmers in the polyacrylamide backbone during a batch polymerization shows a compositional drift as a function of conversion which is attributed to micellar effects. A semi-continuous process has been designed which allows the correction for this compositional drift. The presence of well segregated H- and F-microdomains in terpolymers could be inferred from viscosity and fluorescence experiments. Furthermore, the solubilization of decaline is enhanced in terpolymer solutions with respect to that of copolymer solutions. This was attributed to the formation of larger hydrocarbon cores in the former case due to repulsive H/F interactions in the polymeric chains.

RECENT PUBLICATIONS

1. *Polymerization in Microemulsions*
   F. Candau
   in "Hanbook of Microemulsion Science and Technology", P. Kumar and K. L. Mittal eds., Dekker , New York (1999), Chapter 22, pp 679-712.

2. *Polymerization of acrylamide in solution and inverse emulsion: number molecular weight distribution with chain transfer agent.*
   M. Pabon, J. Selb, F. Candau, R.G. Gilbert
   Polymer 40 , 3101-3106 (1999)

International Polymer Colloids Group Newsletter Submission

December 1999

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Unpublished papers:

Predicting the Effectiveness of n-Dodecanethiol Chain Transfer Agent in Styrene Emulsion Polymerization

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(accepted for publication in *Macromolecular Symposia*, August 1999)

Abstract

Chain transfer agents (CTAs) are widely used to regulate molecular weight in emulsion polymerizations. In a homogeneous polymerization (e.g. solution or bulk), it is a straightforward procedure to estimate the molecular weight distribution being produced at any instant during a polymerization if the concentrations of chain transfer agent and monomer are known. Typically the CTA and monomer are consumed at different rates, resulting in either upward or downward drift in the average molecular weight. (If the transfer constant C_{tr} (k_{tr}/k_p)>1, CTA is consumed faster than monomer, while if C_{tr}<1, monomer is consumed faster than the CTA.) The concentrations of CTA and monomer can usually be determined by on-line measurements such as GC (CTA) and densitometry (monomer). However in an emulsion polymerization, the CTA and monomer are partitioned between three phases: monomer droplets, aqueous phase, and particles. It is the concentrations in the particles that determines the molecular weight produced at any instant, but it is often very difficult or impossible to determine the CTA concentration

inside the particles ([Tp]) during a process. (The monomer concentration inside the particles ([Mp]) can be calculated from thermodynamic relationships.) If the CTA is in equilibrium between all phases, then [Tp] can be calculated. In many cases, however, the CTA may not be at equilibrium and thus [Tp] cannot be readily determined. Failure to achieve equilibrium could result from very low water solubilities (large partition coefficients) and/or high transfer constants, which result in the CTA being consumed by reaction faster than it can diffuse from the monomer droplets to the polymer particles. The particles are then "starved" with respect to CTA. Without an accurate method to determine [Tp] during reaction, it is not possible to predict the molecular weight being produced. It is the objective of this work to develop a methodology to determine the CTA concentration within the particles during reaction and study how the instantaneous MWDs are affected.

Measuring the Effects of Dissolved Oxygen in Styrene Emulsion Polymerization

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(accepted for publication in *Polymer*, September 1999)

Abstract

The effects of oxygen in the emulsion polymerization of styrene have been studied by varying the initial dissolved oxygen concentration in the aqueous phase. Using different initial levels of dissolved oxygen corresponding to 0%, 50%, 80%, 90% and 100% of saturation, the induction period, conversion kinetics, molecular weight and particle size were investigated. The length of the induction period did not vary linearly with the initial oxygen level, suggesting diffusion from the headspace to the aqueous phase was an important factor. Partitioning calculations and experimental data suggest oxygen should be modeled as both a water soluble and monomer soluble inhibitor.

Introduction

It has long been recognized that the presence of oxygen in emulsion polymerizations (and other free radical polymerizations) can have detrimental effects on the course of reaction, including causing inhibition periods and retarding the reaction rat. Dissolved oxygen, one of the most common impurities in real systems, consumes radicals and can effect the radical entry rate into the particles and micelles. In an industrial emulsion polymerization, there are two reasons why oxygen is at least partially removed from the system prior to starting the reaction. First is the desire to minimize or eliminate induction periods and/or rate retardation, both which decrease reactor productivity and therefore increase process cost. Second is the safety concern of operating a reactor with potentially explosive organic monomer vapors in an oxygen-rich headspace. However in most industrial settings, it is not practical to achieve the near-zero oxygen levels that are obtained in laboratory experiments. Consequently, low levels of oxygen are present in industrial reactions. As noted by de Arbina et al. [1], inhibition and retardation are typically the cause of run to run variability.

Relatively few publications have addressed the issue of oxygen effects in emulsion polymerization. It is common to assume oxygen behaves as an ideal water soluble inhibitor, and therefore results in an induction period that persists until all oxygen is consumed followed by a normal reaction profile. However it will be seen that this is not true. Experimental data collected in this study show that inhibition and retardation coexist, that there are effects on molecular weight and particle size, and the reaction commences while oxygen is still present.

Experimental

All polymerizations reactions were performed at a constant temperature (60°C) in a one litre glass reactor (10 cm diameter) with a six-bladed, 6 cm diameter, impeller mounted 3 cm above the bottom of the reactor. A Mettler Toledo Model 4300 Dissolved Oxygen Microprocessor Transmitter with an Ingold Dissolved Oxygen Sensor was used to determine the oxygen levels in the emulsion at the beginning of reaction.

Summary

Measurements of initial aqueous phase dissolved oxygen levels in styrene emulsion polymerization show that oxygen is most appropriately treated as both a water soluble and monomer soluble inhibitor. Induction periods increase nonlinearly with initial oxygen levels, suggesting diffusion of oxygen from the headspace to the latex can have a significant impact on reaction rates and polymer properties. Partitioning calculations showed that the headspace can be a large source of oxygen, much greater than either the aqueous or styrene phases. At higher initial oxygen levels, low molecular weight polymer was produced early in the polymerization, signifying retardation in the particle phase. As the oxygen was consumed during reaction, the molecular weight gradually increased. Higher initial oxygen levels also resulted in lower mean particle diameter due to a prolonged nucleation period.

References

1. de Arbina, L.L., Gugliotta, L.M., Barandiaran, M.J. and Asua, J.M., *Polymer*, 1998, **39**, 4047-4055.

Supermicron Polymer Particles with Core-shell Type Morphologies

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Abstract

Polymer particles with controlled morphologies and having diameters from about 1-20 microns can be prepared using a new suspension polymerization based procedure. In contrast to existing procedures using emulsion polymerization, this process allows efficient preparation of supermicron particles that can be easily isolated as a dry powder. Control of the particle morphology is obtained by manipulating the monomer conversion at the beginning of the second stage of the reaction (when the second monomer is added). Two systems are studied. The first system uses styrene added to a partially polymerized MMA host particle, while the second system uses styrene added to a partially polymerized 45wt% styrene – 55wt% butyl methacrylate host particle.

Calculating Molecular Weight Distributions in Emulsion Polymerization Under Conditions of Diffusion Limited Chain Transfer

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Work in Progress:

Living Radical Styrene Polymerization in Miniemulsion

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Living radical polymerization is a recent innovation that enables the design of polymeric materials with tailored chemical and physical properties, including preparation of narrow molecular weight distribution resins, block copolymers, and polymers with functional endgroups. Prior research has made considerable progress in elucidating the mechanisms in homogeneous systems such as bulk and solution polymerizations. However an emulsion-based process offers significant engineering and economic advantages. Previous efforts revealed the difficulty of conducting nitroxide-mediated living radical polymerizations in emulsion [1]. We have chosen to use miniemulsion polymerization in order to provide a more controlled system for studying and understanding the underlying mechanism. The feasibility of using miniemulsion for nitroxide-mediated polymerizations was recently demonstrated by Prodpran et al. [2].

Styrene miniemulsion polymerizations initiated by potassium persulphate and mediated by TEMPO were run at 135°C. Two level experimental designs were used to identify the critical factors in determining the molecular weight distribution, reaction rate, particle size distribution, and degree of "livingness" of the polymer chains. Factors studied include initiator concentration, ratio of initiator to TEMPO, and concentration of swelling agent (hexadecane). Both primary and interaction effects between the factors have been identified.

1. Bon, S.A.F., Bosveld, M., Klumperman, B., and German, A.L., Macromolecules, 1997, 30, 324-326.
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Recent Papers:

Microsuspension Polymerization of Methyl Methacrylate

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Titles and abstract of unpublished papers, work in progress and theses:

1. "Polymer Composite Particles Synthesized by Dispersion Polymerization in supercritical Carbon Dioxide", Jennifer L. Young and Joseph M. DeSimone

Polymer composite particles containing polystyrene (PS) and poly(methyl methacrylate) (PMMA) were synthesized by a sequential polymerization technique in supercritical carbon dioxide. The morphology, or distribution of the PS and PMMA phases within the particles, was determined by transmission electron microscopy (TEM) with selective staining by ruthenium tetroxide (which stains PS) and uranyl acetate (which stains the background). For the particles containing 50 mol% PS, several reaction parameters were varied, including the polymerization order of the two monomers, the surfactant composition, the rate of the second monomer addition, and the pressure and temperature of the second monomer polymerization. Independent of these conditions, the morphology was half-moon with the PMMA forming an incomplete shell around the PS. Varying the monomer ratio resulted in two other morphologies: a PMMA particle containing PS microdomains and an inverted core-shell structure, which contained a PS core and a PMMA shell. Based on the morphologies, the proposed thermodynamically stable morphology contains a PS core and a PMMA shell. Currently, the partitioning of monomer between the CO_2 phase and the polymer phase at the beginning of the second monomer polymerization stage is being determined. Another area of investigation is the synthesis of particles containing polyvinylpyrrolidone and PS.

2. "Heterogeneous Polymerization of Isopropyl Acrylamide in Carbon Dioxide", Terri Carson, Joseph M. DeSimone

Current studies involve the heterogeneous polymerization of isopropyl acrylamide (IPA) in carbon dioxide, specifically precipitation polymerizations. Polymerization of IPA at 65°C and 413 bar results in the formation of well-defined particles that possess spherical morphologies. The particle formation process has been investigated as a function of monomer concentration, reaction time, reaction temperature, and solvent medium. It appears the interfacial tension of the polymer and its non-tacky nature may contribute to the mechanism of particle formation. The synthesis and precipitation polymerization of methyl and ethyl acrylamide derivatives are underway.

3. "Solid Supports for Carbon Dioxide Applications", Stephanie Creete, Joseph M. DeSimone

Current investigations focus on swellable copolymers as solid supports for diverse applications into either liquid or supercritical carbon dioxide. Indeed, one of the main interests of those CO_2-soluble cross-linked copolymers is their swellability due to the incorporation of variable amounts of fluorinated monomers. Several potential fields of applications are envisioned including separation processes, enzymatic catalysis, transition metal catalysis as well as combinatorial science. In this study, we discuss our efforts in designing and synthesizing CO_2-soluble cross-linked fluorinated copolymers by suspension polymerization in water, yielding micron-sized beads. Different cross-linkers at various concentrations have been used, as well as various amounts of fluorinated comonomer. In addition, we will report on the swelling of these supports in gaseous, liquid and supercritical carbon dioxide.

4. "Partitioning of Monomer Between Polymer and Supercritical CO_2 at Polymerization Reactions Conditions", Danni Wang, Joseph M. DeSimone

The partitioning of methyl methacrylate (MMA) between poly (methyl methacrylate) (PMMA) and supercritical carbon dioxide ($SCCO_2$) has been studied at conditions that is identical to that of the polymerization. PMMA, MMA monomer, and $SCCO_2$ were mixed at various temperatures and pressures. A high-pressure sampler was used to take certain amount of sample from the continuous phase of the mixture and then the MMA/CO_2 sample was transferred to methanol (MeOH). The amount of the MMA was determined by using gas chromatography (GC). It was found that the MMA partition coefficient between $SCCO_2$ and PMMA increased with increasing the pressure of $SCCO_2$. Under the condition that is similar to a dispersion polymerization of MMA in $SCCO_2$ (345 bar) at 50% conversion, it was found that almost all of the MMA (> 95%) is partitioning in the $SCCO_2$ phase. The effects of other parameters such as temperature, molecular weight of polymer, and the concentration of monomer/polymer on the partition coefficient are also under investigation.

5. "Synthesis of Sugar-containing Amphiphiles for Liquid and Supercritical Carbon Dioxide", Weijun Ye, Joseph M. DeSimone

Carbon dioxide as a useful processing fluid is limited by its inability to solubilize highly polar compounds. This problem can be alleviated by the addition of CO_2-philic amphiphiles. Our primary objective is to design and synthesize novel materials that have both strong polar moieties and highly CO_2-philic segments. Sugar-based hydrophobic/hydrophilic fluorinated copolymers were synthesized by free radical polymerization. The degree of solubility of the amphiphiles in CO_2 was found to be heavily influenced by their structure, including the polarity of the sugar head (acetal protected and deprotected), and the fraction of CO_2-philic groups. We also found that the presence of water in CO_2 phase could decrease the solubility of hydrophilic copolymer. Dispersion polymerization of 2-hydroxyethyl methacrylate in CO_2 was tested by using the hydrophilic amphiphile as a stabilizer and spherical polymer particles in submicron-size range were obtained.

6. "Siloxane-based Surfactants for Supercritical Carbon Dioxide Applications", Sarah Folk, Joseph M. DeSimone

A variety of siloxane-based surfactants are desired for use in CO_2 as they offer a less expensive alternative to fluoropolymer surfactants. Quaternary ammonium salt terminated poly(dimethylsiloxane) (PDMS) surfactants for CO_2 applications are being synthesized via standard living anionic polymerization techniques. The influence of the PDMS chain length, the nature of the counterion, and the substituents on the amine headgroup are being studied. The surfactants will be characterized by light scattering in CO_2 to determine aggregation behavior and the percent solubilization of water possible in water/CO_2 emulsions.

7. "Synthesis and Light Scattering Study of Poly(tert-butyl methacrylate)-block-Poly(1,1-dihydroperfluorooctyl methacrylate) in Supercritical Carbon Dioxide: Towards the Reversible Control of Self-Assembly", Eri Yoshida, Joseph M. DeSimone

The synthesis of poly(tert-butyl methacrylate) (PtBMA)-block-poly(1,1-dihydroperfluorooctyl methacrylate) (PFOMA) was attained through anionic polymerization by the sequential addition of tBMA and FOMA using 1,1-diphenylhexyl lithium and lithium chloride initiating system. The PtBMA-b-PFOMA (PBF) having a PtBMA length longer than PFOMA, was soluble in supercritical CO_2, with cloud point densities between 0.79-0.86 g/cm3. The PBF copolymer had the cloud point density between the cloud point densities for the respective homopolymers of tBMA and FOMA. The cloud point behavior of the copolymers was investigated holding the PFOMA block constant (PFOMA = 50K). The cloud point density increased with an increase in length of PtBMA block, and decreased with an increase in temperature. Dynamic light scattering studies demonstrated that the copolymers having a PtBMA length greater than 4K, self-assembled into micelles with narrow molecular weight distributions. The copolymers having micelle size between 13 and 21 nm, exhibited a transition from micelles to unimers (mtu) in the CO_2 density range of 0.87-1.04 g/cm3. The exact transition density is dependent upon the length of both polymer chains composing the diblock. Phase diagrams were determined for a series of the block copolymers holding the PFOMA block constant (PFOMA = 50K) in order to investigate the relationship between the block length of PtBMA and mtu transition. For the copolymers with 6K < Mn (PtBMA) <20K, three regions were observed in the phase diagram: a two-phase region, a region of spherical micelles, and a phase of isolated copolymer chains dissolved in CO_2. The copolymer with Mn (PtBMA) < 4K didn't form micelles, with the result that only two regions of two phase and isolated copolymer chains were observed. The copolymer with Mn (PtBMA) > 25K showed micellization, but exhibited no mtu transition, and two regions of a two phase and spherical micelles were observed. For the copolymers with 6K < Mn (PtBMA block) < 20K, mtu transition was shifted to higher densities with an increase in length of PtBMA. The phase diagrams were also determined for a series of PBF copolymers holding the PtBMA block constant (PtBMA = 13K). The copolymer with Mn (PFOMA block) < 20K showed micellization, but exhibited no mtu transition. On the other hand, the copolymers with Mn (PFOMA) > 50K, exhibited mtu transition, and three regions were observed. However, the region of spherical micelles for the copolymer with Mn (PFOMA block) = 91K was observed at higher concentrations than the region for the 52K PFOMA copolymer, indicating that the transition for the copolymer with 91K PFOMA block occurs at lower transition densities than the transition for the 52K PFOMA copolymer. The shift in the transition region to lower CO_2 densities with the larger PFOMA segments is accounted for by the fact that the 91K PFOMA copolymer formed micelles with smaller aggregation number than the 52K PFOMA copolymer. The temperature-dependence on mtu transition was also investigated using PBF copolymer with Mn (PtBMA-b-PFOMA) = 7K-48K. It was found that the transition was shifted to lower densities as a result of increasing temperature. This indicates that the micelles reverts to unimers more easily at higher temperature.

The List of recently published papers:

1. "Critical Micelle Density for the Self-Assembly of Block Copolymer Surfactants in Supercritical Carbon Dioxide" Triolo, F.; Triolo, A.; Triolo R.; Londono, J.D.; Wignall, G.D.; McClain, J.B.; Betts, D.E.; Wells, S.; Samulski, E.T.; DeSimone, J.M. Submitted to *Langmuir*, **1999**.
2. "Synthesis of Fluoropolymers in Liquid and Supercritical Carbon Dioxide Solvent Systems" Young, J.P.; Romack, T.J.; DeSimone, J.M. In *Fluoropolymers*, ch. 13. Phenum Publishing, **1999**.
3. "Polymerizations in Supercritical Carbon Dioxide" Kendall, J.L.; Canelas, D.A.; Young, J.L.; DeSimone, J.M. *Chem. Rev.* **1999**, *99*, 543-563
4. "Small Angle Neutron Scattering from Polymers in Supercritical Carbon Dioxide" Londono, J.D.; Wignall, G.D.; McClain, J.B.; Betts, D.E.; Canelas, D.A.; DeSimone, J.M.; Samulski, E.T.; Triolo, R *Neutron News*, **1999**, *10/2*, 10-11
5. "Carbon Dioxide-Induced Swelling of Poly(dimethylsiloxane)"; Royer, J. R.; DeSimone, J. M.; Khan, S. A. submitted to *Macromolecules* **1999**.
6. "Preparation of Micron-size Polystyrene Particles in Supercritical Carbon Dioxide"; Shiho, H.; DeSimone*, J. M. *J. Polym. Sci. Part A*, **1999**, 37, 2429-2437.
7. "Homogeneous Radical Copolymerization of Methacryloxypropyl-terminated Polydimethylsiloxane with a Fluorinated Acrylic Monomer in Supercritical Carbon Dioxide" Shiho, H. and DeSimone, J.M. submitted to *Journal of Polymer Science Part A: Polymer Chemistry*, **1999**.
8. "Dispersion Polymerization of Styrene in Supercritical Carbon Dioxide Utilizing Random Copolymers Including Fluorinated Acrylate for Preparing Micron-size Polystyrene Particles" Shiho, H. and DeSimone, J.M. submitted to *Journal of Polymer Science Part A: Polymer Chemistry*, **1999**.
9. "Dispersion Polymerization of Acrylonitrile in Supercritical Carbon Dioxide" Shiho, M and DeSimone, J.M. submitted to *Macromolecules*, **1999**.
10. "Atom Transfer Radical Polymerization in Supercritical Carbon Dioxide" Xia, J.; Johnson, T.; Gaynor, S.; Matyjaszewski, K. *Macromolecules*, **1999**, *32*, 4802-4805.
11. "Perfluoropolyether Synthesis in Liquid Carbon Dioxide by Hexafluoropropylene Photooxidation"; Bunyard, W. C.; Romack, T. J.; DeSimone, J. M. submitted to *Macromolecules* **1999**.
12. "Continuous Polymerizations in Supercritical Carbon Dioxide: Chain-Growth Precipitation Polymerizations" Charpentier, P.A.; Kennedy, K.A.; DeSimone, J.M.; Roberts, G.W. *Macromolecules*, **1999**, *32*,5973-5975.

On-line monitoring of Emulsion Polymerization by Low Resolution Raman Spectroscopy

By Timothy McCaffery and Yvon G. Durant

We have extended our use of Low resolution Raman spectroscopy to the on-line monitoring emulsion polymerization. Our Raman system is made of an Ocean Optics Raman Spectrometer with an optical fiber probe. The probe is placed directly in the polymerization reactor. Spectra are recorded continuously on a computer every 104 seconds. Each spectrum is the result of a 20 second cumulated acquisition. The excitation laser (785nm) is toggled on-off between each acquisition with a warm-up period of 20 seconds.

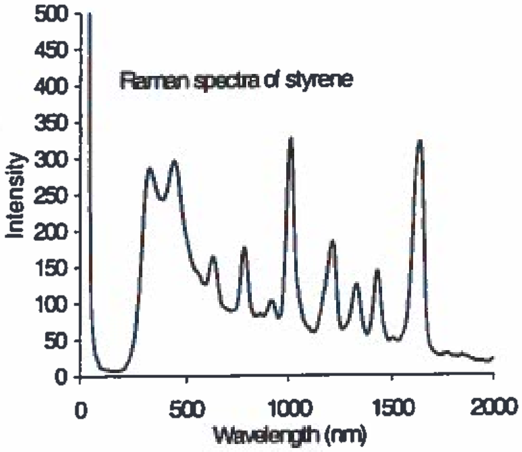
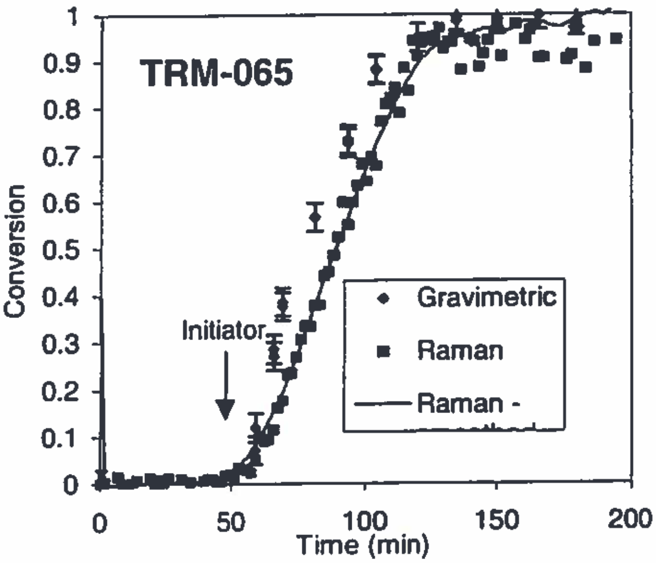


Table1. Experiment	TRM065	TRM066	TRM067
Water (g)	697.994	707.89	700.00
SDS (g)	5.90	5.90	3.00
50nm PS seed (g)	1.95	1.95	-
NaHCO3 (g)	0.30	0.30	0.2
NaS2O8 (g)	0.30	0.30	0.197
Styrene (g)	295.00	371.00	-
Monomer feed	batch	205 min	batch
TRM065 (g)	-	-	100
Butyl Acrylate	-	-	196.7
Dn (nm)	96.8	75.7	140
Dw/Dn	1.04	1.21	

This system has been used to monitor the polymerization of styrene in batch and in semi-continuous, and the second stage polymerization of butyl acrylate from a polystyrene seed. These reactions were carried out in a 1 liter-jacketed reactor under nitrogen at 70°C according to the recipes of table 1.

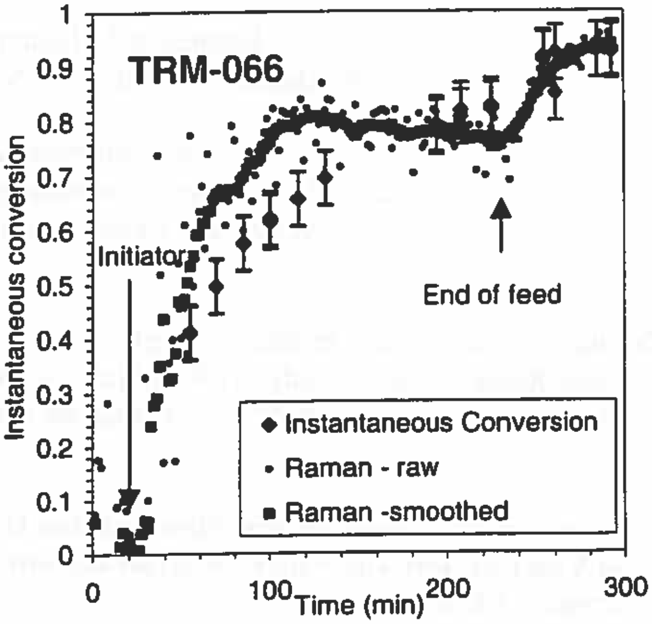
Styrene produces Raman peaks at 1000 nm and at 1600 nm. The 1600 nm peak represents mostly the vinyl stretch and decreases in intensity as polymerization occurs. The 1000 nm peak represents the "breathing" of the phenyl ring and remains independent of polymerization. All vinyl functions have a Raman peak around 1600nm which can be used to quantify monomer concentration. By computing the ratio of the integrated areas of the peaks at 1600 and 1000, we obtain a number independent from scattering intensity, laser intensity and fouling (though it is minimal). The phenyl rings behave serve as internal standard.

Based on the peak ratio and the knowledge of the initial and final condition (i.e. conversion) it is easy to calculate the instantaneous conversion. In the cases of batch polymerization instantaneous and overall conversion are indeed the same. In all cases we have compared the Raman calculations with the conversion obtained



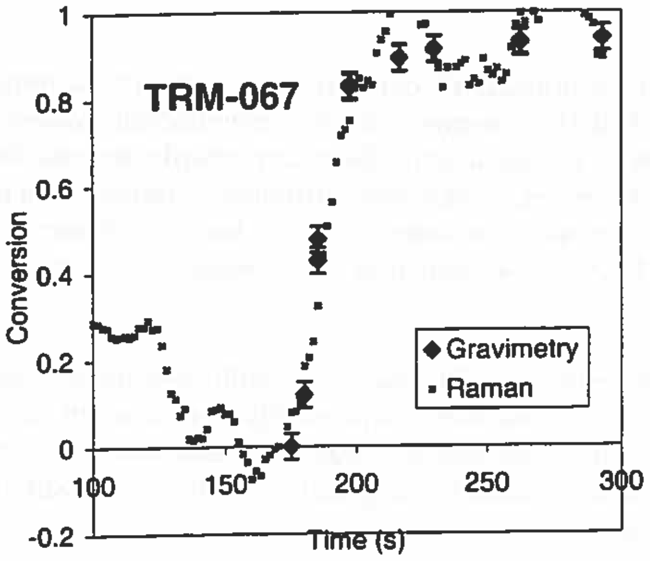
from gravimetric analysis of manual samples.

