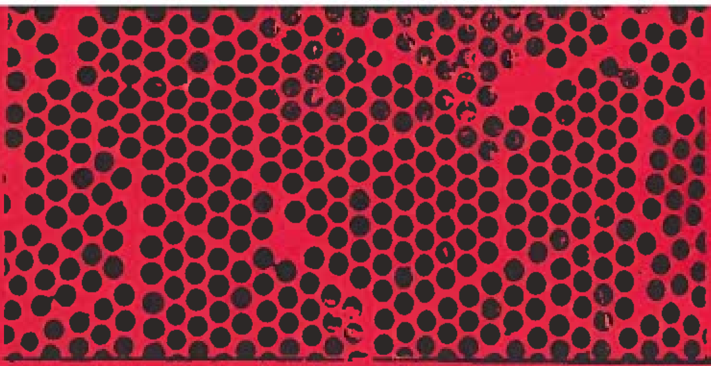


Secretary:
D H Napper
School of Chemistry
University of Sydney
NSW 2006
Australia

IPCG

INTERNATIONAL POLYMER COLLOIDS GROU

DECEMBER 1996

VOLUME 27 NUMBER 2

NEWSLETTER

INDEX

FROM THE EDITOR'S DESK

It is with sadness that I find that I must now step down from being Secretary of the IPCG and Editor of the Newsletter. After almost a decade in the role, which has for me been tremendously rewarding, I find that my changed responsibilities at the University of Sydney preclude me from continuing in these roles. I intend, however, to maintain some research activity in polymer colloids so I hope I will not be drummed out of the Group quite yet! Until the Group can meet at the next Gordon Conference in late June, my colleague, Bob Gilbert has agreed to coordinate the preparation of the next Newsletter.

THE FUTURE OF THE NEWSLETTER

At the next AGM, the IPCG should discuss how best to use modern methods of electronic communication. I know that Gary Poehlein has some interesting ideas on this and Anton German has submitted his contribution to this Newsletter by email. I suppose with the www and home pages, there is a sense in which the Newsletter is obsolete. Yet, given the good response to this edition, members clearly demonstrate that it provides a convenient mechanism for the dissemination of the latest developments in much of Polymer Colloids. The Group will have an interesting discussion of this issue at the Gordon Conference.

Report of the Polymer Colloids Group Meeting 1996

Thanks to Mohammed El-Aasser for the minutes of the IPCG meeting held at the NATO Advanced Study Institute Conference in July 1996 (please see p (ii))

FUTURE MEETINGS

A notice about the 1997 Gordon Research Conference to be held June 29 to 4 July appears on p (iv). Please contact Don Sundberg if you have any queries.

Information about the 7th International Symposium on Advanced Technology of Fine Particles to be held 12 to16 October is included on p (v).

Christian Pichot advises that the Fourth International Conference on Copolymer Latexes in Dispersed Media will be held in Lyon in April 1999. Please make a note in your diaries.

NEXT NEWSLETTER

Please send contributions by air mail or email to me (fo collation by Bob Gilbert) by 1 July 1997

Polymer Colloids Group Meeting
July 3, 1996
Elizondo, Spain

Agenda:
- Attendees
- Review of future meetings
- Additions of new members
- Newsletter

The Polymer Colloids Group met on July 3, 1996, during the NATO Advanced Study Institute Conference. The following people were in attendance:

Jose M. Asua, David R. Bassett, F.M. Candau, J. Delgado (3M), Dieter Distler (BASF), M. S. El-Aasser, Do Ik Lee (Dow), Willem Norde (Wageningen), Shinzo Omi, Christian Pichot, Don Sundberg, Koichi Takamura (BASF), Klaus Taur (Max Planck Institute), Theo van de Ven, Alex van Herk (Eindhoven).

1. The group expressed their thanks to Professor Asua and the local organizing committee for organizing an excellent meeting. Professor Asua is expecting to get all corrected manuscripts from the speakers by no later than September 1, 1996. The expected publication date for the NATO book is early 1997.

2. Future Meetings.

   1997 - The Gordon Conference will be held in New Hampshire during the period of Sunday June 29 - July 4, 1997. Don Sundberg (Chairman) informed the group of the change in format, where the first technical session will be held on Sunday evening after dinner, and there will be no lectures on Friday morning. He requested that the responses to his questionnaire be returned to him as soon as possible.

   1997 - The Yokohama Meeting in Japan is to be held during the period of October 12-16, 1997. Dr. Kawaguchi will send the meeting program to Professor Napper for printing in the next Newsletter. Professor Omi indicated that there is still a need for a few more invited speakers, since Dr. Bassett has decided that he can not participate. Suggestions were made about speakers in the area of Polymer Battery. Delgado promised to check for a speaker at 3M.

   1998 - IUPAC, MACRO 98 in Australia, a symposium on polymer colloids, will be organized during the period of July 13 - 17, 1998. More details will be given in the future by Professors Napper and Gilbert. Delgado (who will be in charge of 3M Corporate Research, in Japan) offered to help in any capacity as needed.

   1999 - A Gordon Conference on polymer colloids is planned with F. Candau as the Chairperson.

2. Future Meetings (continued)

2000 - A symposium on polymer colloids will be held in conjunction with the National Colloids and Surfaces Meeting to held at Lehigh University, Bethlehem, PA during the period of June 14 -17, 2000. More details will be given in the future.

2001 - A Gordon Conference will be held.

2002 - Discussion on organizing a European Gordon Conference (with K. Taur as the Chairman). There was a suggestion by van de Ven to organize it in the year 2000, which is the same year a meeting on polymer colloids will be held at Lehigh. This will be discussed further during the group meeting next year in New Hampshire.

3. Membership.

(I) The following new member was voted in:

Dr. Helmut Zecha
Wacker-Chemie GMBH
Werk Burghausen
P.O.Box 1260
Burghausen, D 84480
Germany
Phone: 8677-83-3705
Fax:: 8677-83-5789

Professor Napper should send him an official letter including the expectations for being an active member.

(ii) The group also indicated interest in getting an updated list of members, perhaps to be included in the next Newsletter.

UNIVERSITY OF NEW HAMPSHIRE

Vice President for Research and Public Service
Thompson Hall
105 Main Street
Durham, New Hampshire 03824-3547
(603) 862-1997
(603) 862-3617 Fax

Gordon Research Conference on Polymer Colloids

June 29 - July 4, 199~~6~~7

Tilton School, Tilton, NH, USA

Donald Sundberg, Chair
Françoise Candau, Vice Chair

Technical Program:
- Particle nucleation, radical capture, polymerization kinetics
- Particle-particle interactions
- Latex particle morphology, film formation
- Biomedical applications
- Microemulsion functionalization, reactive surfactants
- Novel latices

Poster Program: Directed by Françoise Candau
Please contact Françoise to present a poster

Applications for conference attendance can be obtained from Gordon Research Conferences, University of Rhode Island, PO Box 984, West Kingston, RI 02892-0984, USA
Phone (401)783-4011 FAX (401) 783-7644
e-mail app@grcmail.grc.uri.edu

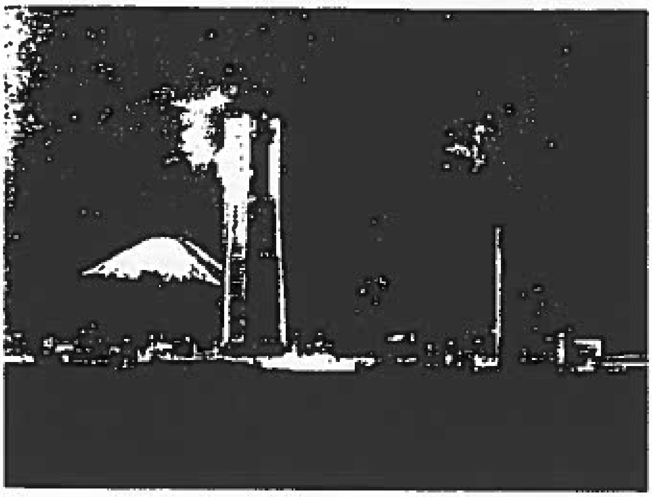
7th
IKETANI
CONFERENCE

INTERNATIONAL SYMPOSIUM ON ADVANCED TECHNOLOGY OF FINE PARTICLES

OCTOBER 12-16, 1997 (SUN - THU)

YOKOHAMA SYMPOSIA,
YOKOHAMA,
JAPAN

First Announcement and Call for Papers



Co-organized by
Polymeric Microsphere Symposium Committee, Japan and
International Polymer Colloids Group

Sponsored by
Iketani Science & Technology Foundation

Topics

Session 1	Polymerization for particle Preparation
Session 2	Design and Characterization of Structured particles
Session 3	Functional Microspheres
Session 4	Colloidal Dispersion Properties
Session 5	Particle-Assemblies and Latex Films and Their Applications

Plenary and invited lectures

Two plenary lectures and about 30 invited lectures will be delivered.

Contributed papers

The program Committee will accept about 20 oral and 100 poster presentations. The type of presentation of each contribution will be decided by the Program Committee considering the author's preference and the number of applications. Fifteen minutes will be allotted to each oral presentation including discussion. Posters will be presented in the early evenings of Oct. 13 and 15. Authors wishing to submit a paper are requested to fill out the attached Application Form and mail it to the Symposium Secretriat by February 28, 1997.