Due to the temperature at the tip of the probe the polymer tends to build up on the tip. When this occurs the probe is not "seeing" what is occurring inside the reactor but rather what is built up on the tip. The operator is not aware of fouling until the tip is visually inspected. All the results presented are using a proprietary material that inhibits fouling during polymerization and in all cases the probe did not have polymer buildup.



We can see that for the batch polymerization of styrene (TRM065) the Raman compares fairly well with the gravimetric analysis. For the semi-continuous polymerization of styrene (TRM066) we also find a surprisingly good comparison, with both clear distinction of the beginning of the polymerization, which always represent an issue in industry, and for the end of the feed. It is important to notice that the Raman data do not require any assumption on the feed rate, while the gravimetric data point have used "mass balance" information in order to be computed.

In all cases the data obtain from the Raman spectrometer is of poor quality at high conversion, mostly because the lack of monomer implies the integration of very small peaks and hence a great influence of the base line background noise. We are currently working on reducing with noise.



In the last case, the second stage polymerization of Butyl Acrylate, using TRM065 as a see at a 200% stage ratio, we found surprisingly poor results. Though the Raman data does follow well conversion, an excessively high back ground noise limits the attractiveness of the Raman setup.

In conclusion we are strongly encourage by those results obtain with relatively inexpensive equipment. We believe that further integration of online measurements is the key to efficient process control.

International Polymer Colloids Group Newsletter

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The titles of our current research projects are given in the **Contents** of our *Graduate Research Progress Reports*, No. 52, July, 1999, which can be found at the end of this report. Abstracts of several recently completed Ph.D. dissertations are given below.

1. Conventional Emulsion and Miniemulsion Homopolymerization and Copolymerization of Vinyl Acetate and Vinyl 2-Ethylhexanoate Monomers

Ervin L. Kitzmiller

"For monomers of significantly low water solubility, in this case V2EH, the use of miniemulsion polymerization can significantly enhance the reaction kinetics compared to conventional emulsion systems. Monomer diffusional limitations tend to slow down reaction kinetics. While the monomer droplets in a conventional emulsion only serve as reservoirs to supply monomer, any restriction of the monomer to get to the site of nucleation and the growing particles effectively slows the reaction; for miniemulsions, the monomer is already at the site and therefore is not as severely afflicted.

When using reactive TREM LF-40 versus its hydrogenated derivative, similar kinetic trends were observed when comparing VAc and V2EH monomers in the conventional emulsion homopolymerization, where the chain transfer to the surfactant effectively retards the reaction. This was not as prevalent in the miniemulsion system, which was attributed to larger particles generated using miniemulsions, where the surface-to-volume ratio is lower compared to conventional emulsions and the role that TREM LF-40 can play in slowing the reaction is diminished.

The polymeric version of TREM is also a reasonably good surfactant in both conventional and miniemulsion homopolymerizations. Despite the fact that there were no allylic groups left in the structure, the kinetics produced as the surfactant concentration was increased lead to a rate reduction. This result is attributed to the polymeric surfactant sitting on the outside of the particle and effectively behaving as a barrier to radical entry.

Copolymerization showed that the V2EH monomer did incorporate well with VAc. Kinetics studies indicated that varying the monomer ratio did not have as much effect in the miniemulsion system as for conventional emulsion copolymerization, which was attributed to the V2EH monomer's low water solubility. VAc possesses higher water solubility than V2EH and the monomer is suspected to facilitate the V2EH's transport through the aqueous phase, therefore enhancing the kinetics as the VAc component is increased. In addition, for miniemulsion copolymerization, each monomer is already present at the site of nucleation and growth and little is gained or lost as the comonomer ratio is altered.

Miniemulsion copolymerization also resulted in better incorporation of the two monomers. The alkaline stability of the miniemulsion copolymer compared with the conventional emulsion copolymer stems from having the two monomers forced to copolymerize at the same location. VAc has the potential to more readily homopolymerize in the aqueous phase than V2EH; therefore, in conventional copolymerization a significant component of the final latex product richer in VAc content exists."

2. The Role of Mixed Anionic-Nonionic Systems of Surfactants in the Emulsion Polymerization of Styrene

Damien Colombié

"The kinetics of the emulsion polymerization of styrene in the presence of mixtures of SLS and Triton X-405 were studied under various conditions.

The competitive adsorption of SLS and Triton X-405 on polystyrene particles was studied. At low surfactant content, Triton X-405 adsorbed preferentially on the surface of the PS particles. In some cases, it was able to displace some of the SLS from the surface. As the surface coverage increased with increasing total surfactant concentration, cooperative adsorption occurred and a large excess of the two surfactants was noted at the surface of the particles.

These mechanisms affected particle nucleation and particle growth in the presence of a mixed anionic-nonionic emulsifier mixture. When the emulsion polymerization of styrene was started with a mixture of the SLS and Triton X-405, most of the Triton X-405 was associated with the oil phase prior to polymerization. However, the partitioning of the nonionic surfactant in the oil phase was decreased by the presence of SLS. At low SLS contents, the nucleation was homogeneous. However, the number of particles initially formed with the mixed surfactant system was much higher than when the nonionic surfactant was used alone. As a consequence, no secondary nucleation was observed at the disappearance of the droplets. At higher SLS contents, there was enough Triton X-405 initially in the aqueous phase to form mixed micelles. The resulting kinetics were fast.

During particle growth, the continuous feeding of increasing amounts of Triton X-405 in neat monomer did not significantly affect the rate of polymerization of the semi-batch emulsion polymerization of styrene using SLS as the initial surfactant for various feed rates. However, the addition of a shot of Triton X-405 in the seeded emulsion polymerization of styrene using SLS as the initial surfactant, lead to a small increase in the rate of polymerization. Local instability may have occurred in the system resulting from the removal of SLS from the surface. Secondary nucleation was likely to be the cause for the increase in the rate, even though the new particles may have not been stable enough to survive until the end of polymerization.

Differences in the composition of the mixed surfactant layer did not seem to significantly affect the pseudo first order entry and exit rate coefficients of the free radicals into and from the particles as determined by the "slope-intercept" approach. Similarly, even though the chain transfer constant to Triton X-405 was large, it did not significantly influence the kinetics of polymerization, both in bulk and emulsion polymerization.".

3. Towards an Understanding of Steric Stabilization when using PEO-PS-PEO Triblock Copolymer as the Stabilizer in Non-Aqueous Emulsion Polymerization Systems

Xiaorong You

"The unique surface activity of PEO-PS-PEO triblock copolymers makes them useful as stabilizers in the preparation of polymer dispersions, either in aqueous or in non-aqueous media.

Sixteen PEO-PS-PEO triblock copolymers were successfully synthesized via an anionic polymerization process. They were characterized by means of GPC, NMR, and intrinsic viscosity methods. From the intrinsic viscosity versus temperature data, a transition temperature at 35°C was observed for all the PEO-PS-PEO triblock copolymers in propylene glycol. The transition temperature was interpreted as a conformational change in the copolymer molecule.

A non-aqueous emulsion copolymerization model system, composed of ethyl methacrylate (EMA) and lauryl methacrylate (LMA) monomers, 2,2'-azobis(isobutyronitrile) (AIBN) as initiator in the propylene glycol medium, and the PEO-PS-PEO triblock copolymer, was used for evaluating the polymerization, kinetics and stability performance of well-defined PEO-PS-PEO triblock copolymers. The influences of the sizes of the PEO and the PS blocks were studied. Stable latexes were formed when the molecular weights of the PEO blocks were in the range of 5300-7700 g/mol, and the PS anchor block molecular weight was between 2000 and 4000 g/mol.

The adsorption of PEO-PS-PEO triblock copolymer on latex particles was measured. A minimum was observed for the amount of PEO-PS-PEO triblock copolymer that was physically adsorbed on the latex particles for a PS block length of about 30 units. The amount of PEO-PS-PEO which is anchored onto the latex particle surface increases monotonically with the PS block length by virtue of a greater binding energy for longer PS unit lengths. In addition, the effects of stabilizer concentration as well as monomer concentration on the adsorption behavior were investigated. It has been found that both the physically adsorbed and anchored molecules decreased with increasing stabilizer concentration. On the other hand, when the monomer concentration was increased, the physically adsorbed molecules, as well as the anchored molecules, increased. Furthermore, polynomial equations were derived for calculating the total number of PEO-PS-PEO triblock copolymer chains needed for providing stabilization.

Several kinetic parameters, including the rate of polymerization, particle density, and total surface coverage, were measured independently. A homogeneous nucleation mechanism was supported by all the data, seeded polymerization, kinetics, and monomer partitioning behavior."

4. Miscibility of Vinyl Acetate-Ethylene Copolymers with Vinyl Chloride-Ethylene Copolymers

William R. Dougherty

"Over the past several decades, much research has been focused on identifying polymers that form miscible blends. The tasks of defining and characterizing polymer miscibility, as well as determining and modeling the conditions that are necessary for it to occur have been unique and all encompassing. Numerous studies have looked at the miscibility between poly(vinyl chloride) (PVC) and vinyl acetate-ethylene (VAE) copolymers. Regions of miscibility have been identified depending on VAE copolymer composition, molecular weight, and blend preparation conditions. The existence of the miscible region has been rationalized in terms of the specific rejection model. Others have disputed the validity of this model, and instead have used specific interactions as an explanation. The current study looks at VAE blends with vinyl chloride-ethylene (VCE) copolymers. The copolymers were synthesized by solution and emulsion polymerization, and blends were prepared via solution casting, emulsion casting, and compressing molding. Fourier Transform Infrared (FTIR) Spectroscopy, Differential Scanning Calorimetry (DSC), and Dynamic Mechanical Spectroscopy (DMS) were used to analyze the blends and ascertain the region of miscibility. Miscibility behavior was found to depend on both copolymerization method, and sample preparation method. Annealing and casting solvents enhance miscibility, although no difference was observed when casting from either THF and MEK. No specific interactions were observed regardless of copolymer type or blend preparation method. The results suggest that the specific interaction theory does not accurately predict the observed miscibility. Specific rejection predicts miscibility more closely, but the low molecular weight analog compounds used for the calorimetry-based predictions do not mimic the copolymer structures used in this study. Lastly, VAE-VCE emulsions prepared by a staged technique yielded miscible systems without annealing or the addition of solvents."

5. Enhanced Droplet Nucleation in Miniemulsion Polymerization—A Kinetic and Mechanistic Study

P. John Blythe

"Predissolving polymer into the monomer prior to homogenization in miniemulsions created using cetyl alcohol as the cosurfactant results in a large enhancement in the polymerization kinetics compared to similar systems with no predissolved polymer. This phenomenon is termed 'enhanced droplet nucleation'. This work studies the effect of varying the molecular weight and end-group of the predissolved polystyrene in styrene miniemulsions. Predissolving polystyrene with either H or SO_3^- end-groups and molecular weights over a range from M_n=39,000 g/mol to 206,000 g/mol results in the same level of enhancement in the kinetics when cetyl alcohol was used as the cosurfactant. However, when hexadecane is used as the cosurfactant, there is a much smaller level of enhancement of the kinetics caused by predissolving the various types of polystyrene. In homogenized emulsions, there is again a significant enhancement in the kinetics resulting from predissolving polymer prior to homogenization.

A direct relationship is noted between whether the system exhibited 'enhanced droplet nucleation' and the stability of the miniemulsion droplets. Measurement of droplet size when the droplets are either not stabilized or are stabilized with cetyl alcohol indicates the droplets undergo degradation from the extremely small droplet sizes produced by the Microfluidizer. However, hexadecane is able to eliminate degradation even in the extremely small droplets produced in the Microfluidizer. These results indicate that 'enhanced droplet nucleation' is primarily a result of the polymer adding extra stability to the miniemulsion droplets both prior to and during the polymerization. Thus, the largest effect of the polymer is seen in systems with measured droplet instabilities.

The effect of the level of shear imparted to create the miniemulsion is reported. The most important finding was when cetyl alcohol is used for the cosurfactant and the level of shear imparted to create the miniemulsion is reduced to a point where droplets have been measured to be stable, there is no enhancement in the kinetics resulting from predissolving polymer. This was taken as further evidence that 'enhanced droplet nucleation' is primarily caused by preservation of droplet number. A mathematical model is proposed that accurately predicts the kinetics using concepts gained from the experimental work."

EMULSION POLYMERS INSTITUTE

Lehigh University

Graduate Research Progress Reports
No. 52 July 1999

CONTENTS

Aggregation Behavior and Coronal Structure of Novel Polyelectrolyte Micelles

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We study a class of novel block copolymers which aggregate to form micelles in neutral to basic aqueous solutions. We focus our attention on four copolymer samples, each of which contain the same pH sensitive 2-(diethylamino)ethyl methacrylate (DEAEMA) hydrophobic block. With each copolymer containing a different hydrophilic block with varying electrostatic properties we seek to provide a detailed picture of their pH and salt dependence. We use small angle neutron scattering (SANS) and Dynamic Light Scattering (DLS) to characterize the micellar structures under these varying conditions. Examination the low q region of the SANS scattering profiles allows us to determine how the aggregation behavior changes with varying pH and ionic strength. Analysis of the intermediate scattering region at higher q enables us to probe finer details in the micelle corona, and provides a picture of the swelling properties of the corona with varying pH and salt concentrations.

Optical Trapping in Magnetorheological Suspensions

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The key to understanding and controlling the rheological response of a colloidal system lies in characterizing the microstructure and its response to perturbations [1]. The formation of well-defined microstructures in magnetorheological (MR) and electrorheological (ER) suspensions offers a clear example. When an external magnetic or electric field is applied to an MR or ER suspension, the particles acquire dipole moments. At field strengths sufficient to overcome thermal disordering, the particles aggregate into chains of dipoles in the field direction. Because energy is required to deform and rupture the chains, this microstructural transition is responsible for the onset of a large, ``tunable," finite yield stress. Applications for MR and ER suspensions include active shock absorbers, clutches, and brakes.

We apply optical trapping techniques in an MR system, allowing us to directly measure the mechanical properties of a dipolar chain, such as the rupturing stress and strain under tensile and affine deformations. Our results under these conditions are in good agreement with calculations of the rupturing stress and strain using a self-consistent point dipole model of the particle interaction that takes into account induction and multi-body effects along the chain. Additionally, we observe energy-dissipating "rearrangements" of chains as a stress is applied, such as the inclusion of neighboring particles into the chain. Similar mechanical measurements on columns of laterally-aggregated chains show that column formation significantly increases the microstructure resistance to applied stresses. Also, rearrangements in columns possibly provide mechanisms for "shear-hardening" effects at intermediate field strengths.

Direct microscopic manipulation allows us to investigate the lateral interaction between chains. In MR suspensions, strong Landau-Peierls thermal fluctuations are thought to cause a lateral attraction between chains that influences the long-time suspension structure, such as the formation of columns or "cross-linking" between chains at high particle concentrations. [2]

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Density Functional Theory of Crystallization

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First-order phase transitions, such as crystallization, are phenomena observed in nearly all known classical systems, ranging from the basic elements to mesoscopic colloids to complex biological macromolecules. Examples abound in both natural and industrial settings, including the freezing of water into ice, the disorder-order transition of polystyrene particles, and the preparation of very pure crystals from the melt. Despite the ubiquity of the crystallization process, however, a full theory of crystallization has remained elusive. Such a model would begin with the interactions present in the fluid phase of a system and be capable of predicting all equilibrium thermodynamic and structural properties at freezing.

In the past twenty years, a promising new avenue of research into the crystallization problem has been pursued. These density functional theories all involve obtaining properties of the equilibrium solid from fluid state input data. In spite of the early triumphs of these models in predicting phase transitions for many systems, however, it was soon realized that these successes could not be replicated in other systems and applications. These failures were traced to the inability of fluid state properties in modeling the static Madelung solid, or even a very highly ordered solid. To correct these deficiencies, a more general model, the Modified Weighted Density Approximation with a Static Solid Reference State (MWDA-SRS), has been proposed [1]. This model incorporates properties of the static solid, which are easily calculable, into existing density functional theory models.

The MWDA-SRS model is applied to a myriad of different systems to test its predictive abilities. For the high density hard sphere solid, correct equations of state up to near close packing are obtained [2]. For soft sphere systems, including the power law and Yukawa fluids, crystallization into face-centered cubic (FCC) solids for short-range, hard potentials and into body-centered cubic (BCC) solids for long-range, soft potentials is observed [1,3-4]. This is in agreement with both computer simulation findings, as well as observations on charge-stabilized colloidal systems.

For attractive systems, including the Lennard-Jones and attractive Yukawa systems, crystallization is also observed under the MWDA-SRS model. This is an improvement over previous theories, which could not predict a freezing transition for attractive systems. The range and hardness of the repulsive portion of an attractive system is found to be the determinant for the slope of the crystallization curve [5]. By varying ranges of attractions and repulsions, therefore, phase diagrams can be custom-tailored to yield desired properties.

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4. D. C. Wang and A. P. Gast, *J. Chem. Phys.*, in press (1999).
5. D. C. Wang and A. P. Gast, in preparation.

Chiral Domain Formation in Co-crystallization of Wild Type and Mutant Streptavidin

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We are studying the macroscopic morphology and molecular arrangement of two-dimensional streptavidin crystals bound to biotinylated lipid monolayers at the air-water interface. At pH 4, wild type streptavidin forms thin needle-like crystal structures with P1 lattice spacing. Using molecular modeling we identified the protein-protein contacts characteristic to this lattice structure. One of these contact points, an aspartate residue at position 36, was mutated to a lysine residue through recombinant protein techniques. The lysine residue was introduced to create steric and electrostatic repulsion at this contact point so as to disrupt formation of the P1 crystals. Unlike the wild type streptavidin at pH 4, the mutant streptavidin forms dendritic x-shaped crystals with P2 lattice spacing. Co-crystallization of wild type and mutant streptavidin was performed at pH 4 in varying ratios of each protein type. When 25% mutant streptavidin is introduced into the system, the needle-like crystals normally formed by wild type streptavidin begin to form chiral ends. At 50% mutant concentration, the streptavidin crystals emerge with inverse-S shaped chiral morphologies. And when the mutant streptavidin concentration is increased to 75%, the crystals maintain their chirality, but become thinner. We believe that the chirality observed in these intermediate crystals is due to a combination of P1 and P2 lattice spacing within each crystal domain. These crystals are analogous in shape and structure to those formed from wild type streptavidin at lipid monolayers over a subphase pH range of 5 to 6. Here the electrostatic interactions cause a mixture of crystal types near the isoelectric point. We discuss these analogous systems and the nature of the solid-solid phase transition.

Contribution from the group of Ton German at Eindhoven University of Technology to the IPCG Newsletter (H.M.A.van.der.Heijden@tue.nl, http://www.chem.tue.nl/spc/)

I. Surfactant Vesicles in Templating Approaches[#]

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[#]This is a brief summary of the Ph.D. thesis of Dominique H.W. Hubert "Surfactant Vesicles in Templating Approaches", Eindhoven University of Technology, 1999.

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The development, characterisation and exploitation of novel materials based on the assembly of molecular compounds is an active and rapidly expanding field. Typically, supramolecular assemblies are exploited as chemically and spatially specific interfaces for morphological patterning. In this thesis, the theme 'surfactant vesicles in templating approaches' has been addressed. Surfactant vesicles were used as templates in two fundamentally different ways. One approach focused on the use of the vesicle bilayer as a compartmentalised reaction space for the polymerisation of organic (hydrophobic) monomers. The other approach exploited the outer leaflet of the bilayer as a receptive surface involved in the controlled growth of silica from precursor solutions (sol-gel synthesis). Morphological imprinting of the surfactant vesicle onto the synthesised matter was pursued. It was anticipated that surfactant vesicles represent a unique opportunity to construct submicron hollow particles. The thesis aimed at a phenomenological understanding of the processes that occur during templating in these systems. In doing this, special attention has been paid to the trine: vesicle (bilayer), precursor and growing material. Their mutual interactions during the process of templating, as well as their combined influence on the morphological evolution of the total system has been examined and explanations have been offered.

Surfactant vesicles exhibit many interesting chemical and physical properties. The general and relevant features of these structures are discussed. Vesicles represent a special class of surfactant architectures and have to be pictured as colloidal structures with intrinsic meta-stability. These entities are characterised by their unique structure, their phase transition behaviour, dynamics, colloidal and mechanical stability. What is more, external parameters, like temperature or solutes, may greatly affect these characteristics. Consequently, thorough morphological characterisation by means of cryo electron microscopy is of utmost importance.

A novel kinetic model for vesicle formation is developed, based on the concept of formation via the intermediation of bilayer fragments. Essentially, this model supposes that vesicle formation is merely the outcome of the kinetic balance between fusion and closing of intermediate bilayer fragments. Model calculations show the relation between the actual kinetic balance and the evolution of vesicle formation. The model may be powerful in designing novel processes and appropriate experimental conditions to control the product outcome.

Various methods of preparing and characterising of dioctadecyldimethyl ammonium bromide (DODAB) vesicles (See Figure 1) have been investigated. Extrusion is examined as a technique to reproducibly prepare unilamellar vesicles (d_p~160nm). It is demonstrated that the formation of vesicles is a complex process involving hydration reactions and fusion/fission phenomena, rather than simple dissolution and aggregation of surfactant unimers. Importantly, a hydrated crystalline phase represents the true equilibrium state of the DODAB/water system at room temperature. As a crystalline phase cannot adopt a curved structure, vesicles cannot be preserved in the long term. However, their extremely retarded relaxation phenomena renders these vesicles kinetically stable. Further, easy and readily available techniques are presented, *i.e.* conductometry and turbidity measurements, to determine the phase transition behaviour of these vesicles.

The strategy of the exploitation of surfactant vesicles as compartmentalised reaction spaces for the polymerisation of monomer solubilised in the bilayers has been addressed in considerable detail. Monomer addition is the first step in this approach. It is required to ensure fast and controlled addition of monomer to the vesicle solutions without destroying the vesicle structure. To this end, a novel hollow fibre membrane set-up was developed, where a membrane ensures controlled transfer of monomer and prevents supersaturation of the vesicle solution. Kinetic and thermodynamic aspects of the monomer transfer process are investigated and corresponding parameters are quantified. Styrene is taken as monomer. The solubilisation of styrene has a significant effect on the characteristics of the bilayer: the presence of monomer brings about a marked reduction of the phase transition temperature, as it acts as a 'plasticizer'. Also, styrene is shown to give rise to shape transformations of the vesicles dependent on the actual degree of loading (See Figures 2 and 3).

Investigations on the polymerisation in monomer laden vesicles show that intra-bilayer phase separation processes occur during polymerisation and that, as a consequence, the templating approach as such fails. It is shown, though, that this polymerisation gives rise to the formation of interesting novel parachute-like structures in which polymer is confined to the bilayer of the vesicle, collapsed to a *single* bead (See Figure 4). Control of the bead size, *i.e.* $30< d_p< 70$ nm, is possible by tuning the monomer loading. The polymer bead is retained or expelled dependent on the degree of rigidity of the bilayer. As such, the vesicle can be regarded as a nano-reactor for small polymer latex particles. The parachute-like vesicle/polymer hybrids embody a novel class of polymer colloids with multicompartmental features. Further, numerous experiments are conducted, varying monomer type and concentration, temperature and even mode of polymerisation. Irrespective of these conditions, polymer clustering is always apparent. In contrast to current opinion in literature on polymerisation in vesicles it is stated that this template polymerisation is bound to fail at the very beginning of the polymerisation due to the incommensurability of the bilayer and the polymer. Mechanistic, thermodynamic and kinetic considerations are presented to support this picture.

Quantitative data on size and shape of the parachute-like vesicle/polymer hybrid particles and of the bare DODAB vesicles are obtained by combination of transient electro-optic birefringence (Kerr Effect) and dynamic light scattering. Also, the study qualitatively assesses the influence of the confined polymer bead on the electro-optic behaviour: the presence of the bead gives rise to a special response, typical of the existence of permanent dipoles, whereas bare vesicles couple to the electric field via induced dipoles. Unlike other vesicles, DODAB vesicles and polymer/vesicle hybrids do not display a deformation step in their electro-optic response. To the best of our knowledge, this is the first vesicular system that acts as rigid particles under the action of an electric field.

The second template approach that has been addressed in this thesis exploits the outer leaflet of the bilayer as a receptive surface for the controlled growth of silica from precursor solutions (sol-gel synthesis). The successful synthesis of silica coated unilamellar surfactant vesicles by using DODAB vesicles as templates in the growth of silica from the hydrolysis and condensation of silicon alkoxides is reported. Evidence of 5-10 nm silica coating is provided by independent methods. The cationic surface of the vesicles is shown to represent an excellent receptive surface that likely directs nucleation and growth of silica from solution. In addition, it is demonstrated that structural and mechanical stability of the template are essential. Lack of stability of the first kind inevitably results in a failure of oriented growth as the directing surface disintegrates. Deficiency of the latter stability leads to deformation of the template during the process. Moreover, the construction of vesicle based inorganic/organic hybrids as an exemplar of meeting challenges in nanotechnology is reported: 'Petrification' of parachute-like vesicle/polymer hybrid particles is demonstrated.

Morphological transformations of vesicles reminiscent of cellular endocytotic uptake and vesicular trafficking are reported (See Figure 6). Explanations for the observations are given in terms of basic physico-chemical processes and intrinsic vesicle properties. The reported findings allow a basic understanding of the physico-chemical nature of the complex morphological transformations in biology.

In retrospective, the work presented in this thesis illustrates the paradigm that templating demands compatibility of the template with the generated material, *e.g.* polymer or inorganic matter, and, of course, structural and mechanical stability of the template.

Finally, the present results emphasise that special attention, with ultrastructural detail, has to be paid to the trine: template matrix, precursor and growing material when developing templating procedures and techniques, or, generally speaking, when exploring the theme of molecular tectonics.

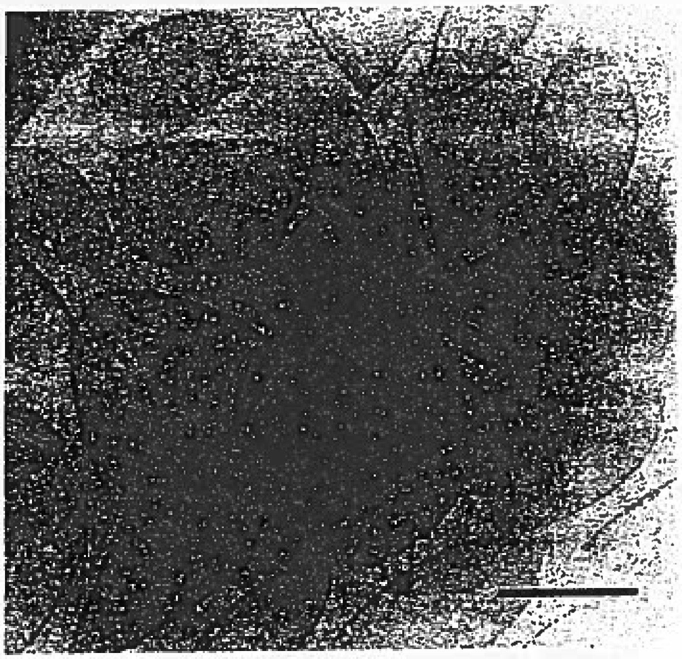

Figure 1: A micrograph of a typical vesicle solution obtained by the standard extrusion protocol. Vitrified sample quenched from room temperature (bar=100nm).

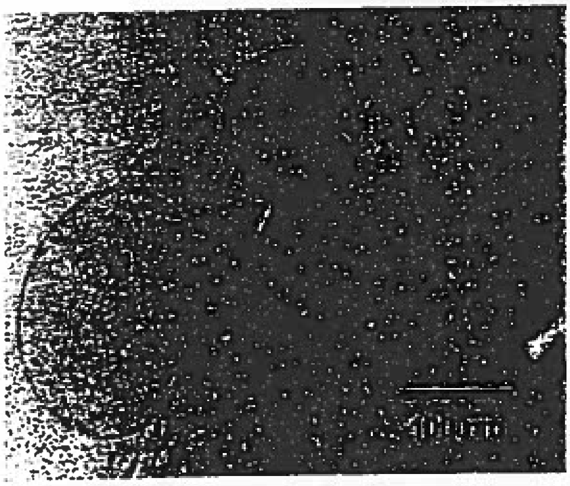

Figure 2: A cryo-micrograph of extrusion vesicles with a low loading with styrene (quenched from room temperature).

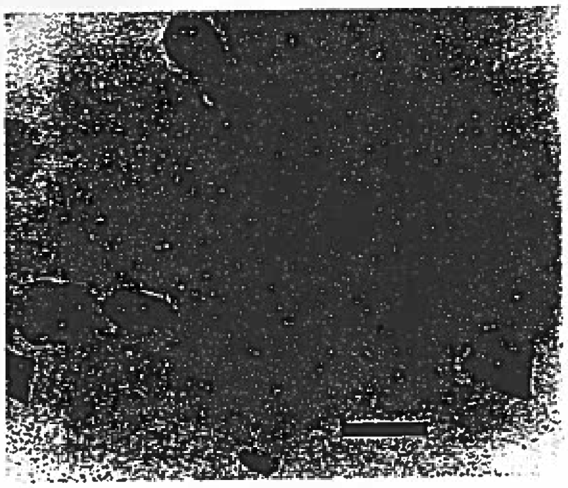

Figure 3: A cryo-micrograph of extrusion vesicles with a high loading with styrene (quenched from room temperature) bar=100nm.

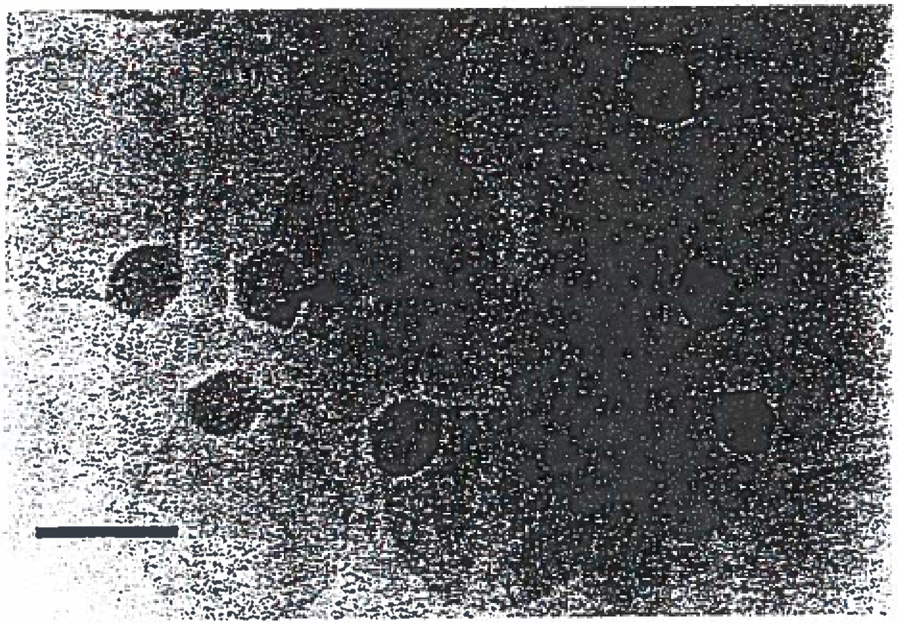

Figure 4: A Cryo-TEM micrograph (bar=100nm) of a photopolymerised product of styrene laden extrusion vesicles ($1.0 \cdot 10^{-2}$ kmol/m^3 DODAB) at T=25°C.

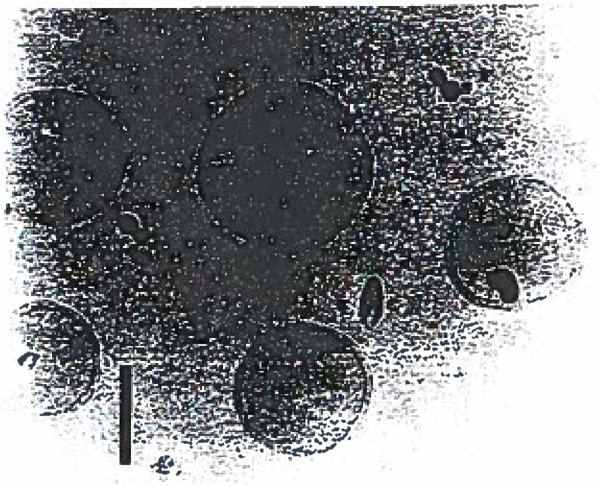

Figure 5: Cryo-Micrograph of silicificated surfactant vesicles. Bar correspond to 200 nm.

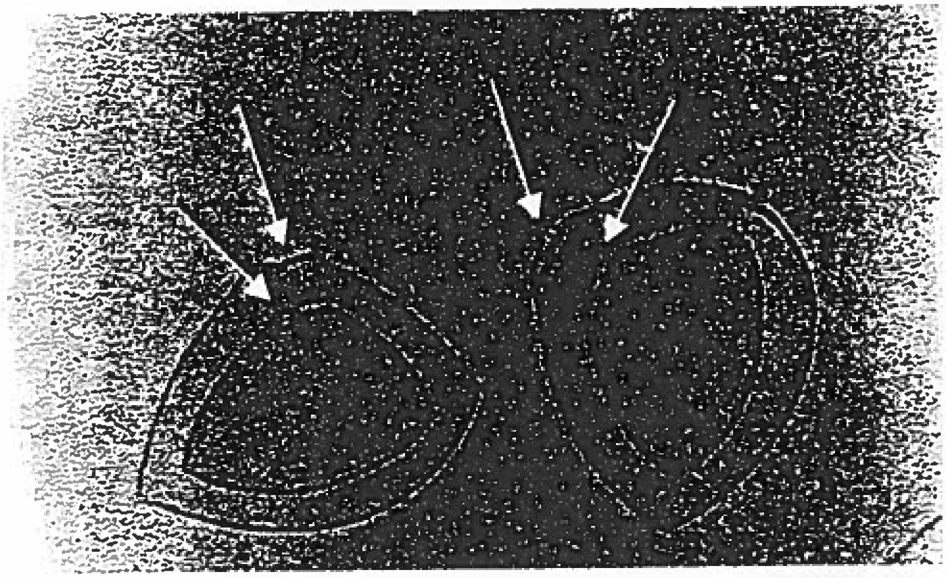

Figure 6: Cryo-TEM micrograph. Morphological transformations of vesicles reminiscent of cellular endocytotic uptake (*cf.* Figure 1).

II. Oil-Acrylic Hybrid Latexes[#]

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[#]This is a brief summary of the Ph.D. thesis of Eelco van Hamersveld "Oil-Acrylic Hybrid Latexes", Eindhoven University of Technology, 1999.

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INTRODUCTION

The objective of the investigations described in this thesis was the development of systems that enable use of vegetable oils as binders for VOC-free waterborne coatings. For this purpose research was directed towards the preparation and characterization of oil-acrylic hybrid latexes and towards the analysis of the film formation behavior of these oil-acrylic hybrid latexes.

OIL-ACRYLIC HYBRID LATEXES

The first part of the thesis describes the study on the preparation of oil-acrylic hybrid latexes using mini-emulsion polymerization. The mini-emulsion polymerizations were initiated by fatty-acid hydroperoxides (SFO-HP) or by *tert*-butyl hydroperoxide (*t*-BHP) in an ROOH/Fe^{2+}-EDTA/sodium formaldehyde-sulfoxylate (SFS) redox initiation system. In this part MMA was used as the monomer. It was shown that the formation of a second generation of all-acrylic particles was strongly reduced with the use of the mini-emulsion polymerization process. The mini-emulsion system was established using *n*-hexadecane as hydrophobe.

Oxidized sunflower oil was used as initiator in the SFO-HP initiated system and the process was compared with that initiated by *tert*-butyl hydroperoxide (*t*-BHP). Cryogenic transmission electron microscopic analysis (cryo-TEM) of the particle morphology of hybrid latexes prepared from the two different types of initiators showed that initiation by SFO-HP resulted in a more homogeneous particle morphology. The cryo-TEM images of the particles prepared from t-BHP and from SFO-HP are presented in Fig. 1A and Fig. 1B

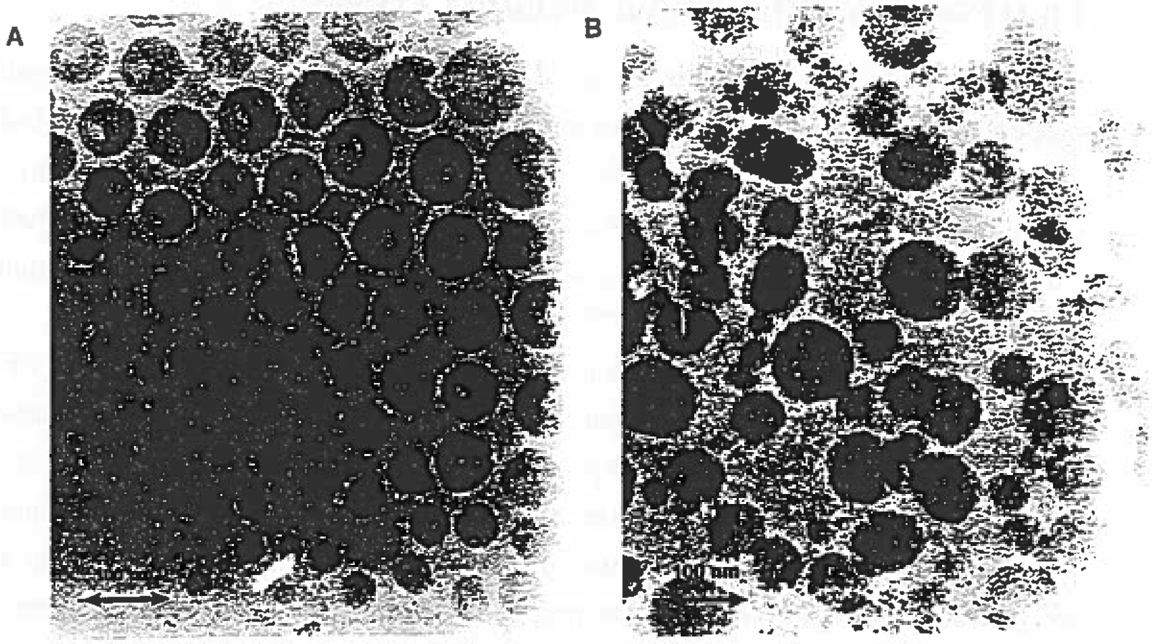


Figure 1. (a) Cryo-TEM image of hybrid latex of SFO and pMMA initiated by t-BHP. (b) Cryo-TEM image of hybrid latex initiated by fatty-acid hydroperoxides (SFO-HP).

The kinetics of the SFO-HP initiated mini-emulsion polymerization were studied by analysis of the polymerization rate of MMA at various conditions. It was shown that the rate of MMA polymerization depended on the concentration of hydroperoxide groups, represented by the hydroperoxide value (HPV) of the oxidized sunflower oil, and on the polymerization temperature. The concentration of SFS and of Fe^{2+} did not influence the rate of polymerization. This suggested that the availability of fatty-acid hydroperoxides was the rate-limiting step during initiation[1].

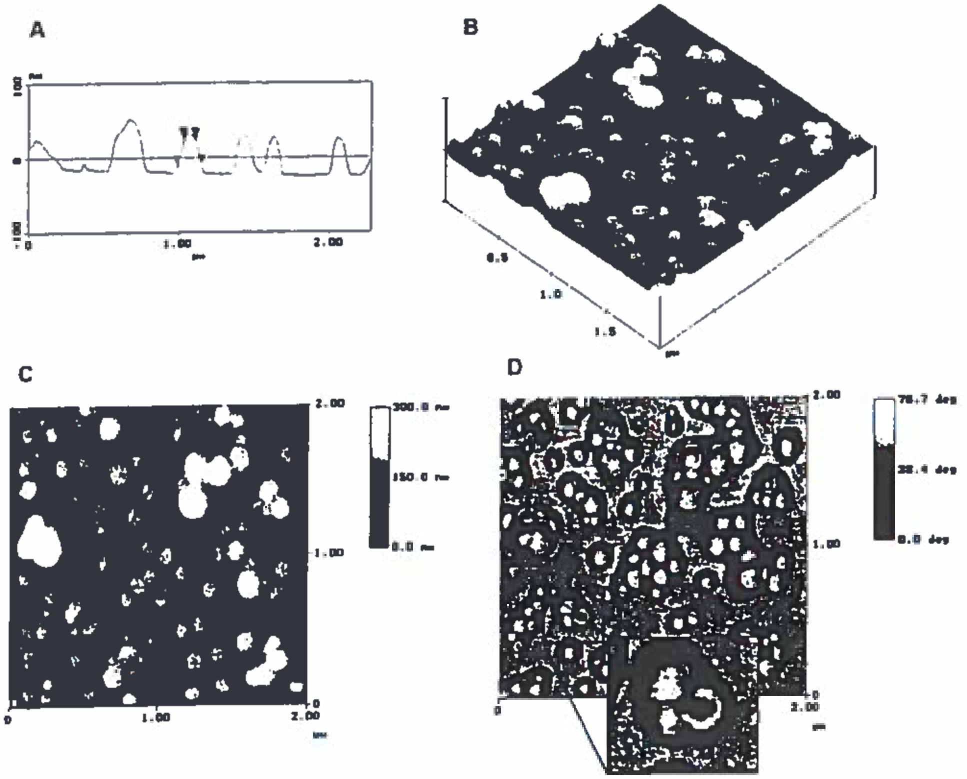
The preparation of emulsions of sunflower oil with different levels of hydroperoxides was studied by oxidation of emulsions of sunflower oil at high partial oxygen pressure and by bulk oxidation of sunflower oil followed by emulsification. At high oxygen pressure the rate of formation and concurrent decomposition of hydroperoxides was found to increase with increasing oxygen pressure. In the bulk the oxidation temperature was of major influence. As the bulk method appeared to be the most flexible oxidation method that yielded the highest HPVs, it was used throughout the rest of the work described in this thesis for the preparation of SFO-HP initiated oil-acrylic hybrid latexes.

FILM FORMING OIL-ACRYLIC HYBRID LATEXES

The preparation of high-solids oil/alkyd-acrylic hybrid latexes with film forming properties and the analysis of the film formation of these hybrid latexes is described in the second part of the thesis. Ethyl methacrylate was used as monomer in the preparation of the film forming hybrids. The hybrid latexes could be prepared with a solids content of 45 w% in various compositions of oil/alkyd to acrylate. The studied compositions varied from 25 w% to 75 w% of oil/alkyd.

Cryo-TEM analysis of the oil/alkyd-acrylic hybrid particles, initiated either by SFO-HP or *t*-BHP, indicated that the particles had a homogeneous particle structure. Analysis by atomic force microscopy (AFM) of individually adsorbed and dried particles suggested that (partial) phase separation had occurred between the oil/alkyd phase and the acrylic phase as shown in Fig. 2. Contact angle measurements and ESCA analysis of surfaces of films prepared on substrates of various degrees of hydrophobicity showed that this phase separation was not very prominent in bulk films.

Figure 2. *AFM analysis of particles of oil-acrylic hybrid adsorbed and dried onto PEI-modified mica. (A) cross-sectional profile, (B) topographic surface plot, (C) top-view topographic image, and (D) phase image.*



Analysis of films prepared from the hybrid latexes time resolved fluorescence microscopy showed an initial difference in the degree of micro-scale mixing between films prepared from latexes initiated by SFO-HP or from by *t*-BHP.

COATINGS FROM OIL-ACRYLIC HYBRID LATEXES

In the final part of the thesis the coating performance of the developed oil/acrylic hybrid system is compared in a non-pigmented formulation with that of a blend system of alkyd emulsion and an all-acrylic latex with similar composition and with that of an alkyd emulsion. It was shown that the drying time of films prepared from the hybrid systems were shorter than those prepared form the blend system and the alkyd emulsion. The hardness and gloss of the films were related to the chemical composition of the systems. Higher contents of oil/alkyd in the hybrid system and in the blend system resulted in an increase in the gloss of the film and in a decrease in the film hardness. This effect was more pronounced in the blend system.

AFM analysis of the morphology of films prepared from blend systems with different compositions showed that the oil/alkyd phase forms the continuous matrix, in which the acrylic particles were randomly distributed. At higher acrylic contents (higher than ~55 w%) not all of the acrylic particles could be enclosed by the oil/alkyd. This resulted in non-transparent films.

The developed oil-acrylic hybrid latexes show interesting opportunities for use of vegetable oils in waterborne coatings.

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Contribution to the IPCG Newsletter from the Key Centre for Polymer Colloids

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Papers submitted or in press

Living free-radical polymerization and molecular weight characterization of poly(N-isopropyl acrylamide. F. Ganachaud, MJ Monteiro, RG Gilbert, M.-A. Dourges, SH Thang and E Rizzardo. *Macromolecules*, submitted.

A series of relatively monodisperse samples of poly(N-isopropyl acrylamide) was synthesized by reversible addition-fragmentation chain transfer (RAFT), over the molecular weight range $2\times10^3 - 3\times10^5$. For molecular weights below 4×10^4, conditions were found so that polydispersity remained below 1.4 up to high conversion (72%). Molecular weight distributions of polymer obtained using GPC in THF and MALDI were in accord for the low molecular weight range (typically 10^5). Particular care is required in GPC sample preparation: it is necessary to ensure that trace amounts of water are initially present when dissolving a polymer sample in THF to avoid irreversible chain aggregation. The hydrodynamic volume of polyNIPAM chains was found to be proportional to molecular weight only for molecular weights $< 10^5$, after which the hydrodynamic volume seems to be independent of molecular weight. The Mark-Houwink parameters obtained from the lower molecular weight data are $K = 10^{-(4.24\pm0.42)}$ dL g^{-1} and $a = 0.78\pm0.09$. A possible reason for the anomalous GPC behavior at higher molecular weights is that polyNIPAM chains form a superstructure of constant hydrodynamic volume above a cut-off value.

Polymer science and technology in the past and the future: heroism, exploration and enlightenment. R.G. Gilbert. Chinese J. Polym. Sci. in press.

From a contemporary perspective, the interlinked scientific and technical history of polymerization can be divided into three periods. These are illustrated for emulsion polymerization.

The first period, which might be termed the *Heroic Age*, was when emulsion polymers were originally produced. The technique was developed as an attempt to copy natural rubber latex. Indeed, the natural process is quite different from the synthetic process of emulsion polymerization, which in fact does not even need an emulsion to be present: the term is a misnomer! The results were functional but limited. The second period in emulsion polymerization might be termed the *Age of Exploration*. The first theories of the process appeared in the 40's, and from the late 30s to the 80s a huge range of products was made, for surface coatings, adhesives, commodity polymers such as SBR, neoprene, etc. The scientific bases of the industrial research efforts were largely those first laid down by the founders of the field. While these scientists were indeed giants, they were not omniscient, and processes were *semi-empirical*. Many suppositions used were not correct: after all, the analytic tools available then were relatively limited. Nevertheless, many excellent products were made and have evolved to many materials currently in everyday use. However, virtually all common industrial "recipes" are exactly that: some ingredients were put in because they happened to be, for example, a surfactant which was on the lab shelf at the time, and their function, if any, is now uncertain; now, no one dares take them out! The third period of emulsion polymerization might be termed the *Age of Enlightenment* and is now dawning. The scientific efforts of many teams over previous decades, aided by the advent of new physical techniques for investigation, have resulted in better understanding of the fundamentals of emulsion polymerizations. It is now possible to do what has never been done before: design an industrial process based on first-principles sound scientific knowledge rather than evolution from a semi-empirical recipe. A number of examples of this will be given from the author's group (in collaboration with D Lamb, J Anstey, N Subramaniam, C Fellows and M Monteiro): creating novel materials using controlled seeded emulsion polymerization from natural rubber latex, and from other substrates such as polybutadiene where the topology and controlled free-radical chemistry are combined to produce (a) a comb polymer with hydrophobic backbone and hydrophilic "teeth", or (b) with sufficient *in situ* compatibilizer between two otherwise incompatible polymers to yield a spatially uniform material down to the nanostructure level, and (c) to produce controlled nanostructures.

Testing models for penetrant diffusion in glassy polymers. MP Tonge and RG Gilbert. *Polymer*, in press.

Data from forced-Rayleigh scattering studies of diffusion coefficients for camphorquinone and diacetyl in poly(methyl methacrylate) in the glassy regime were used to test two models for this quantity. Free-volume theory with the parameter-choice method suggested by Vrentas and co-workers [Vrentas, J. S.; Vrentas, C. M. *European Polymer J.* **1998**, *34*, 797] predicts an activation energy (*ca.* 260 kJ mol^{-1}) which is a factor of about 2 greater than experiment, and a pre-exponential factor which is several orders of magnitude too large: thus this model underestimates experimental diffusion coefficients by many orders of magnitude at the temperatures studied. This is ascribed to free-volume theory being inapplicable to the actual mechanism for penetrant diffusion in glassy polymers: simulations suggest this occurs instead by occasional jumps between cavities through the opening of a "neck". This jump mechanism is explicitly taken into account by the second model tested here [Gray-Weale, A. A.; Henchman, R. H.; Gilbert, R. G.; Greenfield, M. L.; Theodorou, D. N. *Macromolecules* **1997**, *30*, 7296]. Although this model successfully predicts diffusion coefficients of small nonpolar penetrants, it is found to greatly overestimate observed diffusion coefficients in the present system, perhaps because it underestimates the attractive potentials between the penetrant and the polymer matrix and/or breakdown of the model's assumption of linear elastic deformation for relatively large penetrants.

Penetrant diffusion in poly(methyl methacrylate) near T_g: dependence on temperature and polymer weight fraction. M.P. Tonge, J.M. Stubbs, D.C. Sundberg, R.G. Gilbert. *Polymer*, in press.

Forced Rayleigh Scattering was employed to measure diffusion coefficients for a ternary system comprising camphorquinone or diacetyl in poly(methyl methacrylate) with methyl isobutyrate as diluent. Measurements were made at polymer weight fractions, w_p, over the range 0.78 – 0.90 and temperature 25 – 50°C for camphorquinone (which spans the glass transition regime), and at $w_p = 0.9$ and 0.95 and at room temperature for diacetyl. Results for camphorquinone show a strong temperature dependence, with diffusion coefficients changing as much as two orders of magnitude between 25 and 50°C, and showing high activation energies for diffusion ≈ 125 kJ mol^{-1}. No sharp change in the activation energy for diffusion was observed as the glass transition is crossed. The pre-exponential factor for the diffusion coefficient decreased dramatically through the glass transition. The diffusion coefficients of small penetrants in glassy polymers appears strongly dependent on molecular size.

Using mechanisms to make seemingly impossible latexes and polymers. JF Anstey, N Subramaniam, BTT Pham, X Lu, MJ Monteiro and RG Gilbert. *Macromol. Symp.*, in press.

It is possible to create latex particles wherein the molecular architecture, on the micro- or nano-scale, appears thermodynamically unfavourable. This can be brought about by exploiting both the topology of an emulsion polymerization (i.e., it takes place in a dispersed medium) combined with appropriate free-radical chemistry. Some examples include creating latexes by seeded emulsion polymerization wherein there is (a) extensive grating between hydrophobic and hydrophilic entities, (b) sufficient graft copolymer is created *in situ* to compatibilize two polymers with significantly different solubility parameters, and (c) graft copolymers between styrene and aniline with interesting electrical properties.

Pulsed-laser polymerization (PLP) of N-isopropyl acrylamide in water : a qualitative study. F. Ganachaud, MJ Monteiro and RG Gilbert. *Macromol. Symp.*, in press.

Pulsed-laser polymerization results are presented for N-isopropyl acrylamide (NIPAM) in water; the data show the overtones that satisfy one of the PLP consistency tests. Apparent propagation rate coefficients $k_{p,app}$ were measured; these decrease with increasing concentrations of initiator, monomer and polymer, suggesting significant association between the various species involved. The PLP data also qualitatively show the presence of low rates of termination and transfer.

Grafting kinetics of vinyl neo-decanoate onto polybutadiene. BTT Pham, M.P. Tonge, MJ Monteiro and RG Gilbert. *Macromolecules*, in press.

The kinetics and mechanism of the bulk free-radical polymerization of vinyl neo-decanoate in the presence of polybutadiene are studied in a series of rate and molecular weight distribution measurements over the temperature range 50 – 90°C. The polymerization of the vinyl ester is greatly retarded by the presence of polybutadiene. The dependences of the rates and molecular weight distributions on the ratio of monomer to the amount of polybutadiene are quantitatively in accord with a retardative chain transfer mechanism, whereby an alkanoate radical undergoes hydrogen transfer with polybutadiene, leaving an unreactive radical species (probably allylic in character) which cannot propagate and instead undergoes termination with another radical. The data yield Arrhenius parameters for the transfer to polybutadiene as $k_{\mathrm{tr,P}} = 10^{6.9}$ dm^3 mol^{-1} s^{-1} exp(– 27.6 kJ mol^{-1}), which, although subject to high uncertainty, are consistent with the rate-determining step being either (a) diffusion to a hindered butadiene unit of the chain end of an alkanoate macroradical, or (b) the actual (chemically-controlled) hydrogen transfer event, which would then have to have an unusually low activation energy.

The following publications have appeared since the previous Newsletter:

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Contribution to the International Polymer Colloid Group Newsletter
December 1999

from

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Titles and abstract of unpublished papers,

The Adsorption and Surface Dilatational Rheology of Unmodified and Hydrophobically Modified EHEC, Measured by Means of Axisymmetric Drop Shape Analysis

Rolf Myrvold[1,3], Finn Knut Hansen[1,4] and Björn Lindman[2]

Studies of adsorbed and spread layers of ethylated hydroxyethyl cellulose (EHEC) and a hydrophobically modified analogue (HM-EHEC) at the air-water interface have been performed by means of four different experimental routes. The adsorption characteristics visualized by means of dynamic surface tension measurements, dilatational elastic behavior measured by means of a oscillating sessile bubble method, and the surface pressure response to surface area reductions measured by means of a Langmuir surface balance all give the same result. Relatively strong interactions can be observed when adding sodium dodecyl sulfate (SDS) to the polymer solutions. The SDS concentration for optimal enhancement of surface properties is 5-6 mM, indicating the formation of the most surface-active polymer/SDS complex. Despite the fact that the bulk properties of these two polymer/SDS systems are quite different, both the dynamic surface tension and the surface rheological properties are practically the same. This emphasizes the different effect of hydrophobic modification on bulk and surface behavior.