Registration Fees

	Advanced registration before July 22, 1997	Register on-site or after July 23, 1997
Company	50,000 Japanese Yen *	55,000 Yen
University	35,000 Yen	40,000 Yen
Full-time Student	20,000 Yen	20,000 Yen
Family	15,000 Yen	15,000 Yen
Post-Conference Tour	10,000 Yen	10,000 Yen

* From the 3rd person in a company : 35,000 Yen

Important deadlines

Preliminary Registration	February 28, 1997
Application for Paper Presentation	February 28, 1997
Receipt of Manuscripts for the Preprints	July 22, 1997
Registration with Payment	July 22, 1997
Application for Accommodations	July 22, 1997

All correspondence should be addressed to:
Dr.Keiji Fujimoto
Secretariat of 7th Iketani Conference
Dept of Appl. Chem., Keio University
3-14-1 Hiyoshi, Yokohama 223 Japan
Fax: +81-45-562-7625
E-mail: polymer2@applc.keio.ac.jp

CONFERENCE SCHEDULE

CONFERENCE	LOCATION	DATE/CONTACT
	1997	
213 ACS National Meeting	San Francisco	13-17 April
Gordon Conference on Polymer Colloids	Tilton School, NH	29-4 July (Sundberg)
7th Colloid & Surface Science Symposium	Newark, DE	29 June - 2 July
214th ACS National Meeting	Las Vegas	7-11 September
Polymers and Surfactants	North East Wales Institute	8-10 September (RSC meeting)
2nd International Conference on Emulsions	Bordeaux	23-26 September
7th Iketani Conference	Yokohama	12-16 October (Kawaguchi)
	1998	
215th ACS National Meeting	St Louis	29 March- 3 April
37th IUPAC Symposium	Gold Coast, Australia	13-17 July (Gilbert/Napper/El-Aasser)
216th ACS National Meeting	Orlando	23-28 August

EMULSIFIER-FREE FILM-FORMING LATEXES AND THEIR MODIFICATION BY EPOXY-ADDITIVES

T.R.Aslamazova, S.V.Bogdanova
Institute of Physical Chemistry of Russian Academy of Sciences
Leninskij prospect, 31, 117915 Moscow, Russia
Fax 7 095 952 5308

Polymeric binders for coating on metals can be obtained by using emulsifier-free latexes (EFL). The existing concepts and technology related to traditional solvent-based coatings are largely applicable to water-based coatings. Fire hazard and toxicol ogical problems are largely eliminated. Simplicity of application and clean-up as well as lower residual odor in the coating are also appreciated.

Although emulsion paints have been used for more than 20 years, however these coatings are generally not considered suitable for coatings on metal surface. The film formed by the coalescence of latex particles is more porous than the film from a solution type coating. Water suspectible additives such as emulsifier are also detrimental to water resistance and adhesion under humid conditions. While coatings formulated from film-forming emulsifier-free latexes have had fairly good success in coating metals, additional improvement is still desirable. For example, greater water resistance and adhesion are needed.

It is well known that besides of chemical modification the properties of EF latexes as water-borne polymer binders for films and coatings can be improved by colloidal-chemical modification of their composition.

In our work the formulation of an improved water borne coating for metal is carried out by using emulsifier-free microcomposite latex of styrene-butylacrylate-methylmethacrylate-acrylic acid (polymer concentration 40%, glass temperature 19°C) and their epoxy modifiers characterized by different water solubility and ability to crosslink during polymerization and thermotreatment of latex polymer as well as under hardener effect.

As modifiers, epoxy modifiers, such as liquid emulsifiable bisphenol A/F epoxy resin (Araldite PY 340-2 of epoxide index 5.5 Eg/kg and 9,2% water solubiltiy under polymerization conditions, Ciba-Geigy) and glycerol-diepoxide (GDE of epoxide index 27.7Eq/kg and complete water solubility at 40°C, Fluka AG), are used. For formulating cold-curing coating, epoxy modifier PY is mixed with hardener HZ 340 (Ciba-Geigy) whereas GDE is used with and without polyethylenepolyamine (PEPA) as a hardener. The effect of polymer modification by epoxy containing agent in the course of polymerization and its addition in latex formed is compared.

The epoxy-modifiers effect on properties of polymer after its addition in latex formed or in the course of latex synthesis is discribed more detailed in [1, 2]. As an example, the effect of GDE on peel adhesion (A), tensile strength (σ_t), ultimate elongation (ε) and water uptake (α) of thermotrated polymer of latexes modified by modifier addition is given in Table 1.

As followed from Table, the mixing modification of EF latexes can be occured by higher concentration of GDE in the absence of hardener but under hugh temperature effect.

The dependence of polymer properties upon concentration of GDE (C_{GDE}) testifies to their maximum value at the modifier concentration equals to about 25%. In this case peel adhesion of polymer of No.3 is more at about 10 times than of nonmodified polymer of No.1.

Table 1
Effect of GDE on peel adhesion (Al), tensile strength, ultimate elongation and water uptake of latex films and coatings thermotreated

No.exp.	C_{GDE},%	A , g/cm	σ_s , mN/m	ε , %	α , %
1	0	110	14.1	120	66.6
2	11	330	22.0	90	48.7
3	25	1210	23.7	210	65.5
4	43	940	23.6	210	80
5	100	630	17.4	120	198.6

The extremum value of peel adhesion and mechanical properties indicates to the double effect of epoxy-modifier on polymer properties. From one side, the crosslink of its structure increases with increasing concentration of epoxy groups of modifier and as a result increase of peel adhesion and tensile strength values. From the other side, the plasticization effect decreases these value.

The effect of GDE and PY on polymer weight loss in aceton (β) and gel-fraction (GF) of non- and thermotreated polymer of latexes modified by adding the modifier and hardener is given in Table 2.

Table 2
Effect of epoxy modifiers on polymer weight loss in aceton (β) and gel-fraction (GF) of latex films before (1) and after thermotreatment (2)

No.exp.	EM,%	CEM ,%	β,%		β, %	GF,%	β ,%	GF,%
			24 hrs			48 hrs		48hrs
			(1)	(2)		(1)		(2)
1	-	0	100	100	100	0	100	0
2	PY	10	34	22	38	62.2	26	74.3
3	GDE	5	31	29	37	63.2	32	68.0

As followed from Table, the EFL polymer crosslinked under hardener effect at ambient and high temperature are characterized by solvation resistance whereas nonmodified polymer completely dissolves in aceton.

Thus the colloidal-chemical modification of latex polymer is based on forming crosslinking structure and content of epoxy-groups in polymer composition. The mixing modification can be realized in the presence or in the absence of hardener (but under high temperature condition in the latter case) by using the higher concentration of epoxy-modifier than in case of the polymerization modification.

References

1. Aslamazova T. Intern.Conf.on Structural Adhesives in Engineering. UK. 1995, p.239.
2. Aslamazova T. Progress in organic coatings, in press.

INTERNATIONAL POLYMER COLLOIDS GROUP NEWSLETTER

Contribution from the Grupo de Ingeniería Química, Facultad de Ciencias Químicas, Universidad del País Vasco, Apdo. 1072, 20080 San Sebastián, Spain.
Reported by José M. Asua

SYNTHESIS AND CHARACTERIZATION OF FUNCTIONALIZED POLYMER COLLOIDS FOR BIOMEDICAL APPLICATIONS

Rosa Mª. Santos, José Sarobe, Alexander Búcsi, Kari Berte Daasvatn and Jacqueline Forcada

The use of latex particles in biomedical applications, mainly in developing new immunoassays, is of great interest. The latex particles with antibodies or antigens adsorbed on the surface are used as carriers of diagnostic reagents for the clinical evaluation of a great variety of analites. The covalent bonding of protein to the particle surface avoids the later desorption of the protein and keeps the native chemical conformation of the biomolecules, improving the specific character of the test, the reactivity and stability of the immunoassay. With the objective of bonding the amino groups of the biomolecules covalently and in a direct way, without preactivation, a new generation of latex particles with different functional surface groups: Aldehyde, Acetal, Chloromethyl and Macromonomer-acetal, were synthesized. In the different synthesis, monodisperse core-shell type particles were produced by means of a two-step emulsion polymerization in a batch reactor. In the first step, the cores were synthesized by batch homopolymerization of styrene, and in the second step, the shells having the desired co/termonomers which carry the desired functionality, were formed, using the monodisperse seeds of polystyrene obtained in the first step. The latexes were characterized by transmission electron microscopy and potentio-conductimetric titrations, in order to obtain the particle size distributions and the amount of surface groups, respectively. The applicability of the synthesized latexes in immunoassays was demonstrated by covalently coupling anti-CRP IgG antibody to the surface of some of the particles obtained. The latex-protein complexes were immunologically active against the CRP antigen.

EMULSION COPOLYMERIZATION MECHANISM INVOLVING THREE ANIONIC POLYMERIZABLE SURFACTANTS (SURFMERS) WITH STYRENE-BUTYL ACRYLATE-ACRYLIC ACID

Harold A.S. Schoonbrood, Maria J. Unzué, Ole-Jacob Beck, and José M. Asua
Grupo de Ingeniería Química, Departamento de Química Aplicada, Facultad de Ciencias Químicas, Universidad del País Vasco, Apdo. 1072, 20080 San Sebastián, Spain

Amaia Montoya Goñi and David C. Sherrington
Department of Pure and Applied Chemistry, Thomas Graham Building, 295 Cathedral Street, University of Strathclyde, Glasgow G1 1XL, UK

Three anionic polymerizable surfactants (surfmers) - a methacrylic and a crotonic ester and a maleic diester - were investigated with respect to their copolymerization behaviour in emulsion copolymerizations of styrene, butyl acrylate and acrylic acid at high solids contents. The methacrylic ester surfmer appears to be extremely reactive and causes premature coagulation. The crotonic ester surfmer reacts only to a small extent, and is not incorporated well enough into the polymer latex. The maleic diester surfmer appears to have intermediate conversions varying between 50% and 95%. It has been clearly shown that the degree of conversion of this surfmer depends on the particle diameter, with the conversion decreasing significantly at diameters higher than 100 nm. In the case of very high conversion part of the maleic diester surfmer appears to be buried in the latex particles if no special addition strategy for the surfmer is used. It is concluded that "ideal surfmer behaviour" would involve low conversion throughout the semi-continuous reaction with a sharp rise at the end of the feeding period.