Adsorption and surface elastic properties of corresponding fluorinated and non-fluorinated cationic polymer films measured by drop shape analysis.

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Introduction

Within the large class of water-soluble, associating polymers, polysoaps can be seen as a series of individual surfactants linked by a polymeric backbone (1,2). They show primarily intra-molecular association, contrary to ordinary surfactants and amphiphilic block copolymers. The polysoaps are also lacking a critical micellar concentration, contrary to the corresponding monomeric surfactants. The adsorption of polysoaps may be expected to show peculiar features due to the competition between the intra-molecular associations and surface activity. Usually, polysoaps consist of simple hydrocarbons, therefore it has been interesting to investigate some novel compounds containing the more hydrophobic fluorocarbon side-chains, as these may be expected to give even more pronounced effects than their hydrocarbon equivalents (3).

The development of our instrument for automatic drop shape analysis has allowed the measurement of dynamic surface tensions and surface dilatational viscoelastic properties by means of the oscillating bubble (4). Several polymeric surfactants have been investigated by this technique, and the results have shown great differences in dynamic surface tension and especially dynamic surface elasticity between different polymer types (4,5). Polymer surfactants generally produce lower equilibrium surface pressures but higher surface elasticities than simple surfactants and dynamic experiments allow the measurement of surface elasticities even for soluble, adsorbing polymers.

Experimental

Chemicals. Two different types of cationic polysoaps have been synthesized from divalent quaternary ammonium monomers with a hydrocarbon or a corresponding fluorocarbon side chain. The structures of the compounds are given in Figure 1. For both the monomers and the corresponding polymers we have measured dynamic surface tension and surface dilatational rheologic properties by means of automatic axisymmetric drop shape analysis.

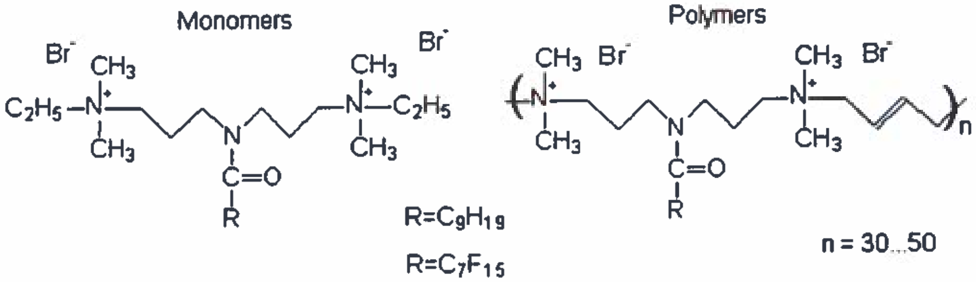


Figure 1. Structure of monomers and polysoaps.

Instruments. The instrument for drop shape analysis (Fig.2 - not shown here) has been described earlier.

Data analysis. The theoretical foundation for the measurement of surface rheological properties is well established (6-8). In this framework the necessary theoretical background for the methods utilized has been derived. The surface elasticity, E , follows the definition given by Gibbs, but it turns out, however, that many surfaces both contain an elastic and a viscous component, and the term "surface dilatational modulus" has been used for this more general case. The contribution of the elastic and viscous terms depend on the different types of relaxation processes that occur in the surface layer and on the interaction of the surface with its surroundings, i.e. the bulk liquid(s). For a dynamic process, a complex surface elasticity may be written as

$$E^* = E' + iE'' \quad [1]$$

Where E' is the storage modulus and E" the loss modulus. The storage modulus will be equal to the pure elastic contribution, and E" proportional to the viscous contribution. For an oscillating bubble, we vary the surface area by changing the bubble volume in a sinusoidal manner, and provided that the volume change is small, this results in a corresponding sinusoidal variation in the bubble surface area. This also leads to and a corresponding surface tension variation. We can write this

$$\Delta A = A - A_0 = A_a \sin(\omega t) \qquad [2]$$

$$\Delta\gamma = \gamma - \gamma_0 = \gamma_a \sin(\omega t + \delta) \qquad [3]$$

Here A_a is the area amplitude and A_0 is the equilibrium surface area, γ_a is the measured amplitude, γ_0 is the equilibrium surface tension and δ is the phase angle. In the usual manner, the (complex) surface dilatational modulus is then expressed by

$$E^* = E' + iE'' = |E| \cos\delta + i|E| \sin\delta \qquad [4]$$

where

$$|E| = \frac{\gamma_a}{A_a / A_0} \qquad [5]$$

The loss modulus E" represent a combination of internal relaxation processes and relaxation due to transport of matter between the surface and the bulk.

Results and Discussion

All compounds show slow adsorption kinetics. The monomers reach equilibrium adsorption after some time, dependent on the concentration, whereas the polymers hardly attain adsorption equilibrium in the observed time span. Figure 3 shows the dynamic surface tension for the fluorinated monomer. The equilibrium surface tensions are less than 20 mNm^{-1} that are very low, but typical for fluorine containing surfactants. We also see that this compound shows a behavior typical of low molecular surfactants, and that the critical micellar concentration (CMC) is ca 200 ppm. The hydrocarbon mono-

Figure 3. Dynamic surface tensions for the fluorinated monomer.

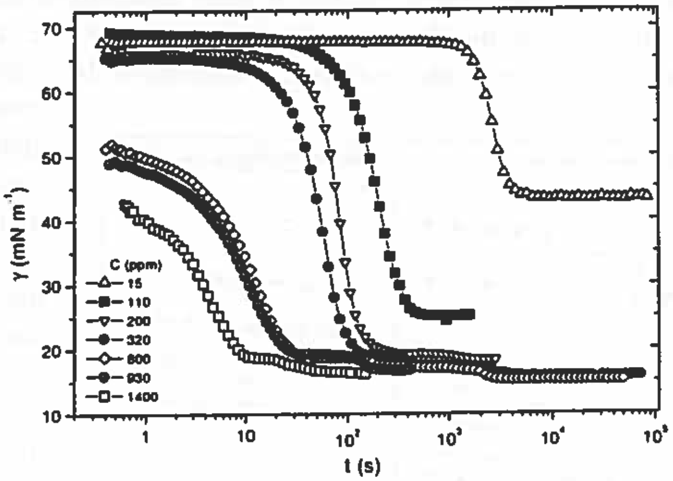
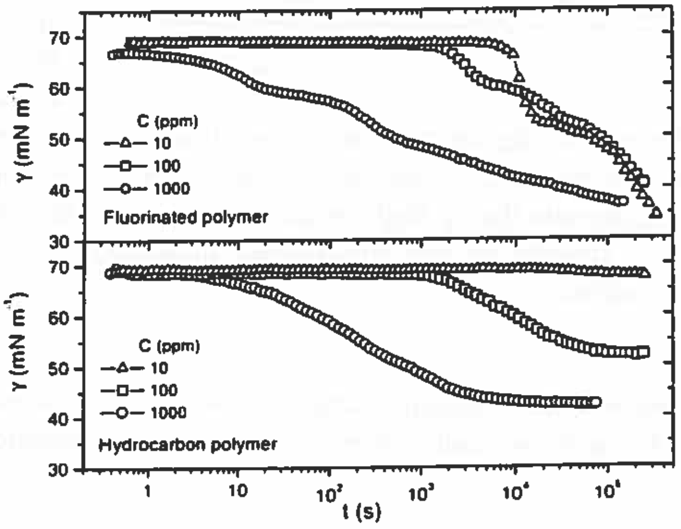


Figure 4. Dynamic surface tensions of both polymers.



mer (not shown) is quite different from the fluorinated analog; it adsorbs much slower and its equilibrium surface tension is higher, similar to other ionic hydrocarbon surfactants.

The dynamic surface tensions of the polymers are shown in Figure 4. We see that the difference between the polymers is less than between the monomers, and that the adsorption kinetics is not that much different for high concentrations. However, the fluorinated polymer displays more complex kinetic curves that indicate several processes and may be due to degradation of the polymer. Also, not even the highest concentration of the fluorinated polymer seems to be getting close to equilibrium adsorption.

Figure 5.

Surface rheological modules for the hydrocarbon compounds.

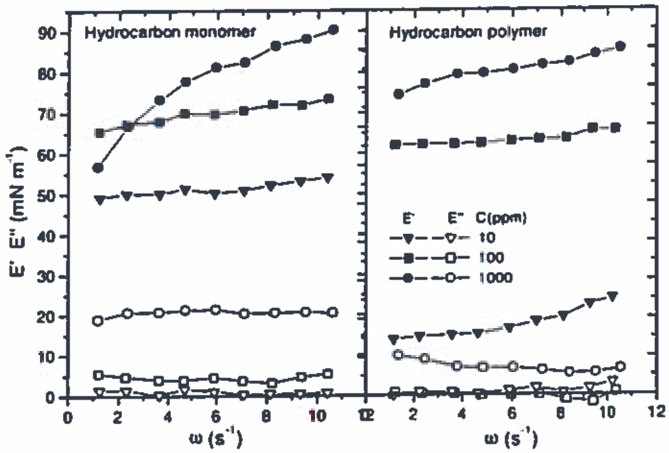
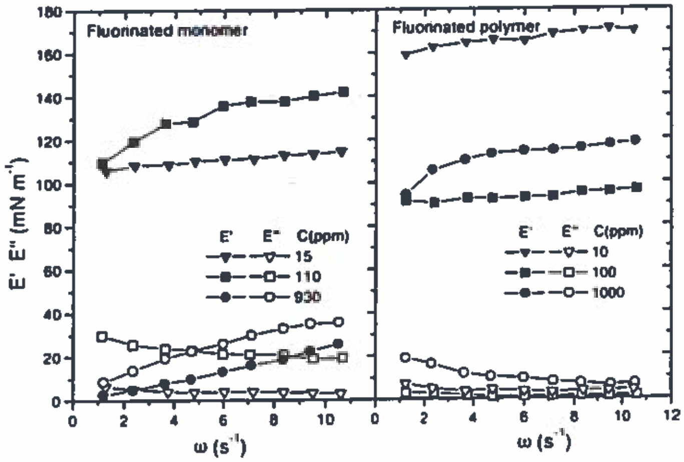


Figure 6.

Surface rheological modules for the fluorinated compounds.



Surface rheological results are given in Figures 5 and 6, for the hydrocarbon and fluorinated compounds, respectively. We see that for most concentrations, the elastic modulus is much greater than the viscous contribution, meaning that the phase angle is low. All compounds also show very high elastic moduli at most concentrations, especially is the extremely high surface elasticity of the fluorinated polymer remarkable. If compared at the same frequency, the results also show both maxima and minima in the elastic module that are probably connected to the shape of the surface pressure/area (ΠA) isotherm. Depending on the orientation of the molecules in the surface film, the Gibbs elasticity may go through both a maximum and a minimum (5), and a similar behavior may be expected for the elastic module from these experiments. A theoretical derivation also shows that a maximum in elasticity is expected for surfactants below the CMC, given that transport between the bulk and the surface is slow. It is also interesting to note that at high concentrations (100 ppm) the elastic module of the monomers decreases strongly at low frequencies, indicating increased influence of transport between bulk and surface.

Conclusions

Both monomers and polymers are strongly surface active and the fluorinated compounds show especially low surface tensions and extremely high surface dilatational elasticity. A maximum in elasticity is observed for the monomer, as also described by a theoretical derivation.

Work in progress.

Most work in our group is still being done with the Drop Shape instrument. The method of measuring surface dilatational rheology by beans of the oscillating drop or bubble is being further developed, and such measurements have become more or less standard now. The work described in the extended abstract above is being extended to liquid/liquid interfaces. The methods seem to be convenient also for these interfaces, and the possibility for better evaluation of the effect of polymer surfactants on emulsion stability are very exiting.

For those who are interested in the method, see http://www.uio.no/~fhansen/dropinst.html

Recently published papers (1999).

1. K.H.Hansen and J.Hveem, The Interfaciel Tension between Acrylic Monomers and Polymers and Non-ionic Surfactants Investigated by the Autiomatic Sessile Drop, J. Colloid Interface Sci. 210, 144-151 (1999).
2. R.Myrvold, F.K.Hansen, B.Balinov, and R.Skurtveit, Monolayers of Some Poly(oxyethylene)-Based Surfactants at the Air-Water Interface: The Effect of Structural Variations and Salt Concentration, J.Colloid Interface Sci., 215, 409-419 (1999).
3. H.B.M.Kopperud, H.Walderhaug, and F.K.Hansen, Polymer self-diffusion and surfactant bindig in aqueous solutions of unmodified and hydrophobocally modified polyacrylamide studied by pulsed field gradient NMR and surface tension measurements, Macromol. Chem. and Phys. 200, 1839-1845 (1999).

CONTRIBUTION TO IPCG 99 NEWSLETTER FROM DEPT OF CHEMISTRY, UNIVERSITY OF MALAYA, MALAYSIA. REPORTER : C.C. HO

LIST OF RECENT PUBLICATIONS :

1. L.P. Mok, **C.C. Ho** and K.K. Chee
"Surface tensions of miscible poly(2,4-dimethyl-1,4-phenylene oxide)/polystyrene and poly(methyl methacrylate)/poly(vinylidene fluoride) blends" *Malaysian J. Chem.* 1 12-19 (1998)

2. **C.C. Ho** and M.C. Khew
"Surface characterization of chlorinated unvulcanised natural rubber latex films" *International J. Adhesion & Adhesives* **19** 387-398 (1999)

3. **C. C. Ho** and K. Ahmad
"Electrokinetic behaviour of palm oil emulsion in dilute electrolyte solutions" *J. Coll. Interface Sci.* **216** 25-33 (1999)

4. **C.C. Ho** and M.C. Khew
"Surface morphology of prevulcanised natural rubber latex films by atomic force microscopy : new insight into the prevulcanisation mechanism" *Langmuir* **15 (19)** 6208-6219 (1999)

5. **C.C. Ho** and M.C. Chow
"The effect of the refining process on the interfacial properties of palm oil" *J. American Oil Chem. Soc.* (in press)

6. D.Y. Lee, J.S. Shin, Y.J. Park, , M.C. Khew, **C.C. Ho** and **J.H. Kim**
"Surface morphology of latex film formed from of poly(n-butyl methacrylate) latex in the presence of alkali soluble resin"
Surface & Interface Analysis **28 (1)** 28-35 (1999)

7. **C. C. Ho** and M.C. Khew
"Surface free energy analysis of natural and modified natural rubber latex films by contact angle method" *Langmuir* (in press 1999)

8. **C. C. Ho** and M. C. Khew
"Low Tg rubber latex film formation studied by atomic force microscopy" *Langmuir* (accepted)

9. D.Y. Lee, H.Y Choi, M.C. Khew, **C.C. Ho** and **J.H. Kim**
"Kinetics of film formation of poly(n-butyl methacrylate) latex in the presence of poly(styrene/alpha-methystyrene/acrylic acid) by atomic force microscopy"
Langmuir (in press 1999)

Ph. D. Thesis published :

"Preparation and characterisation of modified natural rubber latices and their film forming properties", by M.C. Khew, *University of Malaya*, 1999

(1) *International J. Adhesion & Adhesives* **19** 387-398 (1999)

Surface characterization of chlorinated unvulcanised natural rubber latex films

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ABSTRACT

Natural rubber (NR) latex film chlorinated by chlorine gas generated in situ from acidified hypochlorite solution at room temperature was characterised by FTIR-ATR, SEM-EDX and contact angle techniques. Chlorinated and oxygenated structures were found on the film surface after chlorination. The level of surface chlorination increased with chlorination duration and chlorine dosage. The hydrophilicity of the surface improved after chlorination. However, cracking of the surface was noted and the surface mean roughness, R_a of the chlorinated surface increased with extent of chlorination. The thickness of the chlorinated layer on the NR latex film was found to be less than 10 µm. Severe cracking of the film surface at high chlorine dosage and extended reaction time was evident. Surface roughening and hardening both would result in a reduction in the adhesive friction of the chlorinated surface against a substrate. Chlorination accelerated the oxidative chain scission of the rubber molecules, especially at elevated temperature, with the attendant introduction of conjugated C=C double bonds into and increase in number and concentration of oxygenated structures of the rubber molecules. Discoloration and poor heat resistance properties of chlorinated NR latex film are perhaps the results of these effects.

* Corresponding author

(2) Surface and Interface Analysis **28**, 28-35 (1999)

SURFACE MORPHOLOGY OF LATEX FILM FORMED FROM POLY(BUTYL METHACRYLATE) LATEX IN THE PRESENCE OF ALKALI-SOLUBLE RESIN

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ABSTRACT

The film morphology of emulsifier-free poly(n-butyl methacrylate) (PBMA) latex in the presence of post-added alkali-soluble resin (ASR) was studied using atomic force microscopy (AFM). The film morphology was monitored, from the nascent stage after water was evaporated from the dispersion, as a function of annealing temperature and its duration. The AFM results suggest strongly the formation of a hard shell of ASR, namely poly(styrene/alpha-methylstyrene/acrylic acid) (SAA) over the soft PBMA particle. During drying of the latex, the incompatibility of the two polymers leads to the migration and accumulation of the SAA at the interstices and interfacial regions among the arrays of PBMA particles and also at the film surface, forming a cellular type of film structure. The hard shell of SAA retards the diffusion of the PBMA molecules across the particle-particle interface and slows down the gradual coalescence of film formation. Annealing at high temperature, ruptures the SAA shells and the PBMA particles interdiffuse at a faster rate than the SAA due to its lower Tg compared to that of SAA. The difference in the rates of fusion of the SAA and PBMA phases leads to the formation of indentations on individual particles at high annealing temperature and long annealing duration. The occurrence of this feature increases with SAA concentration, the annealing temperature and its duration. These indentations are eventually transformed into 'holes' when the SAA collapses into the soft PBMA beneath at sufficient high annealing temperature and long annealing time. The surface enrichment of SAA is confirmed by FTIR ATR results of the film surface.

Keyword : latex film morphology, alkali-soluble resin, atomic force microscopy, poly(n-butyl methacrylate) latex, film formation mechanism

(3) *Langmuir* **15 (19)** 6208-6219 (1999)

SURFACE MORPHOLOGY OF PREVULCANIZED NATURAL RUBBER LATEX FILMS BY ATOMIC FORCE MICROSCOPY : NEW INSIGHT INTO THE PREVULCANIZATION MECHANISM

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ABSTRACT

Prevulcanization of natural rubber latex was investigated as a function of maturation duration. The morphology of the film formed from these latexes was monitored using atomic force microscopy (AFM) as the film aged. The morphology is correlated with the cross-linked density of the rubber molecules. Film formed from prevulcanized latex was further postvulcanized, and their film morpholgies were compared. Inhomogeneous latex particles cross-linked on the surface with an unvulcanized core were obtained during prevulcanization. This gives rise to the characteristic indentation structure when these hard shell-soft core latex particles coalesce to form film. Basically the prevulcanization mechanism is controlled by the relative rates of the diffusion of vulcanizing reagents and the cross-linking reaction within the latex particles. It is clear that the partially vulcanized particles have a profound influence on the film-forming property of the prevulcanized latex.

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(4). Langmuir (accepted)

Low T_g Rubber Latex Film Formation Studied By Atomic Force Microscopy

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ABSTRACT

Latex of very low T_g polymer forms continuous film on drying. The physical and mechanical properties of the film are dependent on the extent the latex particles are able to coalesce and fuse into each other. Any hindrance to the film formation process would result in a poorly formed film and a drop in performance. The film formation process of natural rubber ($T_g \sim -65°C$) latexes and synthetic latexes with low T_g are monitored as a function of time using atomic force microscopy (AFM). The influence of the leaching method of the film, the presence of additives (some post-added after preparation) and non-rubber materials (specific for natural rubber latex only), and gel content on film morphology and flattening of the particles in the film is studied. The influence of the leaching procedure on the effectiveness of non-rubbers removal from NR latex films and their effect on film formation is highlighted. The effects of non-rubbers and high gel content of NR latex in slowing down the NR film formation is discussed and contrasted with the synthetic polyisoprene and chloroprene latexes. The change of the surface mean roughness, R_a, with time provides a convenient means of comparing the rate of flattening of the polydisperse particles in these films.

KEYWORS : Natural rubber latex film, latex film morphology, atomic force microscopy, latex film formation, low T_g latexes

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(5). Langmuir (accepted)

SURFACE FREE ENERGY ANALYSIS OF NATURAL AND MODIFIED NATURAL RUBBER LATEX FILMS BY CONTACT ANGLE METHOD

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ABSTRACT

The contact angles of soft latex dipped films of high-ammonia natural rubber (HA) latex concentrate, deproteinised natural rubber (DPNR) latex and oil-incorporated natural rubber latex were determined by the sessile drop method. The surface free energies were calculated using different procedures available in the literature. For each type of latex film, the harmonic-mean treatment gives the highest polar component of the surface free energy while those from the Lifshifz-van der Waals acid-base method the lowest. This trend is the same for each type of latex films, but the magnitude varies. Among the various latex types, unleached NR latex film surface is the most hydrophilic, deproteinised latex film the least. All the NR film surfaces were found to be monopolar basic in nature, with the unleached NR film being the most basic and those of HA the least. The behavior of the various film surfaces is discussed in terms of the presence of non-rubbers and their removal by washing (leaching) of the film or by deproteinisation of the latex. The polar nature of the film surface is correlated well with the presence of the exuded non-rubber materials at the film surface. The surface free energies of the latex films are comparable to that for synthetic cis-polyisoprene latex film but lower than that for chloroprene. These are in turn in reasonable agreement with the surface free energies of some common solid polymer surfaces. Discussion on the possible implications of the present results in dipped-goods manufacturing process was attempted.

KEYWORDS : Surface free energy, dispersive and non-dispersive components, contact angle measurements, natural rubber latex film, natural rubber latex, deproteinised natural rubber latex, modified latex

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International Polymer Colloids Group Newsletter

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Our papers published or accepted for publication in 1999 are compiled in the following.

Recently Published

(1)Recent study on counterion-mediated attraction between colloidal particles, N. Ise, *Colloids and Surfaces,* **146**, 347-357 (1999) [Festschrift for Professor Tom Healy].

(2)Transitions between ordered and disordered phases and their coexistence in dilute ionic colloidal dispersions. H. Yoshida*, J. Yamanaka**, T. Koga, T. Koga, N. Ise, and T. Hashimoto‡, *Langmuir* **15**, 2684-2702 (1999). Published on Web 03/19/1999.

(3)How homogeneous are "homogeneous dispersions"? Counterion-mediated attraction between like-charged species. N. Ise, T. Konishi, and B. V. R. Tata+, *Langmuir* **15**, 4176-4184 (1999). Published on Web 03/19/1999.

(4)Reentrant order-disorder transition in ionic colloidal dispersions by varying particle charge density. J. Yamanaka, H. Yoshida, T. Koga, N. Ise, and T. Hashimoto, *Langmuir* **15,** 4198-4202 (1999). Published on Web 04/24/1999.

Papers in press

(5)Ordering in poly(allylamine hydrochloride) gels. G. V. Rama Rao, T. Konishi, and N. Ise, *Macromolecules* in press.

Poly(allylamine hydrochloride) gels were prepared using *N, N'*-methylenebis(acrylamide) or glutaraldehyde as cross-linking agents. The gels were found to collapse when equilibrated with sodium salts of various organic acids. A less precipitous volume change was observed when equilibrated with NaCl or NaI. A small-angle X-ray scattering (SAXS) study was performed on the gels. A single broad peak was observed for the collapsed gels with the sodium salts of organic acids such as *p*-styrenesulfonate whereas no peak was found for the inorganic salts. The strong maximum in the SAXS patterns was attributed to the presence of ordered structures in the collapsed gels. The peak position shifted toward lower angles as the size of counterion was increased. A change in the peak position, though small, was noticed with variation in the charge density of the polymer, except for the less charged gel prepared at pH 10.5 which did not even collapse.

(6)Reply to comment on "Monte Carlo study of structural ordering in charged colloids using a long-range attractive interaction". B. V. R. Tata and N. Ise, *Phys. Rev. E* in press.

In the comments by Grier and Crocker, the authors tried to refute our criticism (*Phys. Rev. E.* **58**, 2237 (1998)) on their work (J. C. Crocker and D. G. Grier, *Phys. Rev. Lett,* 77, 1897 (1996)) by simply fitting once again their old experimental data. They did not provide additional experimental proof to counter our criticism. The authors claimed that their pair-potential measurements on aqueous dilute suspension of charged colloidal suspension confined between charged glass walls at gap of about 8 μm provided evidence for the failure of the Sogami theory and demonstrated the applicability of the DLVO theory. It was pointed out that their experimental condition would be proper for discussion of the DLVO theory, which was derived for *two*-particle systems, whereas this was not the case for the Sogami theory, which discussed the electrostatic interaction in *multi*-particle systems. We continued to claim here based on our conductivity and conductometric titration measurements, which allowed estimating the effective charge and determining the number and nature of the dissociable sites, respectively, that their samples had practically no measurable amounts of charges and no strong acid groups at variance with their claim and their measurements using such not well-characterized samples and under unsuitable experimental conditions could not provide clear evidence for the failure of the Sogami theory. With the evidences available in literature, we refuted all the Crocker-Grier comments including the effect of charged wall confinement on the measured colloidal interactions. It was furthermore suggested that much higher charge density particles had to be employed if the Sogami theory was to be correctly tested.

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INTERNATIONAL POLYMER COLLOIDS GROUP NEWSLETTER

Contribution from Johnson Polymer, 8310 16th Street, P.O. Box 902, Sturtevant, WI 53177 – 0902

Reporter: D. Sunil Jayasuriya

Contribution 1:

Presented at the NPIRI (National Printing Ink Research Institute) conference of NAPIM (National Association of Printing Ink Manufacturers) held in Miami Beach, FL during October 13-15, 1999, and will be published in American Ink Maker.

Structure/Activity Relationship of Styrene-Acrylic Resins for Predicting the Quality of Pigment Dispersion and Ink Performance

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ABSTRACT

The polymer used in an ink vehicle affects pigment dispersion, press performance and print quality. This paper probes the relationship between polymer structure and ink properties using a multi-disciplinary approach. Water-borne styrene-acrylic polymers varying in composition and structure were used to prepare pigment dispersions and inks. The rheology profiles of the pigment dispersions were measured using an oscillatory viscometer. Polymer solubility parameters were calculated with a molecular modeling program and correlated with the pigment dispersion's rheology and quality characteristics. It was found that oxygen content and molecular weight were the most important factors in pigment dispersion quality and performance for the polymers studied.

Contribution 2:

Submitted for publication in the Journal of Polymer Science Part A: Polymer Chemistry.

Reactivity Ratios From A Single Experiment:

Copolymerization of Methyl Methacrylate and 2-Ethylhexyl Acrylate

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Johnson Polymer, Sturtevant, WI 53177 – 0902

SYNOPSIS

A novel technique has been developed for the estimation of monomer reactivity ratios. This technique requires a single experiment as opposed to the 5 – 10 runs that have hitherto been used for this purpose. This has been made possible by measuring the individual monomer concentration on line during the course of the copolymerization. The instantaneous conversions were then calculated from the monomer concentrations via a simple mass balance. This technique has been successfully applied for the determination of the reactivity ratios of methyl methacrylate and 2-ethylhexyl acrylate.

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Contribution to International Polymer Colloids Group News letter

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(Dec. 15, 1999)

News

There is sad news from Japan. Dr. Sei Hachisu, the emeritus professor of Tokyo University of Education, passed away at the age of 80 in the beginning of December, 1999. He was a pioneer in the field of colloid crystals. There is a pendant of artificial opal, in my hand, which was the solidified colloid crystal produced by Dr. Hachisu.

I have to apologize to all concerned with the International Symposium on Advance Technology of Fine Particles held at Yokohama in October, 1997 for the delayed publication of the proceedings, which corresponded to the special issue of Colloids and Surfaces A: physicochemical and Engineering aspects. We have waited for the publication almost two years. At last the proceedings, Colloids and Surfaces A (Special Issue) vol. 153 was published this August.

Papers in press

Smart Latexes for Bioseparation and Bioprocessing (H.Kawaguchi and K.Fujimoto) will appear soon in a book "Smart Polymers in Bioseparation and Bioprocessing" ed. by B. Mattiasson and I. Galaev, OPA, the Netherlands. This paper is a review of our studies on biomedical applications of thermosensitive microspheres. The microspheres were employed as protein adsorbents, enzyme carriers, cell activators, and affinity devices.

My colleague, Dr. Keiji Fujimoto, the associate professor of Keio University, is involved in the development of microspheres having chaperon function (to refold a denatured conformation of a protein to its native one) and prepared the second paper in this series, which has been accepted for publication in Colloids and Surfaces B: Biointerface. The paper entitled **Improved refolding of Denatured/Reduced Lysozyme Using Disulfide-Carrying Polymeric Microspheres** (H.Shimizu, K.Fujimoto*, and H.Kawaguchi) included the "chaperon"-like function of latex particles having thiol and disulfide groups on their surfaces. Denatured or reduced protein molecules were adsorbed on the particle, refolded on the surface, and then desorbed spontaneously. The desorbed proteins were confirmed to recover enzymatic activity.

Publications in 1999

Books

1 H.Kawaguchi, Thermosensitive hydrogel microspheres, in "Microspheres, Microcapsules & Liposomes" ed by R. Arshady, Citus Books, London (1999) pp.237-252

2. H.Kawaguchi, Dispersion polymerization, in "Handbook of Radical Polymerization" ed. by M.Kamachi, et al., NTS, Tokyo (1999) pp.264-273 (in Japanese)

Journal

3. K.Fujimoto, C.Iwasaki, H.Kawaguchi, E.Yasugi, M.Oshima, Cell membrane dynamics and the induction of apoptosis by lipid components, FEBS Lett., 446, 113-116 (1999)

4. H.Kawaguchi and K.Fujimoto, Smart latexes for bioseparation, Bioseparation, 7, 253-258 (1999)

5. K.Fujimoto, K.Nakahama, M.Shidara, H.Kawaguchi, Preparation of unsymmetrical microspheres at the interfaces, Langmuir, 15, 4630-4635 (1999)

6. H.Shimizu, K.Fujimoto, H.Kawaguchi, Refolding of protein using thiol-carrying latex particles, Colloids Surfaces A., 153, 421-427 (1999)

7. M.Miyaki, K.Fujimoto, H.Kawaguchi, Cell response to micropatterned surfaces produced with polymeric microspheres, Colloids Surfaces, 153, 603-608 (1999)

8.K.Nakamura, K.Fujimoto, H.Kawaguchi, Dispersion polymerization of methyl methacrylate using macro-azo initiator, Colloids Surfaces, 153, 195-201 (1999)

9. M.Hatakeyama, S.Iwato, H.Hanashita, K.Nakamura, K.Fujimoto, and H.Kawaguchi, DNA-carrying particles for DNA diagnosis 3. Detection of point mutant DNA using an indirect labeled probe, Colloids Surfaces, 153, 445-451 (1999)

10. H.Matsuoka, K.Fujimoto, H.kawaguchi, Stimuli-response of microsphere having poly(N-isopropylacrylamide) shell, Polym. J., 31, 1139-1144 (1999)

From Prof JH Kim
A List of Unpublished Papers

- Synthesis of Phenolic/Furfural Gel Microspheres in Supercritical CO_2

- Kyung-Nam Lee, Hae-Joon Lee, and Jung-Hyun Kim*, *The Journal of Supercritical Fluids*

Abstract

Phenolic/furfural (P/F) gel microspheres were successfully produced by new supercritical CO_2-based process. CO_2-soluble poly(dimethylsiloxane) (PDMS) was used as the stabilizer in this system. Spherical morphology of the gel microspheres was confirmed by scanning electron microscopy. Particle size and particle size distribution of P/F gel microspheres can be modified upon variation of the solids content and the stabilizer content. The resultant P/F microspheres have average particle size in the range of 1-6 μm. The structure of P/F gel microspheres was revealed by IR analysis.

Keywords: Phenolic/furfural; gel microspheres; sol-emulsion-gel technique; particle size; supercritical CO_2

- Effect of Annealing on the Surface Properties of Poly(n-butyl methacrylate) Latex Films Containing Poly(styrene/alpha-methylstyrene/acrylic acid)

- Jin-Sup Shin, Doug-Youn Lee, Chee-Cheong Ho** and Jung-Hyun Kim*, *Langmuir*

Abstract

The effect of alkali-soluble resin (ASR) post-added to emulsifier-free monodisperse poly(n-butyl methacrylate) latexes (PBMA) on the surface properties of the latex films formed was investigated using contact angle method. The contact angles of a probe liquid (containing 50:50 wt % ethylene glycol and water) on the film surface were determined as a function of the annealing temperature of the film and the annealing duration. The ASR, poly(styrene/alpha-methylstyrene/acrylic acid), was found to exude to the air/polymer interface after annealing, as monitored using FTIR-ATR. Thus the surface properties of the films were dependent on the concentration of the ASR employed, the annealing temperature and the duration. Annealing the film at temperature about the T_g of ASR allows them (ASR) unrestricted migration to the film surface and also to expose the hydrophobic region of their chains to the surface. The more hydrophobic character of the film annealed at 150_ with a higher contact angle as compared to that at 50_ is a result of the change in chain conformation of the ASR at the surface brought about by annealing. Also, the results illustrate that the hydrophobic-hydrophilic character of the PBMA-SAA film surface can be changed readily by merely adjusting the annealing temperature.

Key words : poly(n-butyl methacrylate) latex films, surface enrichment of latex film by poly(styrene/alpha-methylstyrene/acrylic acid), contact angle measurement, annealing effect

- Modeling and simulation of equal density seeded emulsion polymerization of styrene

- Jung-Hyun, Kim, In-Woo Cheong, and Do-Ik Lee, *Polymer Reaction Engineering*

Abstract

Equal density polymerization concept was proposed to simulate a micro-gravity environment based on a semi-continuous monomer addition process. A general model for this particular process was derived to calculate the specific monomer addition rate. Dynamic monomer feeding rates for an equal density condition were obtained with different reaction temperatures, initial sizes of seed particles, and initiator concentrations. The average number of radicals per particle was calculated by pseudo-bulk kinetics equation proposed by R. G. Gilbert et al.(1995) in both batch and semi-continuous conditions. A generalized dynamic feeding equation was derived to maintain an equal density condition by using a simple relationship concerning the volume fraction of monomer in growing polymer particles.

■ Preparation and Morphology Characterization of Microcellular SAN Foam Processed in Supercritical CO_2

- Kyung-Nam Lee, Hae-Joon Lee, and Jung-Hyun Kim*, *Polymer International*

Abstract

Microcellular polymeric foam structures have been generated using a pressure induced phase separation in concentrated mixtures of supercritical CO_2 and SAN. The process typically generates microcellular core structure encased by nonporous skin. Pore growth occurs through two mechanisms: diffusion of CO_2 from polymer-rich regions into the pores and also through CO_2 gas expansion. The effect of saturation pressure, temperature, and swelling time on the cell size, cell density, and bulk density of the porous materials have been studied. Higher CO_2 pressures (hence, higher fluid density) provided more CO_2 molecules for foaming, generated lower interfacial tension and viscosity in the polymer matrix, and thus produced lower cell size but higher cell densities. This trend was similar to what was observed in swelling time series. While the average cell size increased with increasing temperature, the cell density decreased. The trend of bulk density was similar to that of cell size.

Key words: microcellular polymeric foam, supercritical CO_2, pressure induced phase separation, cell size, cell density

- Synthesis of Resorcinol/Formaldehyde Aerogel Microspheres by the Sol-Emulsion-Gel Technique

- Hae-Joon Lee, Kyung-Nam Lee, and Jung-Hyun Kim*, *Materials Research Bulletin*

Abstract

The preparation of resorcinol/formaldehyde (R/F) aerogel microspheres by means of the sol-emulsion-gel technique and CO_2 supercritical drying has been studied. The sizes of these microspheres ranged from submicrometer to a few hundred micrometers. The particle sizes were controlled by the composition of the system and the emulsification conditions - agitation rate, shape of agitator, contents and type of surfactant and type of oil. Morphology of R/F aerogel microspheres was observed by scanning electron microscopy and nitrogen physisorption experiments. It's structure of R/F aerogel microsphere was revealed by IR analysis.

Keywords: microporous materials, sol-gel chemistry, electron microscopy, microstructure

- **Mechanistic Study on Latex Film Formation in the Presence of Alkali-Soluble Resin Using Atomic Force Microscopy**

- Doug-Youn Lee, Young-Jun Park, Mei-Ching Khew⁺, Chee-Cheong Ho⁺ and Jung-Hyun Kim*, *Macromolecular Symposia*

Abstract

The mechanism of film formation of emulsifier-free monodisperse poly(n-butyl methacrylate) (PBMA) latex in the presence of postadded alkali-soluble resin (ASR), namely poly(styrene/alpha-methylstyrene/acrylic acid) (SAA) was followed using atomic force microscopy (AFM). The film morphology and peak-to-valley distance (Δz) of latex particles in the film was monitored at different annealing temperatures as a function of annealing duration. The Δz of the PBMA particles in films containing SAA was found to be higher than those in the pure PBMA films. The AFM results suggest very strongly the formation of a hard surface layer of SAA over the soft PBMA particle, and the migration of free SAA to the latex film surface during annealing. The SAA layer adsorbed on and surrounding each PBMA particle retards the viscoelastic flow of the PBMA particles and slows down the gradual coalescence of the particles in film formation. Annealing at high temperature, the PBMA particles fuse at a faster rate than the SAA due to its lower T_g compared to that of SAA. The difference in the rates of fusion of the SAA and PBMA phases leads to the formation of indentations on individual particles at high annealing temperature and long annealing duration.

■ Preparation of Ethylene-Modified Latex using Ethylene-Acrylic Acid Resin

- Jin-Sup Shin, Doug-Youn Lee, Jung-Hyun Kim*, *Macromolecular Symposia*

Abstract

Ethylene-modified latexes were prepared by emulsion polymerization of styrene and n-butyl methacrylate using ethylene-acrylic acid (EAA), [M_n: 18,800, acid number: 140], as a polymeric emulsifier respectively. EAA containing 20% portion of acrylic acid could form aggregates like micelles and the solubilization ability of the aggregates were dependent on the electrolyte concentration above 100% degree of neutralization of EAA. The polystyrene (PS) latexes prepared using EAA showed small particle size and monodispersed particle size distribution in the presence of excess neutralizing agent or relatively high content of electrolyte. The EAA improved the barrier properties of ethylene-modified poly(n-butyl methacrylate) (PBMA) films.

- Miscibility Behaviour of Poly(n-Butyl methacrylate) Latex Films Containing Alkali-Soluble Resin

- Hee-Young Choi, Doug-Youn Lee, Jun-Young Lee, and Jung-Hyun Kim, *Journal of Applied Polymer Science*

Abstract

The dynamic mechanical properties of poly(n-butyl methacrylate) (PBMA) latex films post-added with alkali-soluble resin (ASR) have been studied and compared with those of latex films prepared by emulsion polymerization in the presence of ASR (ASR-fortified latex). The miscibility between PBMA and ASR, poly(styrene/alpha methylstyrene/acrylic acid) (SAA), was found to influence the dynamic mechanical behavior of the films. The dynamic properties of PBMA latex films post-added with SAA show two distinct damping peaks, which correspond to those of PBMA and SAA respectively in the phase separated state. The SAA migrates onto film surface during film formation and, as a result SAA preserved their domains in the matrix phase, showing two distinct relaxations in the dynamic mechanical spectrum. On the other hand, the ASR-fortified films exhibit single damping peak. SAA-fortified latex particles would be core/shell structured and the miscibility between PBMA and SAA is clearly improved by the grafting reaction between PBMA and SAA.

Keywords : dynamic mechanical properties ; miscibility ; alkali-soluble resin (ASR) ; SAA-fortified latex

Work in Progress

- Preparation and Properties of Ethylene-Modified Latexes as Polymeric Emulsifier

- Jin-Sup Shin, Doug-Youn Lee, and Jung-Hyun Kim

- Effect of Immiscibility on Surface Properties of Poly(n-butyl methacrylate) Latex Film in the Presence of Alkali-Soluble Resin

- Jin-Sup Shin, Hee-Young Choi, Doug-Youn Lee, and Jung-Hyun Kim

- Mechanistic Study on Emulsion Polymerization of Styrene in the Presence of Water-dispersible Polyurethane Resins

- In-Woo Cheong, Jung-Hyun Kim

- Molecular Weight Distributions in Terpolymerization of Alpha-methylstyrene /styrene/acrylic acid in CSTR

- Byoung-Jo Lee, In-Woo Cheong, Doug-Youn Lee, Jung-Hyun Kim

- Reaction Mechanism of Chain Extension by 1,6-Hexane Diamine in IPDI-based Aqueous Polyurethane Dispersion

- Young-Kuk Jhon, Jong-Yoon Jang, In-Woo Cheong, Jung-Hyun Kim

- Influence of Process Variable on Molecular Weight and Wet Properties of Water-dispersed Polyurethane

- Jong-Yoon Jang, Young-Kuk Jhon, In-Woo Cheong, Jung-Hyun Kim

- Preparation of Poly(Lactic Acid) Microspheres in Supercritical Carbon Dioxide

- Jun-Young Lee, Jin-Young Bae, Jeong-Ho An, Jung-Hyun Kim

- Preparation and Characterization of PLGA Containing Estrogen by Emulsification-Diffision Method

- Hye-Young Kwon, Jun-Young Lee, Jung-Hyun Kim

A List of Recently Published Papers

- Preparation of core particles for toner application by membrane emulsification
- Young-Kil Ha, Hi-Seok Song, Hae-Joon Lee, and Jung-Hyun Kim, *Colloids and surfaces A: Physicochemical and engineering aspects*, **162**, 1-3, 289-293, 2000

- Kinetics of Film Formation of Poly(n-butyl methacrylate) Latex in the Presence of Poly(styrene/alpha-methylstyrene/acrylic acid) by Atomic Force Microscopy
- Doug-Youn Lee, Hee-Young Choi, Young-Jun Park, Mei-Ching Khew[+], Chee-Cheong Ho[+] and Jung-Hyun Kim*, *Langmuir*, **15**, 23, 8252-8258, 1999

- Surface Morphology of Latex Film Formed from Poly(butyl methacrylate) Latex in the Presence of Alkali-Soluble Resin
- Doug-Youn Lee, Jin-Sup Shin, Young-Jun Park, Jung-Hyun Kim, Mei-Ching Khew, and Chee-Cheong Ho, *Surface and Interface Analysis*, **28**, 28-35, 1999

- Film Formation from Reactive Latex Particles: Influence of Intraparticle Crosslinking on Mechanical Properties
- Young-Jun Park, Jung-Hyun Kim, *Colloids and Surfaces A*, **153**, 583-590, 1999.

- Role of Alkali-Soluble Random Copolymer in Emulsion Polymerization
- Doug-Youn Lee, Jung-Hyun Kim*, and Tae-Ik Min, *Colloids and Surfaces A*, **153**, 89-97, 1999.

- Investigation of Seeded Emulsion Polymerization Using a Calorimetric Method: Effects of Surface Charge Density on Polymerization Rate and Average Number of Radicals per Particle
- In-Woo Cheong, Jung-Hyun Kim, *Colloids and Surfaces A*, **153**, 137-142, 1999.

- The Relationship of Interaction Forces in the Protein Adsorption onto Polymeric Microspheres

Joeng-Yeol Yoon, Jung-Hyun Kim, and Woo-Sik Kim *Colloids and Surfaces A*, **153**, 413-419, 1999.

- Agglomeration of polybutadiene latex by highly carboxylated functional microsphere
- Woo-Churl Shin, Hae-Joon Lee, Young-Jun Park, and Jung-Hyun Kim, *Polymer International*, **48**, 479, 1999.

Recent Activities

Career

1998. 3. - present	Head professor in Chemical Engineering & Biotechnology
1998.3 - 1998.9	Head professor in the Department of Chemical Engineering

Awards and Honors

1999. 6.	Win a prize in 1st Lab-Venture Competition (Korea)
1999. 7.	Endued with Presidential Researcher in NRL (Korea)

Nanosphere Process and Technology Laboratory
National Research Laboratory

Nanosphere Process and Technology Laboratory (NPTL) was founded in 1991. Its aim is to carry out interdisciplinary research to gain fundamental information on the preparation and properties of functional nanosphere and to discover and develop industrial applications also. Last year, NPTL is selected as one of National Research Laboratories. Our NPTL is supported under the KISTEP's National Research Laboratory Program since 1999.

The research activities of NPTL include: mechanistic study on emulsion polymerization mechanisms and kinetics of conventional, resin-fortified, and dispersion polymerizations; investigations for the development of particle morphologies in composite latex systems through both theoretical and experimental means; the role of polymeric surfactants in emulsion polymerization; latex film formation mechanism (also for latex blends); the dispersed condensation polymerization process in supercritical CO_2; the preparation and application of water-borne polyurethane; functional nanospheres in biomedical fields, e.g., latex-based immunoassay, preparation of biodegradable nanoparticles for drug delivery; the encapsulation technique using membrane emulsification or *in-situ* polymerization.

A Colloidal Stability Analysis of a Core/Shell Emulsion Polymerization Reaction

Ed Kostansek, Rohm and Haas Co.
(To be presented at a future meeting)

Abstract

During the course of emulsion polymerization reactions many parameters which affect colloidal stability are varying significantly. Latex parameters include particle size, zeta potential, surface hydrophobicity, surfactant concentration and surfactant coverage. Process parameters include temperature, pH, agitation (shear rate), electrolyte concentration, standing monomer, solids and viscosity. In order to identify potential colloidal stability problem areas in the process, we took periodic samples from emulsion polymerization runs of a three-stage core/shell emulsion polymer and measured/analyzed the previously mentioned parameters. The three stages included MMA, BA/Sty, and MMA , respectively.

Shear stability at the various stages was measured and also calculated from DLVO theory. Viscosity was measured and calculated using a simple model. The results indicated a problem area in the process in terms of shear stability and possible gel formation and coagulation. Hydrophobic interactions appear to be very important during that stage of the reaction. This can be a problem in reactions where the particle surface changes from hydrophilic to hydrophobic.

Contribution to IPCG newsletter fro the

Leiden Colloid and Interface Science group

A complete list of published material is available on http://pobox.leidenuniv.nl/~gkoper

Preprints:

Synthesis and Protonation Behavior of Carboxylate-Functionalized Poly(Propylene Imine) Dendrimers

R.C. van Duijvenbode, A. Rajanayagam, G.J.M. Koper, M.W.P.L. Baars, B.F.M. de Waal, E.W. Meijer, M. Borkovec

Five generations of carboxylate-functionalized poly(propylene imine) dendrimers have been synthesized starting from a double Michael addition of amine-functionalized poly(propylene imine) dendrimers to methylacrylate followed by basic hydrolysis using LiOH in a water/methanol mixture. The dendritic compounds have been characterized using ^{1}H-NMR, ^{13}C-NMR, IR and ESI-MS spectroscopy. Subsequently the protonation behavior of these potential complexing agents is studied with potentiometric titrations in 0.1 M and 1.0 M KCl solutions. The carboxylate-functionalized dendrimers show a characteristic onion-like shell protonation behavior. The titration curves for different ionic strengths cross at pH 8.5 which is exactly after protonation of the outermost shell of amines ($\theta \sim 0.25$). This crossing point is found not to be identical to the point of zero charge $\theta \sim 0.5$, which is observed at pH 4.5. The Ising model was used to rationalize the complete set of titration data simultaneously for five generations with only one microscopic pK value for each additional shell and a set of three nearest neighbor pair interaction parameters.

To appear in *Macromolecules*

Optical Properties of Colloidal Films

G.J.M. Koper

The optical properties of colloidal films with thickness ranging from less than one nanometer, formed by dendrimer molecules, to over one micrometer, formed by proteins and latex particles, are discussed. The experimental technique used is scanning angle reflectometry that is shown to provide extremely accurate information on dielectric thin films. Even though the analysis of these properties requires sophisticated electromagnetic theory, simple approximations are derived and their use is demonstrated. The inherent errors are quantified using the full electromagnetic theory.

To appear in *Colloids and Surfaces A*

Ionization processes and proton binding in polyprotic systems: small molecules, proteins, interfaces, and polyelectrolytes

M. Borkovec, B. Jönsson, G.J.M. Koper

A prerint of this review paper is available upon request from the last author.

To appear in *Surface and Colloid Science*, ed. E. Matijevic

Manuscripts in preparation:

Adsorption properties of poly(propylene imine) dendrimers, statics
R.C. van Duijvenbode, G.J.M. Koper, and M. Böhmer

Adsorption properties of poly(propylene imine) dendrimers, kinetics
R.C. van Duijvenbode, I. Rietveld, and G.J.M. Koper

Electrically induced anisotropy in nanocolloidal dispersions
C. Chassagne and G.J.M. Koper

WContribution to the International Polymer Colloids Group Newsletter

Do Ik Lee
Emulsion Polymers R&D
The Dow Chemical Company

The following paper will be presented at the 74th **Colloid and Surface Science Symposium** sponsored by ACS Division of Colloid and Surface Chemistry in June 19 –21, 2000 at Lehigh University.

HIGH-TEMPERATURE WATER-EXTENDED LATEX TECHNOLOGY

Do Ik Lee
Emulsion Polymers R&D
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USA

ABSTRACT

The alkali-swelling of carboxylated latex particles has been extensively studied by both industrial and academic researchers in the past, and it has been well understood that upon neutralization, their swelling increases with increasing acid content and hydrophilicity of backbone chains as well as with decreasing Tg of backbone chains and crosslinking density of the whole polymeric chains. For this reason, lightly carboxylated, high Tg polymer latex particles were not expected to swell upon neutralization at room temperature, but it has been discovered that they not only swell at high temperatures near their Tg's, but also retain most of their swollen dimensions even after cooling down to room temperature. This discovery was coined as high-temperature water-extended latex technology.

For example, a lightly carboxylated, crosslinked polymethyl methacrylate (MMA/MAA/AMA: 89/10/1) latex of 156 nm did not swell when it was neutralized at room temperature, but when it was neutralized at 105° C, it swelled and its swelling ratio (swollen volume/original unswollen volume: $[D(\text{Swollen})/D(\text{Original})]^3$) at 100% neutralization with NaOH was determined to be 4.26 by HDC (its eluant at pH 8.9) at room temperature.

These high-temperature water-extended latexes based on high-temperature alkali-swellable latexes are a new class of alkali-swellable latexes which would exhibit unique physical, rheological, film-forming (water-plasticization), and end-use properties. They can be used as thickeners for colloidal systems, as bulking agents in coatings, as heat-gelation agents for coating systems, as lubricants for high-shear applications, as low-temperature film-forming, hard, and water-resistant latexes as well as coating binders, etc.

This paper will briefly review the current alkali-swellable latex technology, and then discuss a new high-temperature water-extended latex technology in more detail.

Professor Peter A. Lovell

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UK Polymer Colloids Forum

The Forum now has a simple web site, which is at:

http://www.ph.surrey.ac.uk/polcol/PCF.html

The 7th Meeting of the Forum is planned and will be a full international conference that will be held from 4-6 April 2001 at the University of Surrey. The conference has the theme "Frontiers of Polymer Colloids" and is being organised by Joe Keddie. The first circular for the meeting is given at the front of this issue of the Newsletter. Details can also be obtained at:

http://www.ph.surrey.ac.uk/polcol/Frontiers.html

We would very much welcome offers of papers for inclusion in the meeting.

Current Research Projects in the Field of Polymer Colloids

Studies of Chain Transfer to Polymer in Free-Radical Solution and Emulsion Polymerisations of 2-Ethylhexyl Acrylate
Research Student: Rajan Venkatesh
Collaborator: Frank Heatley, Chemistry Department, University of Manchester

Effects of Particle Size on the Toughening of Poly(methyl methacrylate)
Research Student: Pranee Thongnoi

Studies of Hydroxyethylcellulose Degradation and Grafting in Emulsion Polymerisations
Research Student: Ian Gray

Effects of Crosslinking and Particle Morphology on the Properties of Water-Borne Pressure-Sensitive Adhesives
Research Student: Nikki Errington

Coating of Particles using Emulsion Polymerisation Methods
Research Student: Parnia Navabpour
Collaborator: John Stanford, Manchester Materials Science Centre

Novel Latent Crosslinking Monomers Designed for One-Part Crosslinkable Water-Borne Coatings
Research Associate: Nadia Suliman
Collaborators: David Berrisford and Andy Whiting, Chemistry Department, UMIST

Recent Theses related to Polymer Colloids

Studies of Chain Transfer to Polymer in Acrylate Polymerisations by Nasir M. Ahmad, UMIST, 1999

Investigations of Acrylic Water-Borne Pressure-Sensitive Adhesives by Samantha Gramani, UMIST, 1999

Recent Papers related to Polymer Colloids

"Chain Transfer to Polymer in Emulsion Polymerization", N.M. Ahmad, D. Britton, F. Heatley and P.A. Lovell, *Macromolecular Symposia*, 143, 231 (1999)

Chain transfer to polymer in emulsion polymerizations of acrylate monomers and vinyl acetate has been studied using ^{13}C NMR spectroscopy to elucidate the chemistry by which chain transfer occurs and to quantify the mol% branches resulting from the reaction. In emulsion polymerizations of n-butyl acrylate, ethyl acrylate and methyl acrylate, chain transfer to polymer proceeds via abstraction of hydrogen atoms from backbone tertiary C–H bonds and typically gives rise to 2-4 mol% branches in the polymers obtained at complete conversion, the level of branching increasing with reaction temperature. For these acrylates, there is no evidence for a significant difference between the extent of chain transfer to polymer. In emulsion polymerizations of vinyl acetate, chain transfer to polymer proceeds mainly via H-abstraction from methyl side-groups, though there is a small contribution from abstraction at backbone tertiary C–H bonds. The levels of branching that result are substantially lower than in acrylate emulsion polymerizations, typically being in the range 0.6-0.8 mol% in the polymers obtained at complete conversion. The level of branching increases with temperature and as the degree of monomer starving (and hence instantaneous conversion) increases. Emulsion copolymerization of vinyl acetate with a small amount (5-20 wt%) of n-butyl acrylate gives rise to a significant increase in the level of branching (to values around 1.3-1.6 mol%), which results predominantly from H-abstraction of backbone tertiary C–H bonds in n-butyl acrylate repeat units by propagating radicals with vinyl acetate end units.