EMULSION POLYMERIZATION OF ALKYL SULFOPROPYL MALEATE POLYMERIZABLE SURFACTANTS (SURFMERS) WITH STYRENE

Harold A.S. Schoonbrood, María J. Unzué, Javier I. Amalvy, José M. Asua

The copolymerization of styrene with two polymerizable surfactants (surfmers) based on maleic acid (dodecyl sodium sulfopropyl maleate and tetradecyl sodium sulfopropyl maleate) was studied in batch emulsion polymerizations. The surfmer conversion was obtained by serum replacement with water and subsequent analysis of the recovered, unreacted surfmers with two-phase titration. It was found that both surfmers copolymerized well with styrene, and their partial conversion was higher than that of styrene. These results are contradictory to what was found before in literature using ultrafiltration with methanol, and the differences are explained on the basis of oligomer formation: the oligomers formed are detected if the latices are washed with methanol. It was found that at the end of the polymerization (almost complete conversion of both styrene and surfmer) only 45% of the surfmer groups were present on the particle surface, which is in agreement with a high conversion of the surfmer at the beginning of the reaction.

OPTIMUM SURFMER BEHAVIOR IN EMULSION POLYMERIZATION

Harold A.S. Schoonbrood, José M. Asua

In an attempt to define the conditions for the optimal use of polymerizable surfactants (surfmers), two anionic maleate surfmers were applied in various emulsion copolymerization systems including styrene/butyl acrylate/acrylic acid; vinyl acetate/Veova 10/acrylic acid; vinyl acetate/butyl acrylate/acrylic acid; and methyl methacrylate/butyl acrylate/vinyl acetate. It was found that the reactivity ratios were the most important variable controlling the incorporation of the surfmer into the polymer chains. The surfmer conversion also depended on the particle size: the larger the particle size the lower the surfmer conversion. It was also found that when the surfmer copolymerized well with the monomers attaining high conversions from the beginning of the process onwards, a significant part of the surfmer was buried in the particle interior leading to unstable latexes. On the basis of the results an optimum surfmer behavior is defined. Some preferable combinations of surfmer reactive groups and comonomers in terms of reactivity ratios are suggested. Several strategies are proposed to attain the optimum surfmer behavior, and for some of these strategies experimental examples are given.

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

Reported by **Jaro Barton**

The following papers were published recently :

Polymerization of Acrylamide in Inverse Microemulsions under Special Conditions. J.Barton,Macromol.Symp., 101, 1996, pp.61-70.
Free-Radical Polymerization in Inverse Microemulsions. J.Barton,Progress in Polymer Science, 21, 1996, pp.399-438.
Effect of Polymer Additive on Inverse Microemulsion Polymerization of Acrylamide.J.Barton,M.Stillhammerova,Chem.Papers, 50, 1996, pp.41-44.
Inverse Microemulsion Polymerization of Acrylamide in the Presence of Hexamethylenetetramine.J.Barton,M.Stillhammerova,Macromol.Chem. Phys., 197,1996, pp.1093-1100.
Polymerization of Acrylamide in Inverse Microemulsion in the Presence of Mixtures of Oleophilic and Hydrophilic Surfactants.J.Barton, M.Stillhammerova,Angew.Makromol.Chem.,237, 1996, pp.113-122.
Polymerization of Acrylamide in Single Phase Inverse Dispersion Systems at High Volume Fractions of Disperse Phase.J.Barton,M.Stillhammerova,M.Lezovic,Angew.Makromol.Chem.,237, 1996, pp.99-112.
Effect of Styrene on the Polymerization of Acrylamide in Inverse Microemulsion.J.Barton,V.Juranicova, Macromol.Chem.Phys.,197, 1996, pp.3177-3190.
Microemulsion Polymerization of Butyl Acrylate.1.Effect of Initiator Ty-pe and Temperature.P.Potisk,I.Capek,Europ.Polym.J., 31, 1995, pp.1269-1277.
Emulsion Polymerization of Unsaturated Monomers in the Presence of Inorganic Ultrafine Particles.I.Capek,V.Juranicova,Chem.Papers, 49, 1995, pp.155-161.
Dispersion Polymerization of Styrene and Methyl Methacrylate Initiated by Polyoxyethylene Macromonomeric Azoinitiators.U.Yldiz.B. Hazer,I.Capek,Angew.Makromol.Chem.,231,1995,pp.135-144.
Microemulsion Copolymerization of Butyl Acrylate and Acrylonitrile.I.Capek,V.Juranicova,J.Polym.Sci.,Part A,Polym.Chem., 34, 1996,p. 575.
Polymerization of Butyl Acrylate in Microemulsion.Locus of Initiation.P.Potisk,V.Vaskova,I.Capek,M.Klimova,Angew.Makromol.Chem.,236, 1996 p.43.
Photopolymerization in Butyl Acrylate Microemulsions.1.Postpolymerization.I.Capek,Polym.Internat. 40,1996, p.41.
The Photopolymerization of Butyl Acrylate Microemulsions.The Effect of Reaction Conditions and Additive Fates of Desorbed Radicals.I.Capek, Polym.J.,28,1996

On the emulsion polymerization of vinyl acetate in the presence of poly(vinyl acetate)/polyoxyethylene emulsifier.

Magdy M. H. Ayoub[1] and I. Capek [2]
[1] Department of polymer and pigments, National Research Center, Dokki, Cairo, Egypt.
[2] Polymer Institute, Slovak Academy of Sciences, 842 36 Bratislava, Slovakia

Abstract

The emulsion polymerization of vinyl acetate initiated by a water-soluble initiator (sodium peroxodisulphate, SP) in the presence of nonionic (polyoxyethylene type) emulsifier has been kinetically investigated. The rate of polymerization was found to be proportional to ca the 0.4th power of the emulsifier concentration and to ca the 0.8th power of the initiator concentration. The apparent activation energy was found to be vary from 135 to 38 kJ/mol. The particle size was observed to increase with increasing the initiator concentration a decreases with increasing the emulsifier concentration. The reaction order (N versus [E]) with respect to the emulsifier concentration was found to be 0.1, 2.05 and 0.89 for run 1, 2 and 3, respectively.

Introduction

The area of emulsion polymerization has been the subject of many studies [1]. However, a small amount of work has been devoted to emulsion polymerization of monomers, particularly to systems with various partly - water soluble monomers or to the nonionic emulsifiers of a PEO type. Urquiola et al. [2] reported that the rate of emulsion polymerization of vinyl acetate increases with increasing initiator concentration and the reaction order with to the initiator concentration (the rate of polymerization versus the initiator concentration) is in the range 0.8-1.0. The reaction order close to the 1 was also observed in the dispersion copolymerization of PEO macromonomers [3]. This was attributed to the formation of stable or occluded growing radicals. The bimolecular termination, thus, is restricted. The large reaction order on the emulsifier (PEO type) concentration was observed in the emulsion copolymerization of butyl acrylate [2,4,5]. This was attributed to a certain solubility of emulsifier in the monomer phase. The purpose of this study is to evaluate the effectiveness of polyvinyl acetate-block-methoxypolyoxyethylene copolymer as a nonionic emulsifier in the emulsion polymerization of vinyl acetate.

Experimental

Materials: Vinyl acetate monomer was redistilled and stored at -20 °C before use. Sodium persulfate $Na_2S_2O_8$ and sodium bicarbonate were used as supplied. The nonionic emulsifier (PVAc-b-MPOE block copolymer, where MPEO has $M_n = 2000$) was used [6]. Twice distilled water was used as a polymerization medium

Polymerization procedure: Batch emulsion polymerization of vinyl acetate were carried out at 60 - 70 °C. In all runs the recipe containing 51.75 g water, 11.02 g vinyl acetate and 0.125 g sodium bicarbonate. The initiator and emulsifier concentration varied as shown later. The composition of emulsifier was varied as follows: 35:65, PVAc:PEO, wt%/wt%, run 1, 27:73, run 2 and 19:81, run 3, respectively. All experiments were run with mechanical stirring at 500 rpm. The conversion of monomer was determined by gravimetry. The polymerization technique used has been described in detail elsewhere [3,4]. The particle size and the polydispersity (Dw/Dn) of poly(vinyl acetate) polymer latices were determined by Transmission Electron Microscope.

Results and Discussion

Rate of polymerization

The conversion curves of the emulsion polymerization of vinyl acetate initiated by SP in the presence of nonionic (PEO/PVAc block copolymer) showed a sigmoidal shape typical of a conventional emulsion polymerization [6]. It was observed that with increasing the emulsifier concentration increases the rate of polymerization (in interval 2, 30 - 60% conversion) the final (limiting) conversion (Table 1). However, the interval 1 (up to 25 or 30% conversion) is inversely proportional to the emulsifier concentration. This may be attributed to the competition between the micellar and the homogeneous nucleation. Thus, the results indicate that with decreasing the emulsifier concentration increases both the contribution of the water - phase polymerization (the homogeneous nucleation) and the nucleation time.

Table 1. Variation of kinetic and colloidal parameters of the emulsion polymerization of VAc with the emulsifier concentration [a)].