Contribution to IPCG Newsletter

Peter A. Lovell, Manchester Materials Science Centre, University of Manchester & UMIST, UK

"Water-Borne Pressure-Sensitive Adhesives: Effects of Acrylic Acid and Particle Structure", J. Garrett, P.A. Lovell, A.J. Shea and R.D. Viney, *Macromolecular Symposia*, accepted for publication

Two types of core-shell pressure-sensitive adhesive latexes have been prepared by semi-continuous emulsion polymerization: (a) *soft-soft* latexes with a poly(n-butyl acrylate) core and a poly[(n-butyl acrylate)-*co*-(acrylic acid)] (PBA/AA) shell; and (b) *rigid-soft* latexes with a poly[(methyl methacrylate)-*co*-(allyl methacrylate)] (PMMA/ALMA) core and a PBA/AA shell. Three series of *soft-soft* latexes were prepared in which: (i) the acrylic acid level in the PBA/AA shell was fixed at 5 mol% and the volume percentage (vol%) of the PBA/AA shell was varied; (ii) the vol% of the PBA/AA shell was varied, but with the acrylic acid level in the shell also being varied such that the total acrylic acid level was constant at 5 mol%; and (iii) the PBA/AA shell was fixed at 20 wt% of the total polymer and the acrylic acid level was varied from 0 to 49 mol%. In the *rigid-soft* latexes, the acrylic acid level in the PBA/AA shell was fixed at 5 mol% and the vol% of the PBA/AA shell was varied. The latexes were adjusted to pH 5.5 using aqueous ammonia solution before being used to form adhesive bonds between Melinex and glass, for measurement of shear resistance, and between Melinex and steel for measurement of peel adhesion. The pressure-sensitive adhesive properties of the latex coatings are interpreted in terms of the effects of the changes in latex particle acrylic acid content and particle structure on the interfacial and bulk properties of the adhesive materials.

"Thermal And Mechanical Characterisation Of Epoxy Resins Toughened Using Pre-Formed Particles", R.J. Day, P.A. Lovell and A.A. Wazzan, *Polymer International*, submitted

Pre-formed multi-layer particles have been used to toughen an epoxy resin. The particles were formed by emulsion polymerisation and consist of alternate glassy and rubbery layers, the outer layer having glycidyl groups in order to give the possibility of chemical bonding of the particles in the cured resin. Two variants of this type of particle were used, termed GM(47/15) and GM(47/37); both types have an overall diameter of 0.5 μm, but the former have a thicker rubbery layer. For comparison, acrylic toughening particles (ATP) with no surface functionality and a liquid carboxyl-terminated butadiene-acrylonitrile (CTBN) rubber were used as toughening agents. The epoxy resin system consisted of a commercial diglycidyl ether of bisphenol A (Shell Epon 828) with diamino-3,5-diethyl toluene as hardener, two commercial sources of which were used, namely Ethacure-100 (Albemarle S.A) and DX6509 (Shell Chemicals).

Thermogravimetry in nitrogen shows that the pre-formed toughening particles begin to degrade at 230 °C, whereas the cured resin begins to degrade rapidly at 350 °C. Thus, even though the particles are less thermally stable than the cured resin, their degradation temperature is well above the glass transition temperature of the resin, and their use does not affect the thermal stability of the toughened materials at normal use temperatures.

The performance of the toughening agents was compared using Ethacure-100 as the hardener. The GM(47/15) and GM(47/37) toughening particles gave rise to a greater toughening effect than the ATP and the CTBN. For example, the fracture energies were: 0.26 kJ m^{-2} for the unmodified resin, 0.60 kJ m^{-2} for the resin toughened with CTBN and 0.69 kJ m^{-2} for the resin toughened with the GM(47/15) particles. The ultimate tensile stress of the unmodified epoxy resin was 43 MPa, which increased to 55 MPa when 20 weight percent of GM(47/15) toughening particles were added.

The toughness of resins cured with the DX6509 hardener were superior to those obtained with the Ethacure-100 hardener, most probably due to DX6509 producing a less-highly-crosslinked network. This highlights the sensitivity of the toughening process to the hardener used, even for hardeners of a similar nature.

"Toughened Carbon/Epoxy Composites Made Using Core/Shell Particles", R.J. Day, P.A. Lovell and A.A. Wazzan, *Composites Science and Technology*, submitted

Toughened epoxy resin composites have prepared by resin transfer moulding using a range of toughening agents. Two types of epoxy-functional preformed toughening particles were investigated and have a three-layer morphology in which the inner core is crosslinked poly(methyl methacrylate), the intermediate layer is crosslinked poly(butyl acrylate) rubber and the outer layer is a poly[(methyl methacrylate)-*co*-(ethyl acrylate)-*co*-(glycidyl methacrylate)]. The presence of glycidyl groups in the outer layer facilitates chemical reaction with the matrix epoxy resin during curing. Comparisons were made with acrylic toughening particles that have a similar structure, but which do not have the epoxy functionality in the outer shell, and with a conventional carboxy-terminated butadiene acrylonitrile (CTBN) liquid rubber toughening agent.

The composites were characterised using tensile, compression and impact testing. The fracture surfaces and sections through the moulded composites were examined using optical and scanning electron microscopy. Short-beam shear tests and fragmentation tests were used to investigate the interfacial properties of the composites. In general, use of the epoxy-functionalised toughening particles gave rise to superior properties compared to both the non-functionalised acrylic toughening particles and CTBN.

Contribution to the IPCG Newsletter January 4, 2000

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Main activities of our group are on colloidal crystals, their morphology, crystal structure, crystal growth kinetics and effect of external fields such as an gravitational field, electric field, and centrifugal field. Microgravity effect on colloidal dispersions has been studied systematically using dropping, aircraft and rocket techniques. Multiple absorption phemomena of colloidal spheres, viscosity of colloidal gases, liquids and crystals, and dissipated structures of colloidal dispersions are also included in our research fields.

Publications(1999-)

(1)"**Suspension Viscosity of Colloidal Crystals and Liquids in Exhaustively Deionized Aqueous Suspensions**", T.Okubo, K.Takezawa and H.Kimura, *Colloid Polymer Sci.*, in press.

(2)"**Electric Field-induced Shear Waves of Colloidal Crystals as Studied by the Electro-Optic Reflection Spectroscopy**", T.Okubo, A.Tsuchida, A.Iwata and T.Tanahashi, *Colloids Surfaces*, 148, 87-94(1999).

(3)"**Electro-optics of Colloidal Crystals as Studied by the Reflection Spectroscopy**", T.Okubo, A.Tsuchida, T.Tanahashi, A.Iwata, S.Okada, S.Kobata and K.Kobayashi, *Colloids Surfaces*, A149, 431-441(1999).

(4)"**Electro-Optical Spectroscopy of Colloidal Systems**", M.Stoimenova and T.Okubo, "*Surface of Nanoparticles and Porous Materials*", Eds. Schawartz & Contescu, Marcel Dekker, Inc., New York, chapt. 5, pp103-124, 1999.

(5)"**Relation of Electro-Acoustic Effects to Low Frequency Anomalies in Colloidal Electro-Optics**", M.Stoimenova, A.Alekov and T.Okubo, *J.Colloid Interface Sci.*, 148, 83-86(1999).

(6)"**Propagation of Electrooptic Shear Waves in Colloidal Crystals As Studied by Reflection Spectroscopy**", A.Tsuchida, T.Taniguchi, T.Tanahashi and T.Okubo, *Langmuir*, 15, No.12, 4203-4207(1999).

(7)"**Nucleation and Growth Processes in the Colloidal Crystallization of Silica Spheres in the Presence of Sodium Chloride as Studied by the Reflection Spectroscopy**", T.Okubo, A.Tsuchida and T.Kato, *Colloid Polymer Sci.*, 277, 191-196(1999).

(8)"**Kinetic Analyses of the Colloidal Crystallization in a Sinusoidal Electric Field As Studied by Reflection Spectroscopy**", T.Okubo and H.Ishiki, *J.Colloid Interface Sci.*, 211, 151-159(1999).

(9)"**Giant Colloidal Crystals of Fluorine-containing Polymer Spheres in the Exhaustively Deionized Aqueous Suspensions and in the Presence of Sodium Chloride**", T.Okubo, H.Yoshimi, T.Shimizu and R.H.Ottewill, *Colloid Polymer Sci.*, in press.

(10)"**Kinetic Analyses of Colloidal Crystallization in Microgravity-Aircraft Experiments**", T.Okubo, A.Tsuchida, T.Okuda, K.Fujitsuna, M.Ishikawa, T.Morita and T.Tada, *Colloids Surfaces*, **A153**, 515-524 (1999).

(11)"**Rotational Diffusion of Anisotropic-shaped Colloidal Particles in a Microgravity As Studied by the Free-Fall Experiments**", T.Okubo, A.Tsuchida, H.Yoshimi and H.Maeda, *Colloid Polymer Sci.*, **277**, 601-606(1999).

(12)"**Kinetic Study of the Formation Reaction of Colloidal Silica Spheres by the Transmitted-Light Intensity and Dynamic Light-Scattering Measurements**", T.Okubo, K.Kobayashi, A.Kuno and A.Tsuchida, *Colloid Polymer Sci.*, **277**, No.5, 483-487(1999).

(13)"**Kinetic Study of Formation Reaction of Colloidal Silica Spheres in a Microgravity Using Aircraft**", T.Okubo, A.Tsuchida, K.Kobayashi, A.Kuno, T.Morita, M.Fujishima and Y.Kohno, *Colloid Polymer Sci.*, **277**, No.5, 474-478(1999).

(14)"**Kinetics of Colloidal Alloy Crystallization of Binary Mixtures of Monodispersed Polystyrene and/or Colloidal Silica Spheres Having Different Sizes and Densities in Microgravity Using Aircraft**", T.Okubo, A.Tsuchida, S.Takahashi, K.Taguchi and M.Ishikawa, *Colloid Polymer Sci.*, in press.

(15)"**Absorption of Macroions on the Colloidal Surfaces As Studied by the Electrophoretic and Dynamic Light-scattering Techniques**", T.Okubo and M.Suda, *J.Colloid Interface Sci.*, **213**, 565-571(1999).

(16)"**Alternative Sign Reversal in the _-Potential and Synchronous Expansion and Contraction in the Absorbed Multi-layers of Poly(4-vinyl-N-n-butylpyridinium) Cations and Poly(styrene sulfonate) Anions on Colloidal Silica Spheres**", T.Okubo and M.Suda, *Colloid Polymer Sci.*, **277**, 813-817(1999).

(17)"**Synchronous Alternative Multi-layered Absorption of Poly(4-vinyl-N-n-butylpyridinium) Cations and Poly(styrene sulfonate) Anions on Polystyrene Colloidal Spheres**", T.Okubo and M.Suda, *Colloid Polymer Sci.*, in press.

Contribution to the IPCG Newsletter

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1. Thermodynamics for the preparation of micron-sized, monodispersed highly monomer-"adsorbed" polymer particles utilizing the dynamic swelling method

T. Yamashita, M. Okubo

Colloids Surfaces A: Physicochem. Eng. Aspects, **153**, 153-159 (1999)

In previous articles, micron-sized monodispersed composite polymer particles were produced by seeded polymerizations for highly monomer-swollen polymer particles, in which seed particle dissolves, prepared by the dynamic swelling method (DSM) proposed by authors. This article discusses theoretically the thermodynamic background of DSM with seed particle which does not dissolve in monomer.

2. Adsorption of enzymes onto submicron-sized temperature-sensitive composite polymer particles and its activity

M. Okubo, H.Ahmad

Colloids Surfaces A: Physicochem. Eng. Aspects, **153**, 429-433 (1999)

Temperature-sensitive composite polymer particles were prepared by seeded emulsion copolymerization of dimethylaminoethyl methacrylate and ethylene glycol dimethacrylate with 0.14 μm-sized polystyrene seed particles. Its reliabiality as a carrier for biomolecules was evaluated by measuring the enzymatic activity of trypsin adsorbed on the composite particle at temperature above the lower critical solution temperature (LCST). Conformation of trypsin desorbed from the particle surface by lowering the temperature to below the LCST was examined with circular dichroism spectroscopy and compared with the native one. Both results indicate that enzymatic activity of the trypsin retained during the adsorption/desorption measurment.

3. Penetration/release behaviors of various solvents into/from micron-sized monodispersed hollow polymer particles

M. Okubo, H. Minami, Y. Yamamoto

Colloids Surfaces A: Physicochem. Eng. Aspects, **153**, 405-411 (1999)

The penetration/release behavior of various solvents into/from the hollow of micron-sized monodispersed cross-linked polystyrene (PS)/polydivinylbenzene (PDVB) (1/5.5, w/w) composite particle was examined. The hollow particles were produced by seeded polymerization utilizing the dynamic swelling method which the authors proposed earlier. The penetration into the hollow was affected by viscosity of the solvents and its affinity for the base polymers. Toluene saved in the hollow was released slowly. These results suggest that there is a possibility to apply such hollow particles as a controlled release material.

4. Synthesis of micron-sized monodispersed, core-shell composite polymer particles by seeded dispersion polymerization

M. Okubo, J. Izumi

Colloids Surfaces A: Physicochem. Eng. Aspects, **153**, 297-304 (1999)

Micron-sized monodispersed polymethyl methacrylate (PMMA) /polystyrene (PS) (PMMA/PS=2/1, wt ratio) composite particles consisting of PMMA-core and PS-shell were successfully produced by seeded dispersion polymerization of styrene in a methanol/water medium in the presence of about 2 μm-sized monodispersed PMMA particles. It was experimentally clarified that the morphology was unstable thermodynamically. From these results, it is concluded that seeded dispersion polymerization, in which almost all monomers and initiators exist in the medium, with seed particles having higher glass transition temperature than polymerization temperature has an advantage in producing core-shell polymer particles in which polymer layers accumulate in their order of the formation, even if the morphology is unstable thermodynamically.

5. Analysis of stepwise heterocoagulation for the preparation of soft core/hard shell composite polymer particles

M. Okubo, Y. Lu, Z. Wang

Colloid Polym. Sci., **277** (1), 77-82 (1999)

The stepwise heterocoagulation of small cationic hard particles (SPs) onto a large anionic soft particle (LP) for the preparation of soft core/hard shell composite polymer particles was examined using dynamic light scattering and spectrophotometry. The effects of the pH value the emulsifier content which was pre-added to the LP emulsion, and the heat treatment lime on the covering of a LP by SPs, and the stability of the heterocoagulated emulsion were clarified.

6. Microanalysis of the surface concentration of sulfate groups at polystyrene particles by isothermal titration calorimetry

M. Okubo, T. Suzuki, A. Sakauchi

Colloid Polym. Sci., **277** (6), 579-582 (1999)

Microanalysis of sulfate groups at polystyrene particle surfaces, which were derived as persulfate initiator fragments, was carried out with isothermal titration calorimetry, and compared with a conventional conductometric titration. The quantitative analysis was possible even with an extremely small number of polystyrene particles have 10 μmol sulfate groups.

7. Effect of polymer composition on the production of cationic multihollow polymer particles by the stepwise acid/alkali method

M. Okubo, H. Mori, A. Ito

Colloid Polym. Sci., **277** (6), 589-594 (1999)

The effect of the polymer composition on the formation of multihollow structures formed within submicron-sized styrene-butyl acrylate-dimethylaminoethyl methacrylate terpolymer particles by the acid/alkali method proposed by the authors was examined. The cationic particles were produced by seeded emulsion terpolymerization with 2, 2'-azobis(2-amidinopropane) hydrochloride initiator. The dimethylaminoethyl methacrylate content and the glass-transition temperature of the terpolymer greatly affected the formation of the multihollow structure.

8. Synthesis of greater than 10 μm-sized, monodispersed polymer particles by one-step seeded polymerization for highly monomer-swollen polymer particles prepared utilizing the dynamic swelling method

M. Okubo, E. Ise, T. Yamashita, *J. Appl. Polym. Sci.*, **74**, 278-285 (1999)

The thermodynamic simulation under kinetic control state indicates that 1.77 μm-sized monodispersed polystyrene (PS) particles can absorb 500 times amount of styrene monomer under keeping the monodispersity by the dynamic swelling method (DSM) which the authors proposed in 1991. Actually about 14.1 μm-sized monodispersed styrene-swollen PS particles in which PS seed particles absorbed 500 times amount of styrene monomer were successfully prepared utilizing DSM. By one-step seeded polymerization for the dispersion of the swollen particles at 30°C for 48 h with 2, 2'-azobis(4-methoxy-2, 4-dimethyl valeronitrile) initiator, 13.1 μm-sized monodispersed PS particles were produced

9. Production of core/shell polystyrene/poly(3, 5-xylidine) composite particles by chemical oxidative seeded dispersion polymerization

M. Okubo, H. Minami, S. Fujii, T. Mukai

Colloid Polym. Sci., **277**, 895-899 (1999)

Abstract Micron-sized monodispersed polystyrene (PS)/poly(3, 5-xylidine) (PXy) composite particles were produced by chemical oxidative seeded dispersion polymerization of 3, 5-xylidine at 20°C with 1.6 μm-sized monodispersed PS seed particles in HCl aqueous solution of which pH was always kept at 2.5 with a pH stat. The produced composite particles consisted of PS core and PXy shell.

10. Preparation of a heterogeneous polymer film from the blend emulsion by the stepwise heterocoagulation method

M. Okubo, Y. Lu

Colloids Surfaces A: Physicochem. Eng. Aspects, **153**, 609-615 (1999)

The blend emulsion of two kinds of polymer particles, in which almost all of the cationic soft small particles (SPs) were adsorbed onto the anionic hard large particles (LPs) by utilizing a stepwise heterocoagulation method proposed by the authors in 1990, was cast to a micro-heterogeneous film. In the film, LPs played a discontinuous phase and SPs with a content of 30 wt% played a continuous one as film forming additives. The storage stabilities of the blend emulsions after the stepwise heterocoagulation were examined under various conditions, and the morphology of the film was estimated from the attenuated total reflectance Fourier-transform infrared spectroscopic.

11. Thermodynamics for preparation of micron-sized, monodispersed, monomer-adsorbed polymer particles having snowman shape by utilizing the dynamic swelling method and the seeded polymerization

M. Okubo, T. Yamashita, E. Ise, er, 75, Ser. B, 7, 195-200 (1999)

12. Production of micron-sized monodispersed core/shell composite particles by seeded dispersion polymerization
M. Okubo, J. Izumi, R. Takekoh
Colloid Polym. Sci., **277**, 875-880 (1999)

13. Behavior of nonionic emulsifier molecules on the preparation of nanoparticles from submicron-sized ionized styrene-methacrylic acid copolymer particles by the particle dissolution method
M. Okubo, N. Fukami, R. Shinohara
Colloid Polym. Sci., **277**, 900-904 (1999)

Contribution to IPCG Newletter From
Unité Mixte CNRS-bioMérieux
Lyon-France
By C. Pichot

Effect of a cross-linking agent on the synthesis and colloidal properties of poly(N-isopropylmethacrylamide) microgel latexes, David Duracher, Abdelhamid Elaissari*, Christian Pichot

SUMMARY: Microgel latex particles were prepared by batch precipitation polymerization of N-isopropylmethacrylamide (NIPMAM) monomer, using methylenebisacrylamide (MBA) and potassium persulfate (KPS) as a cross-linker and initiator respectively. Polymerization kinetics and final particle size as measured by quasi-elastic light scattering (QELS) at 20°C was not affected upon varying the cross-linker concentration. In contrast, the final particle size determined using both QELS (at 50°C) and SEM exhibits an increased in particle diameter upon increasing the MBA concentration. In addition, the amount of water soluble polymer was found to be directly related to the amount of MBA. Finally, the electrophoretic mobility behavior of the obtained latexes were investigated as a function of temperature.

Preparation of thermosensitive latexes by copolymerization of N-isopropylmethacrylamide with a chelating monomer, David Duracher, Abdelhamid Elaïssari, François Mallet and Christian Pichot*

SUMMARY: Functional poly(N-isopropylmethacrylamide) (NIPMAM) copolymer latexes were prepared at 80°C using methylene-bisacrylamide (MBA) as the crosslinking agent, and potassium persulfate (KPS) as the initiator in the presence of N-(vinylbenzylimino)-diacetic acid (IDA). Adding functional monomer (IDA) was found to drastically affect particle size, but not size distribution as observed both by scanning electron microscopy and quasi elastic light scattering. However, performing the polymerization reaction at too high functional monomer concentration, led to enhanced the formation of water soluble polymers (WSP). The Lowest Critical Solubility Temperature (LCST) of cleaned latexes was measured by a turbidimetric method reflecting the thermosensitive behavior of the particles. The transition temperature was found to be around 43°C, and was only slightly dependent on the concentration of functional monomer.

NMR investigations into heterogeneous structures of thermosensitive microgel particles

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Summary : Internal properties of submicron poly(N-isopropylmethacrylamide)(NIPMAM) latex particles were investigated as a function of methylene bisacrylamide (MBA) concentration, used as a crosslinker. Two experimental approaches were performed. i) Quasielastic light scattering (QELS) measurements provided the particles size variation as a function of temperature, from which the swelling capacity of the particles as a function of MBA were estimated. In addition, the broadening and the lowering effects of the Lower Critical Solubility Temperature (LCST) were detected from the turbidity of solutions vs MBA concentration. ii) Observations of the transverse relaxation of protons gave evidence for heterogeneous structures inside particles ; several structural parts were discriminated from one another from different proton mobilities detected through magnetic relaxation rates. Corresponding to concentration gradients of the crosslinker, the internal particle structures were found to be looser and looser from the core to the shell. The state of gelation of the polymer particles was found to be governed by the initial amount of crosslinker, introduced in the latex recipe.

Adsorption of Bovine Serum Albumin Protein onto Amino-containing thermosensitive core-shell latexes, David Duracher, Abdelhamid Elaïssari*, François Mallet, Christian Pichot

Summary : Adsorption of bovine serum albumin (BSA) onto positively charged core-shell latex particles with a poly(styrene) core and a rich poly(N-isopropylacrylamide (NIPAM)) shell layer was examined in view of electrostatic and hydrophobic interactions. The adsorption of BSA protein onto such cationic and thermosensitive charged core-shell latexes increases upon raising temperature. In addition, the pH and the salinity dependence of the plateau adsorption is related to surface properties. The above dependency of protein adsorption is discussed by taking into the hydrophilic-hydrophobic balance of the particle interface versus temperature.

Adsorption of modified HIV-1 Capsid p24 Protein onto Thermosensitive and Cationic Core-shell Particles, David Duracher, Abdelhamid Elaïssari*, François Mallet, Christian Pichot

Summary: The adsorption of modified HIV-1 Capsid p24 protein (RH24) onto thermosensitive and cationic core-shell poly[Styrene/N-isopropylacrylamide] latex particles was investigated as a function of pertinent parameters such as time, temperature, pH and salinity. The adsorption of RH24 versus temperature develops three domain which are discussed taking into account the hydrophilic-hydrophobic balanceof the particles. The maximum adsorbed amount was reached above the LCST of the hydrogel shell, whereas negligible adsorbed amount was detected below the LCST. The adsorption isotherms performed above the LCST exhibit well-defined plateaus, which are pH and salinity dependent. These plateaus show a maximum around the IEP of the protein with a decrease in the adsorbed amount in the alkaline pH domain, rather than what is expected and generally reported for model protein adsorption onto polystyrene latexes. In addition, the adsorption isotherms were discussed using both Langmuir and Freundlich adsorption approaches. The estimated standard free enthalpy of protein adsorption was lower compared to the BSA adsorption onto polystyrene particles but comparable to that of fibrinogen

Studying the adsorption of modified HIV-1 Capsid p24 protein (RH24) revealed the complexity of the adsorption mechanism of such a new protein.

Recent Papers :

Expoxy networks toughened by core-shell particles. Influence of the particle structure and size on the rheological and mechanical properties
Becu-Longuet L., Bonnet A., Pichot C., Sautereau H., Maazouz A.
J. Applied Polym. Sci., 37, Issue: 12, 1823-1837,1999

Functional Nanosphere by Emulsion Polymerization, Pichot C., Delair T.
In Microspheres, Microcapsules and Liposomes. Ed. R. Arshady, Citus Book, London, Chap. 5, 125-164, (1999)

Functionalization of Preformed Microspheres, Arshady R., Margel S., Pichot P.
In Microspheres, Microcapsules and Liposomes. Ed. R. Arshady, Citus Book, London, Chap. 6, 165-196, (1999)

Hydrophilic magnetic polymer latexes 1-Adsorption of ferrofluids onto various cationic latexes. ; 2-Encapsulation of adsorbed iron oxides
Sauzedde F., Elaïssari A., Pichot C.
Colloid Polym. Sci ., in press (1999)

Study of cationic N-isopropylacrylamide-styrene copolymer latex particles using fluorescent probes
E.M.S. Castanheira, J.M.G. Martinho, D. Duracher, M.T. Charreyre, A. Elaissari, C. Pichot
Langmuir, 15,n°20, 6712 (1999)

Amino-containing cationic latex-oligodeoxyribonucleotide conjugates:Application to diagnostic test sensitivity enhancement., T. Delair, F. meunier, A. Elaïssari, M.H. Charles, C. Pichot, Colloids and Surfaces, Special Volume of the "International Symposium on advanced technology on fine particles" **153**,341 (1999),

Characterization of Cross-linked Poly(N-isopropylmethacrylamide) Microgel Latexes
Duracher.D, Elaïssari. A, Pichot C.
Colloid & Polymer Science, 277, 905 (1999)

Synthesis of hairy acrylic core-shell particles as toughening agents for epoxy networks
Hazot P., Pichot C., Maazouz
Macromol. Chem. and Phys. (accepted)

Report on PDM 99 (C. Pichot)

The fourth International Symposium «Polymers in Dispersed Media» (PDM 99) was organized in Lyon last April 11-15, following the previous ones, respectively held in 1984, 1989 and 1994. The main objective of this symposium was to deal with several major topics related to the preparation, characterization and properties of dispersed polymers, as obtained not only through heterogeneous media (emulsion, dispersion, suspension, etc.) but also by other methods including blends, reactive processing, ring-opening polymerization, etc, then allowing to synthesize dispersed polymer materials in a broad range of particle sizes and structures. A precise control of the macromolecular, colloidal and morphological characteristics of these materials is proved to be essential, as well as the development of relevant models, so as to provide an appropriate response to the many applications in which they are involved.

This Symposium was very successful since it attracted about 300 people from 26 different countries with a good balance between academic and industrial representatives. It is also noteworthy that a large number of students could also actively participate and contributed to the friendly atmosphere all along the meeting. Twenty-two invited lectures and 28 oral communications were presented, completed with 103 posters. The meeting was concluded by a fascinating lecture of Professor J. Fréchet about dendrimers, a special kind of dispersed material. A special committee selected three posters (one per topic) which were orally presented during the last session of the symposium.

83 invited and contributed papers of this meeting will be published in a special issue of Macromolecular Symposia and which will appear in two Volumes by next spring 2000. In the first volume are collected papers corresponding to topic (I): « Polymerization in dispersed media » and in the second volume those related to topics II and III :« Non-conventional dispersion of Polymers »; « Properties and Applications of Dispersed Polymers ».

Finally,this Symposium was also the opportunity for the scientific community to honour the activity of our colleague, Alain Guyot – Directeur de Recherche CNRS-emeritus – who has played a decisive role in the setting up and the development of the Polymer Science in Lyon as well as in the foundation of laboratories and the training of many researchers in this field.

In Memory of
Jean Guillot, Director of Research, CNRS

(1937-1999)

Jean Guillot suddenly passed away on the April 3, 1999 at the age of 62, one week before the PDM symposium started. He was deeply involved in the topics related to polymers in dispersed media for over 20 years, and contributed greatly to the organization of the three previous Conferences. We will no longer see his familiar silhouette or his jovial face always brightened by a friendly smile.

After completing chemical engineering studies at the Ecole de Chimie de Lyon, Jean Guillot joined the CNRS in 1961 at the Institut de Recherche sur la Catalyse, and rapidly became an excellent and creative scientist. He was a pioneer in many fields, mostly those related to radical copolymerization and to copolymer properties. During his PhD thesis work (which he defended in 1968) under the direction of Alain Guyot, he developed appropriate quantitative techniques to follow copolymerization kinetics. From the beginning of his career, Jean Guillot was always concerned with modeling, since he learned and practiced computer programming very early and with much passion. He started to apply his knowledge by simulating copolymerization kinetics and microstructure of the corresponding copolymers.

When the Laboratory of Organic Materials (LMO) moved to Solaize in 1980, he developed and led a research group in the emulsion polymerization field. He still continued to deal with copolymerization and with the complexity of heterogeneous media. With John Ugelstad, he was the first to introduce innovative thermodynamic concepts with the purpose of establishing reliable models, not only for predicting reaction kinetics but also for modeling various copolymer properties, such as microstructure, glass transition temperature, molecular weight distribution, crosslinking, etc. He initiated and maintained numerous and various collaborations with industry all over the world in these fields. The establishment of the Laboratoire de Chimie des Procédés de Polymérisation (LCPP) brought him back to Villeurbanne in 1995, at the Ecole de Chimie Physique Electronique (CPE).

J.Guillot also served as a diplomat for two years (1975-1977) as a scientific representative at the French embassy in Moscow, which gave him the opportunity to enjoy and to learn much about Russian culture. He also assumed administrative positions in the CNRS national committtee and in various research committee programs.

In all these activities, J. Guillot behaved as a warm and pleasant person with a solid sense of humour. He was curious about everything and quite eclectic in his hobbies. He was fond of literature, painting (he was himself an expert painter), music, languages (in this domain, he learned and practiced Chinese and Japanese). He was also an accomplished sportsman, and used to jog and cycle. Last but not least, J.Guillot loved his wonderful Beaujolais, especially the Bois d'Oingt surroundings and vineyards. When he left the lab in December 1998, he still maintained research activities and computer simulations as a consultant for many industrial companies. However, it is certain that he would have liked to take advantage of his retirement to enjoy more, with his wife Odile and their three children, this Beaujolais region to which he was very attached.

The PDM symposium was an appropriate occasion to pay tribute to the memory of Jean Guillot and that everyone will remember him for a long time.

Contribution to the International Polymer Colloids Group Newsletter

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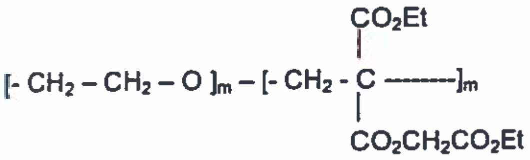
During 1999 we continued our activity on block copolymers and their application as polymeric surfactants.

A review article on "Functional Colloids using block copolymers" by G. RIESS, Ph. DUMAS and G. HURTREZ is in preparation for MML series edited by Reza ARSHADY. It will contain chapters on controlled synthesis of block copolymers, their use in emulsion, microemulsion and dispersion polymerization, the biomedical and non biomedical applications of colloidal particles produced using block copolymers.

Virginie LARRAS has continued her work on poly(methylidene malonates) by preparing amphiphilic block copolymers such as



$$[- CH_2 - CH_2 - O\,]_m - [- CH_2 - \underset{CO_2CH_2CO_2Et}{\overset{CO_2Et}{C}} \text{--------}]_m$$

The micellization behavior of these biocompatible and bioerodible block copolymers was examined. The corresponding publication will be submitted shortly to Macromol. Chem. Phys. – Rapid Comm.

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Recent Publications

"Micellar solutions of associative polymers: the relationship between structure and rheology", *Macromolecules* **32** 5139-46 (1999) [with Q.T. Pham, J.C. Thibeault, W. Lau].

"Linear viscoelasticity of hard sphere colloidal crystals from resonance detected with dynamic light scattering", *Physical Review E* **60** 1988-1998 (1999) [with S.-E. Phan, M. Li, J. Zhu, P.M. Chaikin, and C.L. Lant].

"A process model for latex film formation: limiting regimes for individual driving forces", *Langmuir* **15** 7762-7773 (1999) [with A.F. Routh].

"Polymeric and colloidal modes of relaxation in latex dispersions containing associative triblock copolymers", *Journal of Rheology* **43** 1599-1615 (1999) [with Q.T. Pham, J.C. Thibeault, and W. Lau].

"Distinguishing slip and dynamic yielding in a weakly flocculated colloidal dispersion", *Colloids and Surfaces A* **161** 271-282 (2000) [with M.C. Grant].

"Dispersions containing PEO with C_{16} hydrophobes: adsorption and rheology", *Associative Polymers in Aqueous Media* (ed. J.E. Glass), ACS Symp. Ser. Vol. xx (in press) [with Q.T. Pham, J.C. Thibeault, and W. Lau].

"Controlled growth of hard-sphere crystals", *Nature* **401** 893-5 (1999) [with Z. Cheng, P.M. Chaikin].

Abstracts

Annual Meeting of the AIChE, November 1999, Dallas TX

Stabilization of Colloidal Dispersions with Polyelectrolytes

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We are interested in the properties of adsorbed polyelectrolytes used in stabilizing dispersions at high salt strengths. The thickness of an adsorbed layer depends on the ionic strength within the brush with contributions from both the counterions and the added salt. In our experiments, the ionic strength within the brush is varied to observe the effects on the properties of the polyelectrolyte layer.

The model system consists of monodisperse latex particles with adsorbed poly(methacrylic acid) bound to the latex particles by a polystyrene anchor block. A series of

monodisperse copolymers with controllable block lengths is used in the study. Because the copolymer is not directly soluble in water, it is first dissolved in a water-dioxane mixture in the presence of the bare latex particles. In this mixed solvent, the copolymer forms micelles that adsorb on the latex particles. Dialysis is used to obtain the polymerically stabilized latex particles in water.

Both the bare and polymer coated latex particles are studied using dynamic light scattering, electrophoresis and dielectric spectroscopy. By comparing the results from the bare and coated latex particles, the polyelectrolyte layer can be characterized. Results for the polymer coated latex particles are interpreted using theoretical models for the thermodynamics of polyelectrolyte solutions and the electrokinetics of polyelectrolyte coated particles

Dielectric Spectroscopy as a Probe of Colloidal Surface Structure: Understanding Block Co-Polymers as Stabilizers

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Dielectric spectroscopy (DES) is remarkably sensitive to changes in particle morphology and is therefore well suited as a characterization method for polymer-coated latices. The experimental difficulties of DES have, however, influenced the rather slow progress in this field. We describe a new type of spectrometer cell coupled to a Hewlett-Packard 4194A impedance analyzer. The thin cell design is much simpler than the conventional cylindrical geometry often employed in low frequency measurements. Thus, relatively fast measurements are possible. Other characteristics are: a small sample volume, an unprecedentedly wide frequency range for a single cell (100 Hz to 40 MHz in a single frequency sweep), and a simple residual circuit model for data interpretation. The direct attachment of the cell to the instrument minimizes self-inductance, a critical feature in the megahertz frequency range. A variable electrode spacing technique extends the measurement of complex conductivity into the medium to low frequency range.

Following the necessary cell calibration, dielectric relaxation measurements were made on suspensions of uncoated polystyrene latex particles. Excellent agreement between the zeta potential derived from these results and those from complementary electrophoretic mobility measurements was found using the standard electrokinetic model and the ζ potential corresponding to the lower branch of the mobility-ζ potential relationship. Measurements on polystyrene latex particles coated with a polyelectrolyte diblock copolymer show dramatic differences as compared with the bare particle behavior. The electrokinetic results are interpreted together with photon correlation spectroscopy measurements used to characterize the hydrodynamic permeability of the adsorbed polymer layer.

73rd ACS Colloid and Surface Science Symposium, Cambridge, MA, June 1999

Dielectric Response of Colloidal Suspensions: A new cell design.

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We describe a new type of dielectric spectrometer cell coupled to a Hewlett-Packard 4194A impedance analyzer. The thin cell design is much simpler than the conventional cylindrical geometry often employed in low frequency measurements. Thus, it permits relatively fast measurements. Other characteristics are a small sample volume, an unprecedentedly wide frequency range for a single cell (100 Hz to 40 MHz in a single frequency sweep), and a simple residual circuit model for data interpretation. The direct attachment of the cell to the instrument minimizes self-inductance, a critical feature in the megahertz frequency range. A variable electrode spacing technique extends the measurement of complex conductivity into the medium to low frequency range. The cell is equipped with a temperature regulating system to maintain the sample temperature at 25 ± 0.1° C. To demonstrate the instrument fidelity, permittivity and conductivity measurements were made with standard electrolyte. This protocol established the necessary cell calibration, *e.g.*, the stray capacitance and conductance corrections. Following the calibration, measurements were made on suspensions of polystyrene latex particles. These results, along with an interpretation using the standard electrokinetic model, will be presented.

74rd ACS Colloid and Surface Science Symposium, Lehigh, PA, June 2000

Complementary Techniques for Probing the Layer Structure of Polyelectrolyte-coated Latices: AFM and Dielectric Spectroscopy:

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Optimizing colloidal stabilization with polyelectrolyte diblocks requires knowledge of the polymer layer structure and the influence of ionic strength. We apply complementary atomic force microscope (AFM) and electrokinetic techniques to layers adsorbed on polystyrene spheres. Interaction forces between 6-micron spheres measured with an AFM yield the magnitude and separation dependence of the repulsion, as well as the presence of any attraction. For bare particles the results agree with expectations for the electrostatic repulsion based on surface potentials extracted from electrophoresis measurements.

For particles coated with polyelectrolyte diblocks, the range of the repulsion correlates with layer thicknesses deduced from dynamic light scattering on 300 nm spheres; both the magnitude and range of the force depend strongly on ionic strength. The electrophoretic mobilities of bare and polyelectrolyte coated particles are similar, but dielectric spectroscopy provides a more discriminating characterization, with the low frequency behavior reflecting the greatly increased charge associated with the polyelectrolyte layer. We interpret the ionic strength dependence of the forces by combining models that capture both short- and long-range electrostatic interactions between charged segments within the brush with mean field treatments of interactions between brushes.

Contribution to IPCG Newsletter
Stan Slomkowski, Center of Molecular and Macromolecular Studies, Lodz, Poland

Tailored modification of quartz surfaces by covalent immobilization of small molecules (γ-aminopropyltriethoxysilane), monodisperse macromolecules (dendrimers), and poly(styrene/acrolein/divinylbenzene) microspheres with narrow diameter distribution

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Colloid Polym Sci, 277, 58-65 (1999)

Summary

Quartz plates were modified by consecutive immobilization of γ-aminopropyltriethoxysilane (APTS), phosphorus containing dendrimers with aldehyde groups (generation 5 - G5), Starburst PAMAM dendrimers generation 4 (PAMAM), and poly(styrene-acrolein-divinylbenzene) microspheres (P(SAD)). In this way surfaces with heterogeneity on molecular, macromolecular, and microscopic level which were equipped with functional amino or aldehyde groups, were obtained. Surface layers were characterized by X-ray photoelectron spectroscopy (XPS) and by contact angle measurements. Analysis of XPS spectra revealed that thickness of the layer of G5 on SiO_2-APTS substrate was 3.7 nm, i.e. was typical for macromolecular dimensions. The average thickness of the layer of PAMAM dendrimers on SiO_2-APTS-G5 was found to be equal 0.35 nm and 0.29 nm, depending

whether calculations were based on attenuation of the intensity of the signal Si2p or P2p, respectively. This thickness was unreasonably low for a monolayer of PAMAM dendrimers and indicated that surface of the SiO_2-APTS-G5 substrate was covered with these macromolecules incompletely. XPS method was used also for determination of the degree of coverage of the surface of SiO_2-APTS-G5-PAMAM plate with P(SAD) microspheres which being equal 0.60 approached the maximal theoretically possible value (0.62) for microspheres attached chaotically and irreversibly to the surface in an arrangement one microsphere thick. Subsequent coverage of SiO_2-APTS-G5-PAMAM-P(SAD) substrate with PAMAM dendrimers resulted in formation of PAMAM adlayer 3.2 nm thick, close to molecular dimensions of these dendrimers. Contact angle measurements revealed considerable differences in hydrophobicity of surfaces of quartz plates, depending on their modification. Hydrophobicity increased in the order SiO_2 < SiO_2-APTS-G5-PAMAM < SiO_2-APTS SiO_2-APTS-G5 < SiO_2-APTS-G5-PAMAM-P(SAD).

Tailored Synthesis of Polyesters by Dispersion Ring-Opening Polymerization of ε-Caprolactone and Lactides

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Macromol. Symp., in press

SUMMARY: Polyester microspheres were synthesized by anionic and/or pseudoanionic ring-opening polymerizations of lactides and ε-caprolactone, yielding particles with number average diameters up to 6.5 μm and with a narrow diameter

polidispersity ($\overline{D}_w / \overline{D}_n$), which for the properly determined polymerization conditions did not exceed 1.2. Depending on the polymerization conditions (nature of initiator, initial monomer and initiator concentrations) it was possible to obtain polylactides with $\overline{M}_n$ in the rrange from 8 000 to 270 000 and poly(ε-caprolactone) with $\overline{M}_n$ from 3 000 to 106 000. Molecular weight polydispersities of high molecular weight polyesters were narrow ($1.05 \leq \overline{M}_w / \overline{M}_n \leq 1.3$). It was found that in investigated polymerizations the microspheres are formed at the early monomer conversion and the main part of propagation proceeds in the monomer swollen particles, in which all growing macromolecules are located. Partial degradation of polyesters in microspheres, treated with KOH in ethanol in presence of surfactants, yielded particles with diameters close to those of the parent ones. Surface layers of these microspheres were rich in carboxylic groups suitable for covalent immobilization of compounds with primary amino groups. Partially hydrolyzed microspheres were used for preparation of suspensions of nonaggregated particles in the water-based media. Poly(ε-caprolactone) microspheres suspended in water were loaded with a drug, ethul salicylate, yielding particles with content of the bioactive compound up to 34 wt%.

X-ray Photoelectron Spectroscopy (XPS) as a Tool for Studies of Surface Layer of Microspheres.

The Case of Polystyrene (PS) and Poly(styrene-acrolein) (PSA) Microspheres with Attached Human Serum Albumin (HSA)

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Colloid Polym Sci, submitted

Abstract

Application of X-ray photoelectron spectroscopy (XPS) for studies of surface layers of objects with spherical shape was investigated using as an example polystyrene (PS) and poly(styrene-acrolein) (PSA) microspheres with attached human serum albumin (HSA). Amounts of immobilized protein were determined by standard biochemical Lowry method and by XPS, using the intensity of N1s signals of HSA as a basis for evaluation. The XPS data were treated taking into account the spherical shape of analyzed particles (variable take-off angle of ejected electrons). The best agreement between results of the biochemical and XPS determinations has been found assuming that for the average particle the take-off angle varies from 17.3° to 90°. This reflects the fact that in the multilayer arrangement of particles, placed onto support of XPS apparatus, these from the upper layer partially screen the edges of particles in the layer below.

IPCG Contribution

Amit M Kulkarni and Charles F Zukoski, Department of Chemical Engineering, University of Illinois at Urbana-Champaign, Urbana, IL 61801.

Unpublished work:

(1) Effects of Polyethylene Glycol on Protein Interactions

Amit M. Kulkarni, Avik P. Chatterjee, Kenneth S. Schweizer, and
Charles F. Zukoski

(submitted to Langmuir)

Abstract (extended)

Addition of non-adsorbing polymer to a stable particle suspension produces an attraction between the particles, commonly known as "depletion attraction". This induced interaction arises from an unbalanced osmotic pressure due to excluded volume overlap of polymers from the region between the particles. This phenomenon has significant scientific and technological consequences in diverse fields and has seen extensive investigation. Our interests lie in the use of polymer induced depletion interactions to aid protein separation and crystallization. The interactions between lysozyme molecules in the presence of poly (ethylene glycol) (PEG) are characterized through the measurement of protein solution second virial coefficient (B_2). The solution properties of the PEG are characterized for four molecular weights (400, 1000, 6000 and 12000) providing an opportunity for quantitative comparison of measurements and theoretical predictions of B_2. As a function of polymer concentration, the second virial coefficient is observed to pass through a minimum for PEG molecular weights of 1000 and greater. The attractive minimum in B_2 at roughly $c_p \cong c_p^*$ becomes deeper and shifts to lower c_p as PEG moelcular weight increases. This minimum cannot be predicted by standard depletion interaction energy models, such as the Asakura Oosawa model. We find that it is closely associated with the proximity of the heating-induced

phase separation (LCST behavior) of aqueous PEG solutions. The location and depth of the minima in B_2 as a function of PEG concentration and molecular weight are well predicted by the thermal Polymer Reference Interaction Site Model (PRISM) for depletion interactions where the polymer mesh size is treated as a function of temperature. This suggests the strong N-dependence of B_2, and its nonmonotonic variation with c_p, as primarily due to thermal polymer concentration fluctuations. This agreement suggests that the strength of polymer-mediated attractive forces between small proteins can be tuned by rational manipulation of the mesh size of polymer solutions by modest pre-transitional thermal polymer concentration fluctuations even 75-100°C away from the critical temperature. This effect may be exploited in a variety of scientific and technological contexts, including the important problem of optimizing protein crystallization conditions.

(2) Effects of polymer density fluctuations on depletion interactions.

Amit Kulkarni, Avik Chatterjee, Kenneth Schweizer, and Charles Zukoski

to be published in the Journal of Physics: Condensed Matter; 4th EPS Liquid Matter Conference Proceedings; Feb 2000.

Published work:

A.M.Kulkarni, A.P.Chatterjee, K.S.Schweizer, and C.F.Zukoski, Phys. Rev. Lett. **83**, 4554 (1999).

Thesis:

A. M. Kulkarni, "Depletion Interactions in the Protein Limit", M.S. Thesis, University of Illinois, Urbana Champaign, 1999.

Synthesis and Characterization of Poly(styrene/-*t*-butoxy-vinylbenzyl-poliglicidol) microspheres

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Ivan Panchev[2], Mohamed M. Chehimi[3]

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Colloid Polyme Sci, prepared for submission

Abstract

Polystyrene microspheres with polyglycidol in a surface layer were synthesized in batch radical emulsifier-free emulsion copolymerizations of styrene and surfmers, t-butoxy-vinylbenzyl-poliglycidol macromonomers (VB-polyGL). Macromonomers with a number average molecular weight $\overline{M}_n$ = 950 (VB-polyGL950) and $\overline{M}_n$ = 3000 (VB-polyGL3000) were used for these polymerizations. In all syntheses the initial concentrations of styrene and initiator ($K_2S_2O_8$) were constant. The initial macromonomer to styrene ratios were varied from $1.10 \cdot 10^{-3}$ to $1.64 \cdot 10^{-2}$ mol/mol and from $3.46 \cdot 10^{-4}$ to $3.47 \cdot 10^{-3}$ mol/mol for VB-polyGL950 and VB-polyGL3000, respectively. Diameters of obtained microspheres were lower for the syntheses with higher concentrations of macromonomers. Syntheses with VB-polyGL950 yielded microspheres with number average diameters ($\overline{D}_n$) from 216 nm to 900 nm and with a bimodal diameter distribution. Number average diameters of microspheres obtained with VB-polyGL3000 varied from 220 nm to 650 nm, depending on the initial concentration of macromonomer. Their diameter distributions were monomodal, with diameter polidispersity parameter (ratio of weight and number average diameters) in the range $1.007 \leq \overline{D}_w / \overline{D}_n \leq 1.02$. For each type of microspheres a fraction of polyglycidol in surface layer and surface concentration of sulfate anions were determined. Fraction of polyglycidol in the surface layer was related to the initial monomer composition in the polymerizing mixture. Adsorption of human serum albumin (HSA) onto surfaces of poly(styrene/VB-polyGL) microspheres was up to 10 times lower than for the polystyrene microspheres obtained in the similar emulsifier-free emulsion polymerization of styrene initiated with the same initiator.

Report from the Institute of Polymeric Materials, University of Pardubice
Reporter: Jaromir Snuparek

In the field of polymer colloids the activity of the group has been focused on binders for water-borne paints, their synthesis by emulsion polymerization and evaluation of properties. Acrylic monomers have been investigated predominantly. The investigatrion is focused on preparation of copolymers containing higher contents of functional comonomers as AA, MAA, HEMA, AAm, MAAm. The work has been focused on copolymerization of monomers with different polarity in semi-continuous process as well as on the particle growth. Film-forming propertiers of binders and basic properties of water-borne paints have been investigated mainly from the point of view of their corrosion protection efficiency. New types of corrosion protective pigments have been used in paint formulations. We are collaborating with group for rheology in the Institute of Macromolecular Chemistry, Academy of Sciences of the Czech Republic in Prague. The rheological behaviour of highly carboxylated copolymers and eficeincy of associative thickeners and invetigation of water borne paints has been studied with support by Grant Agency of the Czech Republic, the investigation of paints also with supprt of Ministery of Industry and Trade of the Czech Repuzblic.

Graduate research (PhD. students) in polymer colloids and their applications

Butyl Acrylate/Styrene/HEMA copolymer latices.
(G. A. Baghaffar) finished

Butyl Acrylate/Styrene/methacryl amide copolymer latices - copolymerization, particle formation, properties.
(M. Ka%‰ka)

Interaction between carboxylic latices and reactive inorganic pigments.
(P. G_esová)

Curing of Hydroxyl Groups Containig Latices by Diisocyanates.
(L. Farsk˘ - undergraduate)

Recent papers

Benda D., ·_upárek J. and _ermák V. :
Inverse Suspension Polymerization of Hydrophilic Acrylic Monomers in the Static Phase.
J. Dispersion Sci.Technol. **18** (2), 115 (1997).

Benda D., ·_upárek J. and _ermák V. :
Inverse Emulsion Polymerization of Acrylamide and Salts of Acrylic Acid.
Eur. Polymer. J. **33** (8), 1345 (1997).

Kalendová A., ·_upárek J. and Kalenda P. :
Nontoxic Spinel-Type Pigments in Anticorrosive Coatings in *Symposium Series 689 - ACS Book on Corrosion Control by Coatings.*, pp. 366 - 382, (Ed. Gordon Bierwagen), Washington, D. C. (1998).

Quadrat O., Mrkvi_ková L., Walterova Z., Titkova L., Bradna P., ·_upárek J.:
Structure and Flow Behavior of Crosslinked Ethyl Acrylate-Methacrylic Acid Copolymer Dispersion Particles

Colloid Polymer J. 276, 879-886 (1998)

Horsk˘ J., Quadrat O., Mrkvi_ková L., Porsch B., ·tern P., ·_upárek, J.:
Rheology of Latices of Copolymwers Containing Various Amounts of 2-Hydroxyethyl Methacrylate Units
Rheology of Polymer Systems - IUPAC 58th Prague Meeting on Macromolecules, July 19 - 22, 1999, Proceedings P12

Submitted papers

Effect of alkalinization on carboxylated latices prepared with various amount of a non-ionogenic hydrophilic comonomer 2-hydroxyethyl methacrylate

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Abstract

Incorporation of 2-hydroxyethyl methacrylate (HEMA) as comonomer into styrene/butyl methacrylate/ acrylic acid latices can affect stability and dry-film properties of these materials. Our results show that also the rheological behavior of these latices is considerably influenced by a HEMA content. A series of styrene/butyl methacrylate/ acrylic acid latices with HEMA contents ranging from 0 to 25% and with particle diameters about 160 nm were prepared by semicontinuos emulsion polymerization. The dynamic light scattering experiments revealed the increase in the hydrodynamic diameter of latex particles upon alkalinization, promoted by the presence of HEMA.

The concentration dependence of low-shear viscosity was measured by a capillary viscometer and the Mooney equation was applied to the results obtained. The behavior of original acid latices corresponded to that of hard spheres: the intrinsic viscosity of about 2.5 was found irrespective of the HEMA content, and the critical fractions were about 0.64, the value expected for random packing. Upon alkalinization, the intrinsic viscosity increased and the critical fractions decreased for all samples except the one without HEMA; otherwise, the higher the HEMA content in the sample the stronger was the effect. The data for alkalinized latices could be fitted to Mooney equation only if volume fractions were empirically corrected for swelling of latex particles.

Steady-state and dynamic measurements, made using cone and plate geometry with Weissenberg rheogoniometer and rheometer Haake RT10, respectively, showed that both the pseudoplasticity and elasticity of the alkalinized latices increased with the content of HEMA.. The universal concentration dependence of pseudoelasticity was found for latices with various HEMA content if correction factors for swelling found from the Mooney equation were applied, thus confirming their physical relevance.

Experiments with dialyzed samples demonstrated the effect of ionic strength on swelling of HEMA containing carboxylated latices and explained why different swelling was found at different latex concentrations.

Submitted to *Colloid and Surfaces A.*

* * *

Thickening of butylacrylate/styrene/hydroxy ethylacrylate/acrylic acid latices with dispersion of crosslinked ethylacrylate/methacrylic acid copolymer

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Summary

Thickening of latices of acrylic carboxylated copolymers containing various amount of hydroxyethyl methacrylate (HEMA) with alkali-swellable dispersion of crosslinked ethylacrylate/methacrylic acid copolymer has been studied using capillary viscometry and dynamic and steady shear measurements. The higher amount of HEMA was incorporated into the latex copolymers, the stronger thickening effect appeared. A comparison of flow behaviour of thickened systems with those of neat latices confirmed a significant influence of the effective volume fraction of alkalinized swollen latex particles on the thickening process. Under these conditions to obtain the same rheological properties a necessary amount of the thickener is lower for the latex copolymers with higher amount of HEMA, as a part of the thickener volume fraction is substituted by an increased volume fraction of swollen latex particles. These findings indicate the weakly interacting systems without a strong compression of particle domains.