Run	[emulsifier] g/dm^3	$Rp.10^4$ (mol/l.s)	D_n nm	D_w nm	D_w/D_n	$N.10^{-11}$ /cm^3	$Conv_{lim}$ %	I_{im} min
1	2.02	4.4	98.5	98.5	1	3.45	80	20
	4.03	5.4	95	96.6	1.01	3.5	85	15
	8.05	6	95.9	97.1	1.01	3.7	88	10
2	4.03	9.4	86.8	90.9	1.05	4.5	85	18
	8.05	12	70.3	71.9	1.02	9.3	87	17
	12.08	15	3.37	43.4	1.1	51.2	88	16
3	0.81	6	96.6	92.6	0.96	3.5	85	18
	4.03	11.7	85.6	85.3	0.99	5.3	87	16
	8.05	15	70.3	71.9	1.02	13.6	89	12

a) [Initiator] = 4.03 g/dm^3

The dependence of the rate of polymerization versus the emulsifier composition (PVAc:PEO) is described by a curve with a maximum at the composition 27:73 (wt%/wt%, run 2). The rate of polymerization, thus, increases with increasing the PEO fraction (in the emulsifier molecule) up to ca. 73 wt%. Above this concentration the rate of polymerization is nearly independent of emulsifier composition. Table 1 shows that the rate of polymerization or the PEO fraction of emulsifier parallels the number of particles.

According to the micellar model the relation between the rate of polymerization and the emulsifier concentration can be expressed as follows [7]: $R_p - [E]^{0.6}$

The experimental results listed in Table 1, however, obey the following relationships

$$R_p \sim [E]^{0.33} \text{ (run 1)}, R_p \sim [E]^{0.40} \text{ (run 2) and } R_p \sim [E]^{0.44} \text{ (run 3)}$$

Similar results were observed in the emulsion copolymerization of alkyl acrylate in the presence of PEO type of emulsifier [8]. This deviation from the micellar model may be ascribed to somewhat looser interaction between the emulsifier and the polymer particle surface. The strong hydrophobic interaction between polymer and emulsifier follows the prediction of the micellar model.

The data in Table 2 show that the rate of polymerization and the limiting conversion increase with increasing the initiator concentration. The reaction order x (from R_p versus [initiator]) slightly increases with the increasing the PEO fraction of the emulsifier as follows

$$0.71 \text{ (run 1)} < 0.79 \text{ (run 2)} < 0.87 \text{ (run 3)}$$

Table 2. Variation of kinetic and colloidal parameters of the emulsion polymerization of VAc with the initiator concentration.

Run	[Initiator] g/dm^3	Rp.10^4 (mol/l.s)	D_n nm	D_w nm	D_w/D_n	N.10^{-11} /cm^3	Conv $_{lim}$ %	t_{int} min
1	1.21							100
	2.02	2.1	72.6	79.7	1.09	6.5		80
	4.03	3.4	87.2	88.7	1.02	4.65	80	50
	8.05	6	95.9	97.1	1.01	3.7	88	10
2	0.42						40	80
	0.81						80	50
	2.02	4.2	52.4	52.6	1	19.6	80	25
	4.03	7.1	52.4	60.9	1.16	17.1	86	20
	8.05	12	70.3	71.9	1.02	9.3	86	15
3	2.02	4.6	32.3	35.4	1.09	68.3	70	30
	4.03	7.3	67.5	67.4	0.99	9.2	80	25
	5.64	10	81.2	112	1.4	3.8	85	20

a) [Emulsifier] = 8.03 g/dm^3

The reaction order 0.5 supports the bimolecular termination of growing radicals [9] or the instantaneous termination caused by the entered radical (complete re-entry [10]. This approach was discussed and applied in the emulsion polymerization of acrylates in the presence of PEO type emulsifier [8]. However, the value of x larger than 0.5 results from the contribution of the first radical loss process. Thus, the entanglement of growing radicals, the formation of stable radicals by the chain transfer to emulsifier (PEO segments), and/or the delayed re-entry or complete re-escape of desorbed radicals favour the first order radical loss process [10]. Similar values of reaction order x reported by Urquiola et al [2] and Capek et al. [3].

With increasing the reaction temperature from 60 to 70 °C the limiting conversion strongly decreased as follows: in run1; from 98 to 60% conversion, in run 2; from 90 to 80% conversion and in run 3 from 98 to 50% conversion. The lowest limiting conversions are observed in the emulsifier system with the largest PEO fraction. The gradual decrease in the limiting conversion with temperature may be attributed to the increased solubility of emulsifier in the oil phase, the increased polymerization in water, the thermal disturbance of hydrogen bonds or dehydration of surface hydrophilic EO groups and the temperature range close to the cloud point for PEO emulsifier.

The overall activation energy Ea of the emulsion polymerization of vinyl acetate was calculated to be 135, 56.5 and 38 kJ/mol for the run 1, 2 and 3, respectively. It consists of three contributions

$$E_a = E_p - E_t/2 + E_d/2,$$

the activation energy for propagation (E_p), E_t the activation energy for termination (E_t), and the activation energy for decomposition of initiator (E_d). It is seen that the activation energy strongly decreases with increasing the PEO fraction of the emulsifier. Ea for the homogeneous polymerization is ca. 90 - 100 kJ/mol [11]. However, in the emulsion polymerization of classical monomers the Ea was observed to be much smaller. For example, in the emulsion polymerization of acrylates the Ea was observed in the range 30 - 50 kJ/mol [12]. Similar values were observed in the dispersion copolymerizatiom of PEO macromonomers [13]. These results were discussed in terms of the large activation energy for termination due to the immobilization of growing radicals in the polymer particles.

Colloidal parameters

According to the micellar model the relation between the number of particles and the emulsifier concentration can be expressed as follows: $N \sim [E]^{0.6}$

The experimental results listed in Table 1, however, obey the following relationships

$$N \sim [E]^{0.1} \text{ (run 1)}, N \sim [E]^{2.05} \text{ (run 2) and } N \sim [E]^{0.89} \text{ (run 3)}$$

Similar results were obtained in the emulsion copolymerization of alkyl acrylates in the presence of nonionic (PEO type) emulsifier [11] where the increase in the reaction order was attributed to the higher solubility of emulsifier in the oil phase. Indeed the increase in PEO content in the emulsifier leads to the strong increase of the reaction order. Besides, this trend may results also from the stabilization mechanism [1,2,5].

The data in Table (1) shows that the particle size distribution is very narrow. The polydispersity parameter (Dw/Dn) is very close to 1.0. It is also seen that the particle size distribution is independent of the emulsifier type (the PEO fraction) and concentration and slightly decreases with increasing the initiator concentration. Thus, the decrease of the nucleation period favours the formation of particles with higher monodispersity.

Conclusion

It was reported that he rate of polymerization in the emulsion polymerization of vinyl acetate in the presence of PEO type of initiator increased with increasing the initiator and emulsifier concentration. These data indicate that both the first and second order radical loss processes take part in the termination mechanism. The solubilty of emulsifier in the oil phase is reponsible for deviation of the polymerization behaviour from the micellar model. It is interesting to note that the present emulsifier favours the generation of monodisperse polymer particles.

References

1. J.Barton, I.Capek, Radical Polymerization in Disperse Systems, T.J.Kemp and J.F. Kenedy, Ed., Ellis Horwood.
2. M.B.Urquiola, V.L. Dimonie, E.D. Sudol and M.S.El. Aasser, J. of Polym. Sci., part A Polym. Chem., Vol. 30, 2619-2629 (1992).
3. I.Capek, M.Riza, M.Akashi, Eur.Polym.J. 31, 895 (1995)
4. I.Capek, M.Mlynarova, J.Barton, Makromol. Chem. 189, 341 (1988)
5. Magdy M.H.Ayoub, H.E.Nasr, N.N.Rozik, Polym.International, in press
6. I. Piirma and J.R. Lenzotti, Br. Polym. J. 21 45 (1989).
7. W.V.Smith, R.H.Ewart, J.Chem.Phys. 16, 592 (1948)
8. I.Capek, J.Barton, L.Q.Tuan, V.Svoboda, V.Novotny, Makromol.Chem. 188, 1733 (1987)
9. I.Capek, L.Q.Tuan, Makromol.Chem. 187, 2063 (1986)
10. R.G.Gilbert, D.H.Napper, JMS. Macromol.Chem. Phys. C23, 127 (1983)
11. Polymer Handbook, Eds. J.Brandrup and E.H.Immergut, 3rd edn. Wiley, New York, 1989
12. I.Capek, P.Potisk, Eur.Polym.J. 31, 1269 (1995)
13. M.Riza, I.Capek, A.Kishida, M.Akashi, Angew.Makromol.Chem. 206, 69 (1993)

ICPG Newsletter

Fluorescence Spectroscopy Of Hydrophobically Modified Alkali - Soluble Associative Polymer

R. J. English [a], H. S. Gulati [a], S. A. Kahn [a], R. D. Jenkins [b], and D. R. Bassett [c]
[a] Dept. of Chemical Engineering, North Carolina State University, Raleigh NC 27965-7905
[b] Union Carbide Asia Pacific, Technical Center, #04-01 The Pasteur, Singapore 118227
[c] UCAR Emulsion Systems, 410 Gregson Drive, Cary, NC 27511

A model alkali - soluble associative emulsion polymer latex consisting of methacrylic acid, ethyl acrylate, and ethoxylated macromonomer in the weight ratios of 40 : 40 : 20, respectively, was prepared according to the procedure previously described.[1] Copolymerization yields a material possessing a carboxylated acrylic backbone with a random distribution of ethoxylate side chains, each capped with a complex alkaryl moiety of large molar volume. Hydrophobes of this type impart dramatically improved properties in various associative polymer systems [2]. A forthcoming paper provides the full experimental details regarding fluorescence spectroscopy and rheological properties of this model alkali - soluble associative polymer[3], while previous publications describe the relationship between polymer composition and solution rheology[4].

The existence of both intra- and intermolecular associations in solutions of associative polymers bearing multiple hydrophobic groups is supported from steady state fluorescence spectroscopy employing pyrene as a hydrophobic probe. A typical emission spectrum of pyrene solubilized in a 0.4 g dl^{-1} solution of the HASE polymer is depicted in Figure 1 (inset). The variation in I_1/I_3 as a function of the concentration of the HASE polymer and nonionic surfactant NP-10 is depicted in the main figure. By plotting the molar concentration of hydrophobes as abscissa, a more direct comparison of the two systems is facilitated. The concentration of hydrophobes for the associative polymer were estimated from the stoichiometry of the constituent monomers (i.e., approximately 0.55% macromonomer on a molar basis) and correspond to polymer concentrations between 0.4 and 0.025 g dl^{-1} (c^* estimated from $1/[\eta]$ is approximately 0.2 g dl^{-1}).

An I_1/I_3 value of approximately 1.2 in the presence of the highest concentrations of NP-10 surfactant is typical of pyrene in a relatively hydrophobic environment. As the surfactant concentration is reduced, however, the emission spectrum changes sharply towards that expected for pyrene in an aqueous environment (I_1/I_3 of approximately 1.7). This transition is identified with the existence of a critical micelle concentration. In contrast, the data for the associative polymer reveal a relatively constant I_1/I_3 of approximately 1.25 across the entire concentration range studied. This I_1/I_3 is similar to that of NP-10 surfactant at high concentrations, thereby indicating the presence of hydrophobic domains at all polymer concentrations studied. Note that the value of I_1/I_3 for pyrene in the presence of the associative polymer (~1.25) is somewhat higher than that in a typical alkylaryl hydrocarbon such as toluene ($I_1/I_3 = 1.04$). This is probably indicative of the probe residing in the "core" of the hydrophobic domains, but being influenced by the proximity of the surrounding aqueous phase.

The range of polymer concentrations studied spans the dilute solution regime ($c \ll c^*$) where coil overlap is precluded, and higher concentrations ($c > c^*$), at which rheometrical experiments indicated the establishment of a network. Therefore, the hydrophobic domains formed at the lowest polymer concentrations must involve significant intramolecular associations. Whether the polymer exists as single chains at the lowest concentrations or larger aggregates is impossible to ascertain at this stage. At polymer concentrations exceeding c^* both intra and intermolecular associations are possible.

---

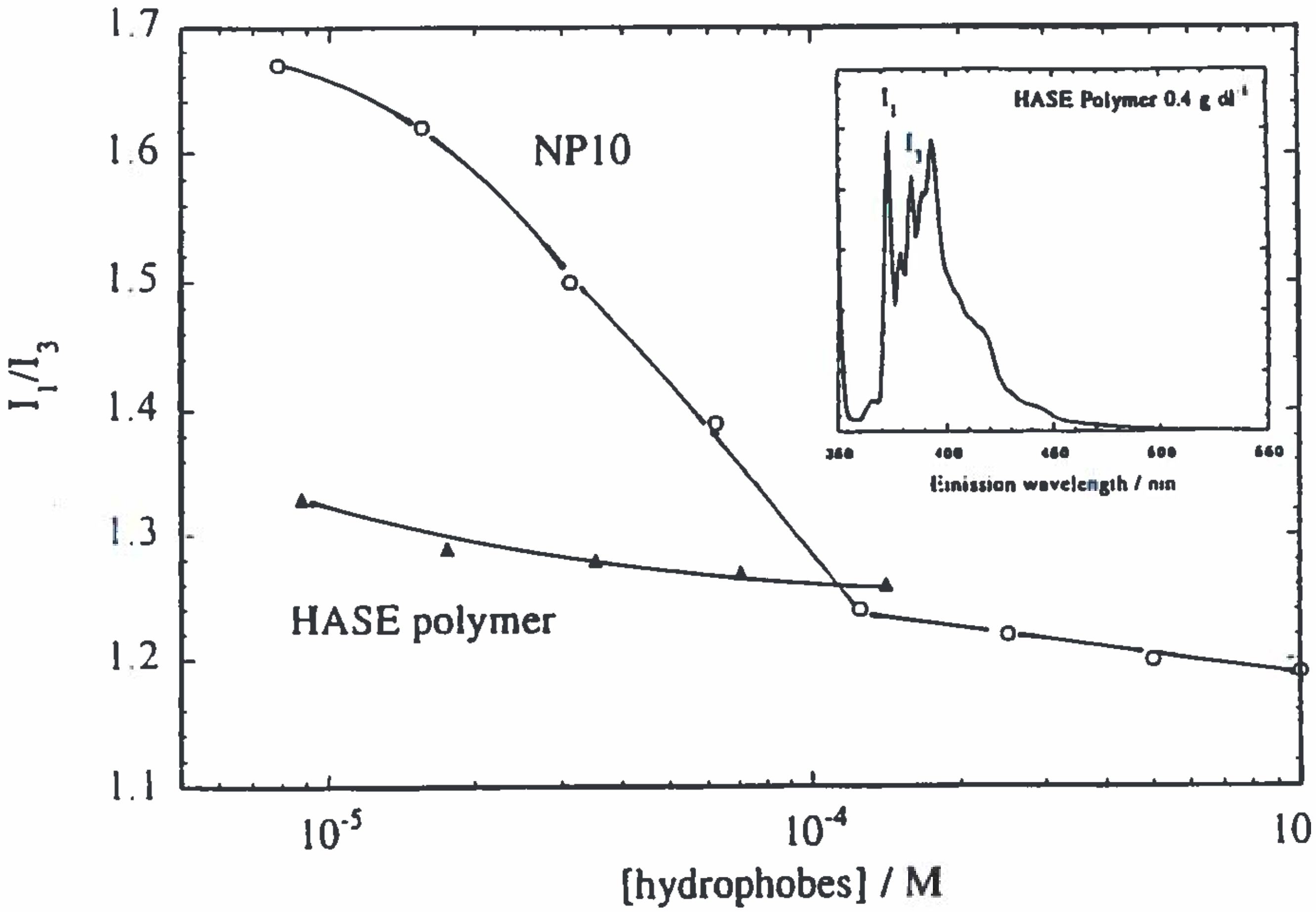
[1] R. D. Jenkins and D. R. Bassett, US Patent 5,292,834.

[2] R. D. Jenkins, B. R. Sinha, and D. R. Bassett, "Associative Polymers with Novel Hydrophobe Structures", Polym. Mat. Sci. Eng. 65 (1991), p. 72.

[3] R. J. English, H. S. Gulati, R. D. Jenkins, and S. A. Kahn, "Solution Rheology of a Hydrophobically Modified Alkali- Soluble Associative Polymer", Journal Of Rheology (1997), accepted.

[4] R. D. Jenkins, L. M. DeLong, and D. R. Bassett, "Influence of Alkali - Soluble Associative Emulsion Polymer Architecture on Rheology", in ACS Advances in Chemistry Series #248, (1995).

Figure 1: Photophysical data illustrating the presence of hydrophobic domains in aqueous solutions of the alkali - soluble associative polymer and comparative data illustrating the behavior of a low molar mass nonionic surfactant (NP-10). (Note that on decreasing polymer concentration, a slight increase in the polarity of the microdomains is apparent. This may be due to changes in the locus of solubilization of the probe, perhaps accompanying changes in the mean aggregation number of the hydrophobes, or from unbound pyrene present in the aqueous phase). Inset: Typical emission spectrum of pyrene probe solubilized in the presence of polymer 0.4 g dl^{-1}, excitation wavelength 340 nm.



POLYMER COLLOID GROUP NEWSLETTER

Contribution from the Institut Charles Sadron
6, rue Boussingault, 67083 Strasbourg Cédex, France.

Reported by Françoise CANDAU

Summaries of progress in several research areas of our Center are presented below.

Synthesis in Microemulsion and Microstructure of Low Charge Density Polyampholytes (S. Neyret, J. Selb, F. Candau)

In our continuing research on water-soluble polymers prepared in heterogeneous media, we have extended the microemulsion polymerization process to the synthesis of low charge density polyampholytes. The samples are terpolymers based on acrylamide (AM), as a neutral monomer, and sodium 2-(acrylamido)-2-methylpropanesulfonate (NaAMPS) and [2-(methacryloyloxy)-ethyl]trimethylammonium chloride (MADQUAT) as charged monomers.

Formulation of monomer-containing microemulsions.