To be submitted to *Progress of Organic Coatings.*

International Polymer Colloids Group Newsletter
Fall 1999 Contribution
University of New Hampshire Polymer Center
Durham, NH 03824 USA
Donald C. Sundberg, Yvon G. Durant

Effect of Initiator Type on Particle Morphology

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Polymer Research Group
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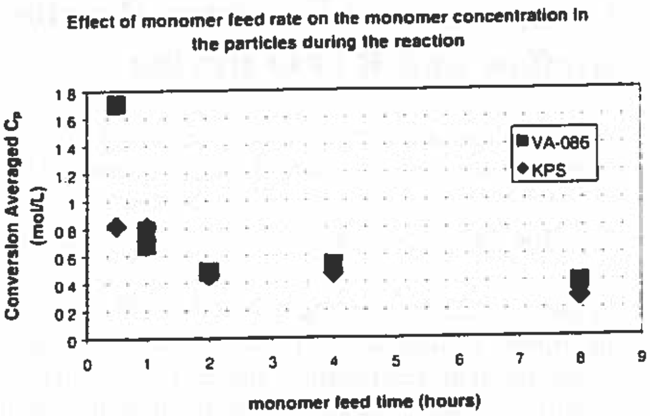
Previous work in our laboratory has shown that it is possible to begin to understand non-equilibrium particle morphology development under kinetically controlled conditions by considering the distance that entering free radicals are able to diffuse into the seed particles. The diffusion rates of these radicals are dependent on the difference between the reaction temperature and the T_g of the seed polymer, as well as the concentration of monomer within the particles during the reaction. We have quantified this by calculating a "fractional penetration" value, FP, which is an estimate of the distance a radical can diffuse before terminating divided by the particle radius. For FP values greater than one, full penetration of the second stage polymer into the seed particles is expected and should result in inverted core shell or occluded morphologies. For FP values much less than one, core shell morphologies are expected. Previous work has shown that these FP calculations agree very well with morphologies observed by TEM[1]. One interesting question is whether or not radicals with ionic end groups anchor to the particle surface, making it more likely to form core-shell morphologies by limiting diffusion of radicals into the particles.

In order to investigate this question it is necessary to use a seed polymer with a T_g such that penetration of radicals, and thus particle morphology, can be controlled easily by changing the monomer feed rate. If a seed polymer with a very high T_g is used, then when monomer is fed slowly the particles will remain glassy during the reaction and the diffusion rates of entering radicals will be very slow. Under these conditions even radicals that are not anchored cannot diffuse far into the seed particles, so core-shell morphologies are expected with either ionic or non-ionic initiators. This was the case for similar experiments performed by Jan-Erik Jönsson at Lund University which used a PMMA seed polymer with styrene fed slowly during the second stage, and compared the morphologies resulting from experiments using either t-BHP (non-ionic) versus potassium persulfate (KPS) initiators[2]. The results indeed showed core-shell morphologies in both cases, which agrees with the predictions of FP calculations for such a high T_g seed polymer. Work conducted in our laboratory by Lina Ivarsson has shown that for a reaction temperature of 70°C, a seed with a T_g near 55°C starts to show considerable penetration of the second stage into the seed particle[3]. For this system it is possible to change for morphology from occluded structures to core shell by decreasing the monomer feed rate (thus decreasing the monomer concentration and diffusion rates within the particles).

Since this time we have conducted experiments to investigate the effect of initiator type by using a poly(methyl acrylate-co-methyl methacrylate) seed latex with a T_g of 54°C. Styrene was then polymerized in the second stage reactions at 70°C and at various monomer feed rates (with total monomer feed times of 1/2, 1, 2, 4 and 8 hours). The two initiators used in the study were KPS and VA-086 (Wako Chemicals USA, Inc.). VA-086 is an azo initiator that is uncharged, water soluble and has a decomposition rate constant similar to KPS. Identical conditions were used in every experiment with the exception of the different initiators, and the initiator concentrations were adjusted to give the same radical production rate in every case. The reactions were monitored by taking samples throughout and analyzing them gravimetrically. Results for the monomer concentrations within the particles during the reactions (values averaged over conversion) for all of the various experiments are shown in Figure 1. As expected, the monomer concentrations decrease with decreasing monomer feed rates (increasing total monomer feed times). The most important point to note from Figure 1 is that, at a given monomer feed rate, the concentration of monomer within the particles is essentially the same for the two experiments with different initiators (except for the experiment with a 1/2 hour feed time). This is an important result because it means that the diffusion rates of radicals with the particles (if they are not anchored) should be the same for either experiment. Then, when the morphologies are compared for experiments at the same feed rate using different initiators, the differences can be attributed to the effects of radical anchoring, without being complicated by possible differences in diffusion rates within the particles.



Particle morphologies were determined from TEM photos of microtomed sections of the particles. The results have shown that there is indeed an effect on the morphologies, although it is not observed in all cases. For the experiments with a total monomer feed time of 1 hour the monomer concentrations within the particles were high enough to facilitate diffusion of the entering radicals towards the particle interior. At this feed rates the latices produced using VA-086 show occluded morphologies with no evidence of a shell, while those having KPS as the initiator show core-shell morphologies. TEM photos of these particles are shown in Figure 2. These results have been confirmed in duplicate experiments. At slower monomer feed rates (2, 4 and 8 hour feed times) the low monomer concentration in the particles restricts diffusion of radicals and core-shell morphologies are observed regardless of the whether KPS or VA-086 was used. For the experiments with the fastest monomer feed rate (1/2 total feed time), occluded morphologies were obtained for either initiator. This result showed that anchoring of radicals is not always a dominant factor in controlling morphology, and that when diffusion rates within the particles are fast enough even charged radicals are able to penetrate into the seed particles and produce morphologies deviating from core shell.

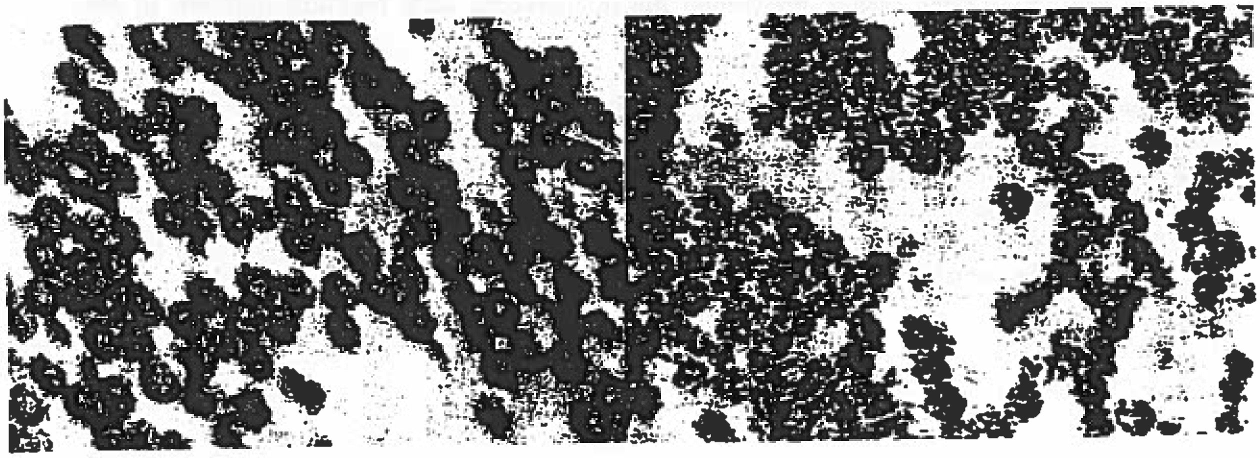


Figure 2: Styrene fed over 1 hour in second stage polymerization with a 1:1 stage ratio (seed:second stage polymer). left: KPS initiator; right: VA-086 initiator.

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2)Jönsson, J.-E.; Hassander, H.; Törnell, B. *Macromolecules* **1994**, *27*, 1932-1937.
3)Ivarsson, L.; Karlsson, O. J.; Sundberg, D. C. *In press* **1999**.

To be presented at AEMA/ISSA Joint Annual Meeting in March, 2000

Comparison of Emulsion Residues Recovered by the Forced Airflow and RTFO Drying

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At the last AEMA meeting in March 1999, we proposed a new residue recovery procedure for the asphalt emulsion. The procedure does not expose the emulsion to extreme heat, but dried in an ambient temperature under forced airflow, thus simulating a typical application condition. Water evaporates freely from the emulsion surface until the total solids are at above 90%. A sufficient amount of the residue samples can be prepared within 3 hours for the Superpave binder characterization. Optical microscope observation confirmed spontaneous formation of a microscopic SBR latex polymer network among asphalt particles upon drying.

M. Heslop and I. Walsh have been working for U.K. Highways Agency to develop a new residue recovery procedure based on the rotating thin film oven test (RTFOT) apparatus. Here, approximately 25g of an emulsion sample is placed in a polytetrafluoroetheylene (PTFF) bottle containing a PTFE S-screw and placed in the carousel. A thin film of emulsion binder is rotated in PTFE bottles at a temperature of 85°C for 75 minute with a flow of heated nitrogen gas jetted over the binder film to evaporate the water phase. The emulsion binder is continuously disturbed by a rotating PTFE S-screw in the bottle, which is designed to draw material away from the entrance of the bottle.

We tested their RTFOT procedure and compared against our forced airflow drying using the SBR latex modified CRS-2 and CSS emulsions. The residue samples were taken every 15-minute during drying with RTFOT, and the Superpave dynamic shear rheometry was applied to characterize their physical properties. Test results demonstrate that these two different drying methods provide the emulsion residue having identical rheological properties. Optical microscope observation, again, confirmed the microscopic SBR polymer network in the residue by RTFO drying.

The emulsion residue of 130-140g can be obtained with the RTFOT procedure using eight bottles. This is enough to complete the Superpave binder characterization using the dynamic shear and bending beam rheometry. Our results indicate that the drying time could be reduced to below 30 minute and airflow instead of N_2 does not affect the residue property. Thus, the residue recovery by the RTFOT apparatus is the most promising method for obtaining the emulsion residue, which closely simulates typical application conditions.

Effects of Temperature on the Flow Dynamics of a Model HASE Associative Polymer in Nonionic Surfactant Solutions

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The interaction between a model hydrophobically modified, alkali-soluble emulsion (HASE) polymer and a nonionic surfactant, $C_{12}EO_4$, was investigated in this work. The addition of the nonionic surfactant increases the viscosity and moduli of the polymer up to the maximum concentration of 0.1 M. The low-shear viscosity, plateau modulus, and hence the effective junction density increase linearly with surfactant concentration up to 0.01 M. However, above 0.01 M, the plateau modulus tapers off while the rise in viscosity becomes steeper. From the Arrhenius plots of both the low-shear viscosity and longest relaxation time, the activation energy of dissociation of the hydrophobes from the aggregated junction for the pure HASE polymer was found to be of the order of 50 kJ mol^{-1}. In the presence of 0.00025-M surfactant, an increase in the activation energy of approximately 10% was observed, and results from the enhancement of the hydrophobic junctions by the surfactant molecules. At higher surfactant concentrations between 0.001 and 0.01 M, the Arrhenius plots show two distinct regions, yielding activation energies of 30 kJ mol^{-1} at temperature T<25 °C and 75 kJ mol^{-1} at T>25 °C. This corresponds to the transition, at approximately 25 °C, from large, mixed, spherical micellar aggregates to a large bilayered structure formed by the polymer-surfactant aggregrates. The size of these bilayers increases dramatically with temperature, as is confirmed by the decrease in the number of effective network junctions at T > 25 °C. At T < 25 °C, the effective junction density remains almost constant with temperature, and the reduction in the activation energy is probably due to a decrease in the functionality of polymer hydrophobes. Above 0.01 M, the surfactant molecules form larger bilayers or vesicles with the associated polymer hydrophobes, resulting in a solid, gellike structure. The gel system exhibits increasing viscosity profiles with increase in temperature, and the transition temperature was shifted from 25 to 8 °C.

To be presented at Advances in Emulsion Polymerization and Latex Techology, 31st
Annual Short Course, Lehigh University, June 5-9, 2000.

An Applied Approach to Film Formation in Waterborne Coatings

J. W. Taylor, Johnson Polymer, P.O. Box 902
Sturtevant WI 53177-0902

The commercialization of latexes by DOW Chemical Company in 1946 created a need to understand film formation from heterogeneous polymeric particles. Environmetal change as well as technological advances have resulted in a continuous shift from sovlent-borne to water-borne polymers. Early theories focused on the film formation of solvent-free latexes; however, in the coatings industry, solvents are often used to improve the performance of industrial and maintenance coatings. A unified approach for the use of filming aids with latexes is under development. Important parameters such as the glass transition temperature of solvents and polymers, the volatility of solvents in the presence of water and polymeric particles, the distribution constants of solvents, the MFT of coating are used in a model to predict the "hydroplasticized" glass transition temperature (Tg_h) of the latex particles at compaction. This model allows the filming aid selection of a water-borne latex-based formulation to be developed from first principles.

Activities in the group of Alex van Herk

A) Composition of the group working on emulsion polymerization, kinetics and related topics:

1	Michel Pepers	PhD	1-7-1999	1-7-2003	Emulsion Copolymerization, on-line Raman
2	Xaviera Reynhout	PhD	1-6-2000	1-6-2004	Reaction Calorimetry (Meuldijk), Emulsion Polymerization
3	Martin Jung	PhD	Defence	28-2-2000	Vesicle polymerization
4	Jens Pusch	PhD	1-1-2000	1-1-2004	Synthesis of microgels for optical applications
5	vacancy	PhD	1-4-2000	1-4-2004	CLD termination rate coefficients
6	vacancy	PhD	1-4-2000	1-4-2004	Copolymerization models
7	vacancy	PhD	1-4-2000	1-4-2004	Aqueous phase polymerization of functional monomers
8	Swapan Ghosh	Post-doc	1-2-2000	1-2-2004	Synthesis of nanocomposites
9	Rainer Vollmerhaus	Post-doc	15-5-1999	15-5-2001	Catalytic chain transfer agents
10	Bas Pierik	PhD	1-8-1997	1-8-2001	Catalytic chain transfer agents
11	Mark van den Brink	PhD	Defence	14-3-2000	On-line Raman spectroscopy in e
12	Mascha Cleven	Twaio	1-1-2000	1-1-2001	Reduction of residual monomer (with CO2)

B) Papers published and submitted in 1999:

M. van den Brink, A.M. van Herk, A.L. German
Non-linear regression by visualization of the sum of residuals space applied to the integrated copolymerization equation with errors in all variables.
I Introduction of the model, simulations and design of experiments
Journal of Applied Polymer Science 37, 3793-3803 (1999)

M. van den Brink, W. Smulders, A.M. van Herk, A.L. German
Non-linear regression by visualization of the sum of residuals space applied to the integrated copolymerization equation with errors in all variables.
II Application to the system methyl methacrylate-α-methylene-γ-butyrolactone using on-line Raman spectroscopy
Journal of Applied Polymer Science 37, 3804-3816 (1999)

M. Van den Brink, A.M. van Herk, A.L. German
On-line monitoring and control of the solution polymerization of n-butyl acrylate by Raman Spectroscopy,
Process Control and Quality 11, 265-275 (1999)

M. van den Brink, A.M. van Herk, A.L. German
Emulsion (co)polymerization of Styrene and Butyl Acrylate monitored by On-Line Raman Spectroscopy
Submitted to Makromol. Symp.

M. van den Brink, A. M. van Herk and A.L. German
On-line monitoring and composition control of the emulsion copolymerization of VEOVA 9 and butyl acrylate by Raman spectroscopy,
Submitted to Polymer Reaction Engineering

M. Jung, D. Hubert, A.M. van Herk, A.L. German
The parachute morphology as equilibrium morphology of vesicle-polymer hybrids ?
Submitted to Makromol. Symp.

M. Jung, D.H.W. Hubert, E. van Veldhoven, P. Frederik, A.M. van Herk, A.L. German
Vesicle-Polymer Hybrid architectures 1: A full account of the parachute architecture
Submitted to Langmuir.

M. Jung, D.H.W. Hubert, E. van Veldhoven, P.M. Frederik, M.J. Blandamer, B. Briggs, A.J.W.G. Visser, A.M. van Herk, A.L. German.
Interaction of styrene with DODAB bilayer vesicles morphology and bilayer properties
Submitted to Langmuir

M. Jung, D.H.W. Hubert, P. Bomans, P.M. Frederik, A.M. van Herk, A.L. German
A Topology map for novel vesicle-polymer architectures
Submitted to Advanced Materials

M. Jung, D.H.W. Hubert, P.M. Frederik, H. Fischer, A.M. van Herk, A.L. German
Vesicle-polymer hybrids
Recent Res. Devel. Macromol. Res. 4 137-156 (1999)

A. Aerdts-Vermeylen, A.L.. German, A.M. van Herk, B. Klumperman, J. Kurja
Materials Science and Technology, A comprehensive treatment, Polymer Synthesis, VCH-verlagsgesellschaft mbH 269-319 (1999)

Alex M. van Herk and Anton L. German
Microencapsulated pigments and fillers, contribution to the book 'Microspheres, Microcapsules & Liposomes', vol 1 : Preparation & Chemical Applications, Citus Books, London , ed Prof. R Arshady 457-484 (1999)

F. Geurts, A.M. van Herk, A.L. German

Encapsulation of Aluminium hydroxide,
Submitted to Journal of Microencapsulation

H. Kaczmarek, A. Kamińska, A. van Herk
Photooxidative Degradation of Poly(alkyl methacrylate)s,
Accepted for publication in European Polymer Journal

F.-D. Kuchta, A.M. van Herk, A.L. German.
Propagation kinetics of acrylic and methacrylic acid in water and organic solvents studied by pulsed-laser polymerization
Submitted to Macromolecules

M. Slawinski, M. Schellekens, J. Meuldijk, A.M. van Herk, A.L. German.
Seeded emulsion polymerisation of Styrene. Influence of acrylic acid on the particle growth process
Submitted to J. Appl. Polym. Sci.

M. Slawinski, J. Meuldijk, A.M. van Herk, A.L. German.
Seeded emulsion polymerisation of Styrene. Incorporation of acrylic acid in latex products,
Submitted to J. Appl. Polym. Sci.

A.M. van Herk
Advantages and disadvantages of dispersions,
European Coatings Journal, *11*, 108-110 (1999)

C) Selected abstracts of submitted papers:

Interaction of styrene with DODAB bilayer vesicles. The influence on vesicle morphology and bilayer properties.

Martin Jung

Abstract.

The solubilisation of styrene in large unilamellar DODAB vesicles is investigated at a styrene to DODAB molar ratio of 2:1. The combination of various vesicle characterisation methods allows a simultaneous look at vesicle morphology (cryo-TEM, DLS) and molecular interactions (micro-DSC, various fluorescence techniques) and gives a complete picture of the DODAB vesicles before and after the addition of styrene.

Cryo-TEM and DLS results reveal that the addition of styrene does not break up the DODAB vesicles as an entity, but the peculiar angular DODAB vesicle morphology becomes smoother and the geometries tend to be more curved. The change in morphology is explained by an enhanced bilayer fluidity and the drastic depression of the phase transition temperature as determined from calorimetry and fluorescence experiments. Moreover, micro-DSC scans and fluorescence experiments with two different pyrene probes suggest a non-homogeneous distribution and partial demixing of solute and bilayer for temperatures below ~27°C. Above this temperature, the solute appears uniformly distributed and facilitates molecular motion in the amphiphile aggregate. The diffusion coefficient for the lateral diffusion of an amphiphilic probe is then increased by a factor of two compared to the pure DODAB vesicles.

The observed solubilisation phenomena are rationalised by interactions of the solute with both the hydrocarbon part and the polar headgroup region of the bilayer.

Vesicle-Polymer Hybrid Architectures: A Full Account of the Parachute Architecture

Martin Jung

Abstract.

We have previously reported that polymerisation of styrene in dioctadecyldimethyl-ammonium bromide (DODAB) vesicles leads to so-called parachute-like morphologies where a polymer bead is attached to a vesicle.

To learn the constructive principles of these novel polymer colloids we present here a full characterisation study. The dual nature of these particles, combining intrinsic vesicle features with polymer colloid properties, requires characterisation methods that address both the morphology (cryo-TEM, AFM, DLS) and the typical vesicle characteristics (micro-DSC, fluorescence techniques, surfactant lysis). It is found that the vesicle characteristics after polymerisation are virtually unchanged when compared to the bare vesicles. This observation can be fully accounted for by the putative complete phase separation between polymer and surfactant bilayer matrix. Several methods to release the polymer bead from its parental vesicle are presented.

In a second part we investigate the relation between polymerisation reaction conditions (i.e. temperature, mode of initiation, molecular weight of the polymer) and the resulting vesicle-polymer hybrid morphology. Unexpectedly, slight modifications in the reaction conditions prove to exert great influence on the produced morphology, resulting in novel vesicle-polymer architectures. It turns out, that these variations in morphology are governed by intrinsic vesicle properties.

As a general phenomenon, we find that polymerisation of styrene in DODAB vesicles – independent of process parameters – inevitably leads to micro-phase separation between amphiphilic bilayer matrix and polymer.

Pulsed-Laser Polymerisation in Compartmentalised Liquids 1: Polymerisation in Vesicles.

Martin Jung

Abstract.

Polymerisation in vesicles is a novel type of polymerisation in heterogeneous media, leading to vesicle-polymer hybrid morphologies. We have previously reported that the polymerisation of styrene in dioctadecyldimethylammonium bromide (DODAB) vesicles gives rise to parachute-like morphologies where a small polystyrene bead is linked to each vesicle. To explore the kinetics of vesicle polymerisations and to learn more about the actual locus of polymerisation we applied the pulsed-laser polymerisation (PLP) technique to the polymerisation of styrene in small and large unilamellar DODAB vesicles.

The analysis of the molecular weight distribution (MWD) allows primarily the determination of the monomer concentration at the site of polymerisation if the propagation rate coefficient, k_p, of the applied monomer is known. Relatively high monomer concentrations (between 2.6 and 4.5 mol/L) were found at the locus of polymerisation at low conversions. PLP experiments as a function of overall monomer concentration, temperature and vesicle size gave insight into the monomer partitioning between vesicle and polymerisation site. The local monomer concentration increased with an increasing overall monomer concentration and decreased with higher temperatures. Larger vesicles lead to elevated monomer concentrations. Surprisingly, the measured monomer concentration stays constant up to at least 40% overall conversion.

With respect to the mechanism of polymerisation in vesicles, these observations seem to indicate that polymerisation does not occur in the complete bilayer, but rather in a small polymer nucleus within this layer where high monomer concentrations are encountered. This shift in polymerisation locus from bilayer to particle occurs within the very early stages of the process.

The present study demonstrates that the PLP technique applied to heterogeneous systems can be a powerful tool to access unique information on mechanistic aspects of the polymerisation.

Strategic aspects of the incorporation of acrylic acid in emulsion polymers

PhD thesis of Martine Slawinski, 20-10-1999

Abstract:

The objective of this thesis was improving our knowledge about incorporation of carboxylic monomers in polymers prepared in emulsion. Therefore, the influence of acrylic acid on the course of emulsion copolymerisation has been investigated with styrene as well as with styrene and butadiene. Attention was focused on the amount of carboxylic groups incorporated into the latex products during the process. The pH of the reaction mixture was studied as the main parameter and ab-initio as well as seeded experiments were performed.

The influence of pH on the polymerisation kinetics of carboxylic monomers in water was investigated with Pulsed Laser Polymerisation experiments in combination with Size Exclusion Chromatography on the polymer product modified by esterification of the carboxylic groups. The investigation was carried out with methacrylic acid at different values of the pH and a constant ionic strength. The experiments revealed that the propagation rate constant is high under acidic conditions, *i.e.* pH 2. The propagation rate coefficient decreases strongly on increasing the pH and passes a minimum at pH 7. This behaviour was extrapolated to emulsion polymerisation of styrene with acrylic acid as comonomer. The influence of pH together with the acrylic acid level on the propagation rate constant as well as on the composition of the copolymer formed in the continuous phase during the process was demonstrated

Emulsion polymerisation experiments with styrene or with styrene and butadiene were performed. The use of acrylic acid in polymerisation recipes together with the pH of the reaction mixture had a strong influence on both the nucleation process and the acid incorporation efficiency. Relatively high acrylic acid concentrations as well as a low pH resulted in high latex particle concentrations, and a relatively large fraction of the initially present carboxylic groups was incorporated at the surface of the polymer particles in the final latex products. With both *ab-initio* and seeded experiments it was demonstrated that acrylic acid was preferentially incorporated at the surface of the polymer particles. Incorporation preferentially occurs during the last stage of the reaction at low pH.

Seeded Emulsion Polymerisation of Styrene:
Influence of Acrylic Acid on the Particle Growth Process

Martine Slawinski

ABSTRACT:

The seeded batch emulsion copolymerisation of styrene and acrylic acid has been studied. The polymerisation rate has been investigated with pH as the main parameter. Some attempts have been made to evaluate the average number of growing chains per particle during stage II of the emulsion polymerisation process. The final latex products were characterised by means of conductometric aqueous titration and potentiometric titration in an organic solvent mixture. The distribution of the acid groups over the aqueous phase, the particle surface and the interior of the particles together with the kinetic results provided insight into important features governing the incorporation of acrylic acid. The results indicate that pH is the dominating parameter for the incorporation process. An optimal incorporation on the surface of the particles is observed for a low value of pH. In that case all the acid groups are protonated.

Seeded Emulsion Polymerization of Styrene:
Incorporation of Acrylic Acid in Latex Products

Martine Slawinski

ABSTRACT:

The seeded batch emulsion polymerization of styrene and acrylic acid has been studied. The influence of pH and acrylic acid content on the polymerization rate and the amount of carboxylic acid groups incorporated in the final latex products has been investigated. The distribution of the functional groups over the aqueous phase, the latex particle surface and the interior of the latex particle has been determined by means of aqueous conductometric titration and non-aqueous potentiometric titration at intermediate and complete overall conversions. Combined with kinetic results, the carboxylic acid group distribution history provided valuable information about the process of incorporation of acrylic acid in latex products. Two-step processes in which a shot of acrylic acid has been performed in the last stage of the emulsion polymerization reaction have been investigated as a strategy to increase the surface incorporation efficiency.

Chain-Length Dependent Bimolecular Termination in Free-Radical Polymerization

Thesis John de Kock 26-10-1999

Abstract:

In his thesis John de Kock describes a new method to obtain model-indepentent chain-length dependent free-radical termination coefficients. The method is based on a single-pulse pulsed-laser technique. It is assumed that the radical population after the initiation step is monodisperse. The resulting molecular weight distribution is linearly related to the derivative of the radical concentration versus time. The chain length dependence of the termination reaction can now simply de determined from this number MWD, its integral and the propagation rate coefficient. The data found in this study on several acrylates (MA, EA and BA) have indicated that, when using a simple power law representation for k_t versus chain length according to:

$$k_t^{ii} = C\, i^{-b}$$

the parameter b this simple universal relation changes according to:
b=0.4 for the oligomer chain-length
b=1.1 for chain length from 15 to 30 monomer units
b=0.3 for chain lengths from 50 to 100.

This new method is one of the most powerful techniques available to study the chain-length dependence of termination reactions.