An optimization of the process for the selection of the different components of the microemulsion has been achieved by applying criteria based on the hydrophile-lipophile balance (HLB) and cohesive energy ratio concepts as already discussed for other types of water-soluble monomers. A typical recipe of the microemulsion is the following : Isopar M = 44% ; monomers in variable proportions : 22% ; water : 22% and nonionic surfactants : 12%. The nonionic surfactant mixture is a blend of Arlacel 83 (sesquioleate sorbitan, HLB = 3.7) and G1083 (polyoxyethylene sorbitol hexaoleate, HLB = 10.2). The values of the optimum HLB $(HLB)_{opt}$ of the surfactant blend and of the corresponding amount of surfactants (S_{min}) needed for the formation of microemulsions have been determined for different monomer compositions. The HLB_{opt} values correspond to the minimum of the curves S = f(HLB). An example is given in Fig.1. These values range from 8.4 to 10.1 depending on the monomer composition (Fig.2). In all cases, the amount of surfactants corresponding to the minimum is quite low since it ranges from 7.2 to 9.4, confirming thus the cosurfactant role of the monomer. The high HLB_{opt} values observed are partly due to the electrolyte character of the charged monomers. Addition of a salting-out type electrolyte leads to an optimum HLB value larger than that would be obtained in the absence of salt. The salting-out effect provokes a decrease in the solubility of the ethoxylated surfactant in water. It is therefore necessary to shift the HLB to higher values in order to

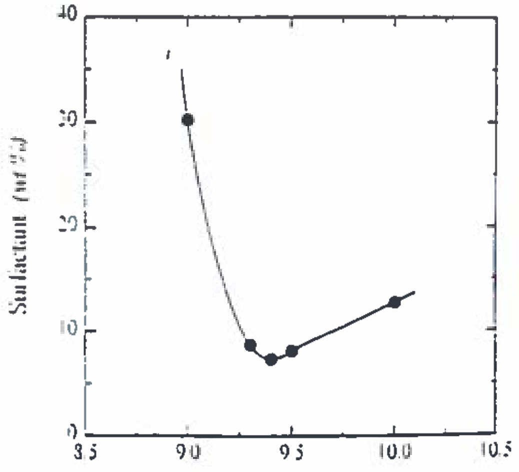


Fig. 1. Surfactant percentage required to produce a microemulsion versus *HLB* for a monomer composition 80/10/10 (mol-% AM/NaAMPS/MADQUAT).

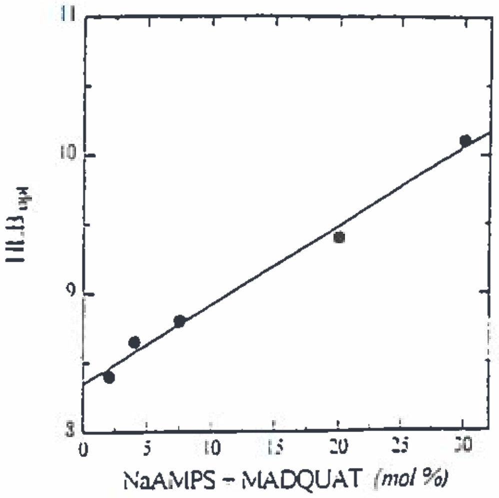


Fig. 2. Variation of the optimum *HLB* versus the molar percentage of NaAMPS and MADQUAT in the monomer blend for systems containing a balanced stoichiometry of these charged monomers.

counterbalance the solubility decrease, for an optimum microemulsification (see Fig.2). These results confirm the generality of the procedure used. Indeed, the CER concept can be applied to any water-soluble monomer (neutral or charged) providing that one takes into account its possible role of cosurfactant and/or electrolyte, since the latter can considerably affect the optimum HLB value.

The free radical polymerization (UV irradiation, 20°C) of the polymerizable microemulsions leads to stable and clear latexes of uniform size (d < 100nm) as determined by quasielastic light scattering.

Terpolymer composition and reactivity ratios.

The variation in copolymer composition with the degree of conversion has been determined for the three following initial monomer feeds (mol-% AM/NaAMPS/MADQUAT) : 70/15/15 ; 39.5/21.3/39.2 ; 33.3/33.3/33.3. An example is reported in Fig.3. The drifts observed with conversion (symbols) are compared to those calculated from the reactivity ratios determined in binary copolymerizations performed in microemulsion (lines). The experimental data were also compared to the values of reactivity ratios determined experimentally in binary solution polymerizations. The disagreement observed between the simulated curves and the experimental data indicates that the reactivity of the monomers in the ternary systems differs from that in the binary systems. The reactivity of the monomers in the terpolymerization seems to be intermediate between that determined in microemulsion binary copolymerizations and in solution binary copolymerizations. These results suggest that the reactivity of the monomers is affected by the ionic strength and therefore depends on the monomer feed composition.

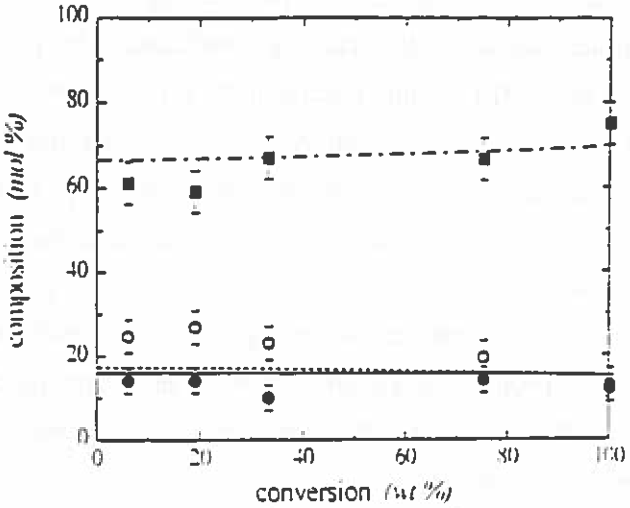


Fig. 3. Terpolymer composition versus conversion for a monomer feed composition 70/15/15 (mol-% AM/NaAMPS/MADQUAT). Experimental data points: AM (■), NaAMPS (●), MADQUAT (O). Calculated curves: AM (—·—·—), NaAMPS (———), MADQUAT (------).

Publications.

S. Neyret, F. Candau, J. Selb.
Synthesis in microemulsion and characterization of low charge density ampholytic terpolymers.
Acta Polymerica, 47, 323 (1996).

F. Candau, J.F. Joanny.
Polyampholytes in "Polymer Materials Encyclopedia".
(J.C. Salamone ed.) 7, pp5476-5488, 1996, CRC Press, Boca Raton.

F. Candau, R. Zana.
Micelle-forming monomers, photopolymerization in "Polymeric Materials Encyclopedia".
(J.C. Salamone ed.) 6, pp4286-4294, 1996, CRC Press, Boca Raton.

Internal Structure of Core-Shell Latex Particles Studied by Fluorescence Nonradiative Energy Transfer (E. Pérez, J. Lang)

The internal structure of core-shell latex particles has been investigated by fluorescence nonradiative energy transfer (NRET). The NRET method has been previously largely used for the study of latex film formation (1-9). This method allows to follow polymer chain migration between adjacent particles in films composed of energy donor-labeled polymer particles and energy acceptor-labeled polymer particles. In the case of core-shell latex particles, an adequat labeling of the core and of the shell of the particles can give information on the extent of mixing between the core and the shell of the particle (10). In order to check for the formation of core-shell particles, latex particles have been synthesized in two-steps emulsion polymerisation under starving conditions. The polymers were based on butyl methacrylate (BMA) and methyl methacrylate (MMA) as monomers. The energy donor monomer was introduced during the first step of the polymerization, and the energy acceptor monomer during the second step. The main purpose of this study was to investigate the extent of core and shell formation after the synthesis. The synthesis were done at 80°C, i.e., above the T_g (34°C) of poly (butyl methacrylate) (PBMA) and below the T_g (110°C) of poly (methyl methacrylate) (PMMA). Energy transfer measurements were done for the core-shell particles in dry film and in dispersion at 10°C. Identical results were obtained in both cases (11). They are the following :

1) The T_g of PBMA is too low, compared to the polymerization temperature, to obtain a separation between the donor and the acceptor-labeled PBMA chains inside the particles. A complete mixing of the core PBMA and of the shell PBMA is observed in this case.

2) The T_g of PMMA is larger than the polymerization temperature, and a separation between energy donor and energy acceptor-labeled PMMA chains is observed with this polymer. The separation has the structure of a diffuse interphase between the two labeled PMMA polymers, i.e., between the core PMMA and the shell PMMA.

3) The study of other particles shows that the fraction of mixing between the core and the shell polymers decreases, as expected, as the incompatibility and the difference in the T_g of the polymers increase.

4) Addition of a cross-linking agent during the first step of the polymerization leads to a decrease of the fraction of mixing between the shell and the core of the particles, even in the case of the PBMA latex particles.

Films as well as dispersions of core-shell latex particles, made of PBMA in the core and of PMMA in the shell, has been annealed at 140°C, i.e., above the T_g of both polymers (11). An increase of phase separation between the core and the shell polymers as the annealing time increases has been observed. This increase is due to the partial incompatibility between PBMA and PMMA. This result indicates that the mixing between PBMA (core) and PMMA (shell) which is observed after the synthesis, is not simply due to the mixing of the two polymers during the synthesis, but rather occurs from the migration of MMA monomers or of small MMA oligomers into the PBMA core during the synthesis of the shell, which then form PMMA chains inside the core. These PMMA polymer chains later phase separate from PBMA upon annealing of the particles at 140°C.

We are presently attempting to modelize the internal structure of the core-shell particles, taking into account the fluorescence decay data, in order to obtain the concentration profile of the donor and acceptor-polymer chains from the center to the surface of the particles.

References.

(1) Pekcan, Ö.; Winnik, M. A.; Croucher, M. D. *Macromolecules* 1990, *23*, 2673.
(2) Zhao, C.-L.; Wang, Y.; Hruska, Z.; Winnik, M. A. *Macromolecules* 1990, *23*, 4082.
(3) Wang, Y.; Zhao, C.-L.; Winnik, M. A. *J. Chem. Phys.* 1991, *95*, 2143.
(4) Wang, Y.; Winnik, M. A. *Macromolecules* 1993, *26*, 3147.
(5) E. M. Boczar, B. C. Dionne, Z. Fu, A. B. Kirk, P. M. Lesko, A. D. Koller, *Macromolecules* 1993, *26*, 5772.
(6) Wang, Y.; Winnik, M. A. *J. Phys. Chem.* 1993, *97*, 2507.
(7) D. Juhué, Y. Wang, and M. A. Winnik, *Makromol. Chem., Rapid Commun.* 1993,*14*, 345.
(8) Juhué, D.; Lang, J. *Macromolecules* 1994, *27*, 695.
(9) Juhué, D.; Lang, J. *Macromolecules* 1995, *28*, 1306.
(10) Winnik, M. A.; Xu, H.; Satguru, R. *Makromol. Chem., Macromol. Symp.* 1993, *70/71*, 107.
(11) Pérez, E.; Lang, J. *Langmuir* 1996, *12*, 3180.

Synthesis and Characterisation of New Structured Latices for Improved Adhesion to Polyester Films

Jean-Yves Charmeau, Joel Richard, G. Lorentz, Louis Vovelle, Yves Holl

The article describes the synthesis in an emulsion polymerisation process of an acrylic copolymer, poly(methyl methacrylate-co-ethyl acrylate) in the presence of a hydrophilic polyester. This polyester has a structure close to poly(ethylene terephthalate) (PET) but is made hydrophilic by sulfonate bearing moieties. It was specially designed as an adhesion promoter of latex films to PET: In water, it forms aggregates with a mean diameter of 20 nm. These aggregates act as seed particles and the synthesis proceeds like an inverted core-shell emulsion polymerisation. The hydrophilic polyester forms the main component of the shell of the final latex particles. The acrylic copolymer is mainly located in the core. Despite of the strong incompatibility between the two polymers, they mix to a certain extent, as clearly shown by the analysis of the mechanical properties of the latex films. This unexpected mixing is due to the synthesis procedure. The acrylic monomers are added slowly and do polymerise as soon as they reach the seed particles, before having time to completely phase separate from the polyester. The knowledge of the particle and latex film structure will be used to interpret adhesion properties of the latex films.

Key words : hydrophilic polyester, emulsion polymerisation, inverted core-shell mechanism, latex film, adhesion, mechanical properties, core-shell structure.

Submitted to Polymer International.

Effects of film structure on mechanical and adhesion properties of latex films

J.Y. Charmeau, R. Berthet, C. Gingreau, E. Kientz, Y. Holl

In order to investigate the effect of the particular structure of latex films on mechanical (stress-strain behavior) and adhesion (measured by peeling) properties, this work compares these characteristics for latex films and corresponding "solution films". Solution films were obtained by dissolving the latex film in an appropriate solvent and forming a new film by evaporating the solvent. In this way, the latex and solution films have exactly the same composition but different structures. Four different systems were studied, namely a homopolymer of 2-ethyl hexyl methacrylate, a copolymer of styrene and butyl acrylate, a copolymer of butyl acrylate with a zwitterionic monomer, and, finally, an ethyl acrylate - methyl methacrylate copolymer partially grafted onto a hydrophilic polyester. It was shown that latex films have Young's moduli systematically higher than the corresponding solution films. This is due to the fact that the hydrophilic shells of the latex particles form a continuous phase in the latex film which increases the modulus thanks to polar interactions. Modeling was possible using an appropriate equation (Palierne's model) which allowed the determination of the modulus and volume fraction of the shell phase, without adjustable parameter. On the other hand, adhesion energy for latex films is always smaller than for solution films. This is interpreted in terms of structure of the film-support interface and dissipative processes within the bulk of the film.

KEY WORDS emulsion and dispersion; latex film; adhesion; destructive testing by peel; mechanical properties of adhesives;

Submitted to International Journal of Adhesion and Adhesives

Langmuir **1996**, *12*, 3675−3681

Formation and Stability of Multilayers of Polyelectrolytes

Nynke G. Hoogeveen, Martien A. Cohen Stuart,* and Gerard J. Fleer

Department of Physical and Colloid Chemistry, Wageningen Agricultural University,
P.O. Box 8038, 6700 EK Wageningen, The Netherlands

Marcel R. Böhmer

Philips Research Laboratories Eindhoven, Prof. Holstlaan 4,
5656 AA Eindhoven, The Netherlands

Received December 20, 1995. In Final Form: April 24, 1996[●]

Sequential addition of anionic and cationic polyelectrolytes may lead to the formation of multilayers at a solid surface. The buildup of such multilayers is characterized by a stepwise increase of the adsorbed amount and layer thickness and by alternating highly positive and highly negative values for the ζ-potential. The prime variables which determine the stability of these structures are the polymer charge and the ionic strength. Very stable multilayers are formed when both polymers are highly charged and when the ionic strength is low. For weakly stable multilayers complexation at the surface may first occur, followed by desorption of the complexes. For strongly charged polyelectrolytes the charge stoichiometry, which is not always 1:1, seems to be unique for each pair of polyelectrolytes; no influence of the substrate, of the pH, or of the ionic strength could be observed.

Introduction

Pairs of oppositely charged polyelectrolytes in aqueous solution are well-known to form complexes.[1] The complexation is mainly due to the attractive electrostatic interaction between the chains. The stability of the complexes therefore depends on the strength of this attraction and, hence, on the polymer charge densities and the ionic strength.

Both stoichiometric and nonstoichiometric complexes can be formed.[2,3] In stoichiometric complexes (complex coacervates[4]) the charges are nearly completely neutralized, so that these aggregates are insoluble and constitute a separate phase. Classical work on this phase separation was carried out by Bungenberg de Jong,[5] and the thermodynamics of these systems was considered by Voorn.[6] Nonstoichiometric complexes,[7] however, remain in solution, stabilized by the uncompensated polymer charge.

The tendency of pairs of oppositely charged polyelectrolytes to form complexes can be used to form multilayers. In the first step of the assembly process a polyelectrolyte (say, cationic) is adsorbed onto a suitable substrate. Then alternately anionic and cationic polymers are supplied. In every step the supplied polymer adsorbs on top of the previously adsorbed layer. Decher and Hong[8−10] showed that all kinds of strongly charged molecules can be combined into ordered multilayers and that this technique can be used to obtain well-defined layers with specific, *e.g.*, optical or electrical, properties.

In most of the studies published so far, the conditions which determine the stability of the multilayers have not been studied systematically. Little is known about the conditions under which stable multilayers can be formed. The aim of this study is therefore to achieve a better understanding of the formation, stability, and stoichiometry of multilayers by measuring the total adsorbed amount, the ζ-potential, and the hydrodynamic layer thickness upon subsequent additions of anionic and cationic polymers.

Materials

As the cationic polymers we used partially quaternized polyvinylimidazole (PVI$^+$), poly((dimethylamino)ethyl methacrylate) (PAMA), and poly-1-methyl-2-vinylpyridinium (PVP$^+$), and as the anionic polymers we used poly(acrylic acid) (PAA), poly(methacrylic acid) (PMA), and polystyrenesulfonate (PSS$^-$). Some of these polyelectrolytes carry a constant charge indicated by the superscript "+" or "−"; the others are pH-dependently charged. The structural formulas of these polymers are given in Figure 1. Some characteristics of the samples are summarized in Table 1. PVI was synthesized and subsequently quaternized by Deratani as described in ref 11. The number of charged groups is given by their degree of quaternization d_q. PAMA was synthesized by Dr. Arnold's group in Halle (Germany) by anionic polymerization as described in ref 12.

The reflectometric measurements were performed on silicon wafers (Aurel GmbH, Germany) bearing a 100 nm thick SiO_2 or a 25 nm thick TiO_2 layer. The ζ-potential and the hydrodynamic layer thickness were measured on monodisperse colloidal silica particles with a radius of 100 nm (Monospher 200 of Merck). All other chemicals were of analytical grade.

Methods

Reflectometry. Adsorption measurements were performed using optical reflectometry combined with a stagnation-point flow-cell.[13] The relative change in the

---

[●] Abstract published in *Advance ACS Abstracts*, June 15, 1996.

(1) Petrak, K. In *Polyelectrolytes: Science and Technology*; Hara, M., Ed.; Marcel Dekker: New York, 1992; p 265.

(2) Tsuchida, E.; Osada, Y.; Sanada, K. *J. Polym. Sci.* **1972**, *10*, 3397.

(3) Koetz, J.; Linow, K. J.; Philipp, B.; Hu, L. P.; Vogl, O. *Polymer* **1986**, *27*, 1574.

(4) van Oss, C. J. *Polym. Prepr.* **1991**, *32*, 598.

(5) Bungenberg de Jong, H. G. In *Colloid Science*; Kruyt, H. R., Ed.; Elsevier Publishing Company: Amsterdam, 1949; Vol. II, Chapters VIII and X.

(6) Voorn, M. J. Ph.D. Thesis, Utrecht University, 1956.

(7) Kabanov, V. A.; Zezin, A. B. *Makromol. Chem., Suppl.* **1984**, *6*, 259.

(8) Decher, G.; Hong, J. D. *Makromol. Chem., Macromol. Symp.* **1991**, *46*, 321.

(9) Decher, G.; Hong, J. D. *Ber. Bunsen-Ges. Phys. Chem.* **1991**, *95*, 1430.

(10) Decher, G.; Hong, J. D.; Schmitt, J. *Thin Solid Films* **1992**, *210/211*, 831.

(11) Böhmer, M. R.; Heesterbeek, W. H. A.; Deratani, A.; Renard, E. *Colloids Surf., A* **1995**, *99*, 53.

(12) Hoogeveen, N. G.; Cohen Stuart, M. A.; Fleer, G. J.; Frank, W.; Arnold, M. *Makromol. Chem.*, in press.

(13) Dijt, J. C.; Cohen Stuart, M. A.; Fleer, G. J. *Adv. Colloid Interface Sci.* **1994**, *50*, 79.

S0743-7463(95)01574-5 CCC: $12.00

International Polymer Colloids Group Newsletter

Contribution from

Professor Joseph M. DeSimone

Department of Chemistry
University of North Carolina at Chapel Hill
Chapel Hill, NC 27599-3290

Our group is currently composed of 18 graduate students and 8 postdoctoral fellows. One of our interests is in the synthesis of tailored amphiphilic (CO_2-philic /CO_2-phobic) block copolymers and the characterization of their self-assemblies in supercritical carbon dioxide. The following abstracts outline some of the research topics currently being pursued by members of our group.

THE SYNTHESIS OF NOVEL SURFACTANTS FOR CO_2-BASED APPLICATIONS.

D. E. Betts, and J. M. DeSimone.

We are currently considering the design and synthesis of several amphiphilic block copolymers composed of a CO_2-philic fluorocarbon block and a CO_2-phobic block being either lipophilic or hydrophilic. These block copolymers will find use primarily as surfactants and viscosity modifiers for CO_2. In addition we propose the design and synthesis of amphiphilic block copolymers in which the aggregation of such a material would be tailored by the density of the CO_2 continuous phase, existing as micelles at lower densities and unimers at higher densities. The density below which micellization occurs and above which unimers exist is termed the critical micelle density (CMD). The synthesis of these amphiphilic materials will be accomplished using either iniferter, atom transfer radical polymerization, or group transfer polymerization techniques.

ATOM TRANSFER RADICAL POLYMERIZATION OF ACRYLATES AND METHACRYLATES. J. C. Anderson, T. Romack, T. Johnson, and J. M. DeSimone.

We are investigating the use of Atom Transfer Radical Polymerization (ATRP) for the synthesis of low polydispersity block copolymers. Several fluorinated and aliphatic vinyl monomers have been determined compatible with ATRP. Block copolymers composed of a CO_2-philic fluorocarbon block and a CO_2-phobic block will find use as CO_2 surfactants and dispersion stabilizers. Currently, the CO_2-phobic material poly(2-ethylhexyl acrylate) is being used in conjunction with the CO_2-philic material poly(1,1-dihydroperfluorooctyl methacrylate) to create such a block copolymer.

CHARACTERIZATION OF SURFACTANTS IN CO_2 J. B. McClain, E. T. Samulski, G. D. Wignall, J. M. DeSimone. Department of Chemistry CB# 3290, University of North Carolina - Chapel Hill, Chapel Hill, NC 27599

Block copolymer amphiphiles which are interfacially active in carbon dioxide have been synthesized and their self assembly has been characterized using small angle neutron scattering. These materials demonstrate the design criteria for molecularly-engineered surfactants which can stabilize and disperse insoluble matter in a CO_2 continuous phase. Hydrophilic-based micelles (comprised of poly(FOA-*g*-PEO)) are capable of dispersing significant amounts of water in CO_2 through hydration of PEO monomer repeat units in the micelle core.[1] Taking advantage of the contrast variations afforded by SANS the degree of aqueous swelling was measured by comparing the scattering curves for dry, H_2O swollen, and D_2O swollen micelles. Poly(1,1-dihydroperfluorooctyl acrylate) - *b* - poly(styrene) copolymers (poly(FOA)-*b*-PS) were found to spontaneously self-assemble into polydisperse core-shell type micelles as a result of the disparate solubility characteristics of the different block segments in CO_2 (i.e. poly(FOA) is soluble while PS is insoluble at molecular weight greater than 400 g/mol). Smaller more polydisperse micelles are observed at higher densities where CO_2 is a better solvent. The effect of density on the association behavior of surfactants in CO_2 is explored which indicates the existence of a critical micelle density (CMD) whereby at a given density self-assembled structures will undergo an aggregate to unimer transition. Poly(FOA)-*b*-PS surfactants were also shown to be capable of emulsifying up to 20 wt% of a CO_2 insoluble hydrocarbon in the micelle core. Swelling of the core proceeded linearly with hydrocarbon oligomer concentration.

HIGH-PRESSURE, HIGH-RESOLUTION NMR ANALYSIS OF POLYMER SOLUTIONS IN SUPERCRITICAL CARBON DIOXIDE. Alexander Dardin, Joseph M. DeSimone, and Edward T. Samulski

High-Pressure, high-Resolution nuclear magnetic resonance spectroscopy has been used to study the solution behavior of poly(1,1-dihydroperfluorooctyl acrylate) (PFOA) and poly(FOA-*b*-styrene) in supercritical carbon dioxide. The proton chemical shift of PFOA as a function of solvent density at constant temperature provides information about medium effects as well as possible van der Waal's or solute-solvent interactions. A transition between two different sets of ^{1}H NMR spectra has been found indicating a distinct change in the polymer coil's environment. Analysis of the signal intensities as a function of increasing CO_2 density imply that at solvent densities of about 0.5 gcm^{-3} the molecular dynamics of the polymer change, followed by a transition to a different state at a CO_2 density of 0.7 gcm^{-3}. The findings are interpreted as a transition of the solvent quality of CO_2 from a poor solvent to a good solvent for PFOA. The chemical shift data suggest that this transition involves dramatic changes in the polymer-solvent interactions which deviate from the CO_2 bulk-effect.

An identical transition can be observed for the PFOA block of the micelle forming poly(FOA-*b*-styrene) copolymer. Here, there is no signal of the polystyrene core observable at low densities resulting from completely immobilized polystyrene segments. Only when the solvent quality of CO_2 is increased at densities above 0.7 gcm^{-3}, polystyrene resonances do become visible indicating an increase in molecular dynamics, i.e. a plasticization of the polystyrene core. Most likely, at low densities the PFOA block is highly collapsed forming a 'cover' around the 'CO_2-phobic' micelle core not allowing CO_2 to penetrate and to plasticize polystyrene.

The following publications have appeared since the previous Newsletter:

Kassis, C. M.; Steehler, J. K.; Betts, D. E.; Guan, Z.; Romack, T. J.; DeSimone, J. M.; Linton, R. W. "XPS Studies of Fluorinated Acrylate Polymers and Block Copolymers with Polystyrene." *Macromolecules* **1996**, *29*, 3081-3089.

Mistelle, C. D.; Thorp, H. H.; DeSimone, M. J. "Ring-Opening Metathesis Polymerizations in Carbon Dioxide." *J. Macromol. Sci., Pure Appl. Chem.*, **1996**, *A33*, 953-960.

International Polymer Colloids Group Newsletter

E.S. Daniels, V.L. Dimonie, M.S. El-Aasser, A. Klein,
O.L. Shaffer, C.A. Silebi, E.D. Sudol, and J.W. Vanderhoff

Emulsion Polymers Institute
Lehigh University, Mountaintop Campus, Iacocca Hall
Bethlehem, Pennsylvania 18015-4732 USA

The titles of our current research projects are given in the **Contents** of our *Graduate Research Progress Reports*, No. 46, July, 1996, which can be found at the end of this report. Abstracts of several recently concluded Ph.D. research programs are included here.

1. Emulsion Polymerization of Styrene Using an Automated Reaction Calorimeter

Luis Varela de la Rosa

The calorimetric technique was applied to study in detail the emulsion polymerization kinetics of styrene using different emulsifier, initiator, and monomer concentrations. This technique provides in an almost continuous way, the heat of reaction which is directly proportional to the rate of polymerization, R_p, providing in this manner details of the process that can not be seen by other techniques.

The classical description of emulsion polymerization states that the process can be divided into three intervals, whose specific features can be found profusely described in the literature, the main characteristic being that, in Interval II, the number of particles, N_p, and R_p are constant, and micelles disappear at the beginning of this interval.

Under the experimental conditions studied, the following observations were made:

- For experiments carried out above the CMC of SLS, the absence of a constant rate period was noted. Instead a relatively long nucleation period was observed after which R_p decreased.
- The R_p curve showed a first change in slope (a decrease) at 5 - 10% conversion, independent of the experimental conditions.
- The end of nucleation and the disappearance of monomer droplets took place at approximately the same conversion (36 - 43%).

The combination of the surface tension of the latex samples as a function of time, with the calorimetric and N_p data, indicates that micellar nucleation dominates up to the first change in slope of R_p, after which the emulsifier concentration drops below the CMC and nucleation takes place mainly by homogeneous nucleation.

Using this information, the emulsion polymerization process was divided into the following manner:

Interval I: R_p and N_p increase; particle formation takes place mainly by micellar nucleation.

Stage II: No constant rate period is observed, N_p still increases; micelles disappear and particle formation is by homogeneous nucleation; nucleation generally ends at the maximum in

R_p, between 36 and 43% conversion.

Interval III: Monomer droplets disappear; R_p and the monomer concentration in the particles decrease.

The changes in slope of the calorimetric R_p curves show that: the first change in slope marks the end of micellar nucleation; the maximum in R_p indicates the end of nucleation and monomer droplet disappearance.

2. Control of Relative Particle Growth in Emulsion Polymerization

Vincenzo Liotta and Christos Georgakis

The feed back control of a discrete representation of emulsion polymerization particle size distribution (PSD) is investigated. The relative particle growth of a bidisperse polystyrene seed is controlled via manipulation of the monomer feed in a custom-built reactor control facility.

The facility is designed and constructed to overcome obstacles which impede the implementation of advanced control methodologies to emulsion polymerizations. It is capable of isothermal conditions, semi-batch operation, creating a suitable mixing and reaction environment, and measuring critical latex characteristics on-line. The on-line sensors include a density meter for near-continuous conversion information and an on-line adaptation of capillary hydrodynamic fractionation (CHDF) for particle size. A distributed-intelligence computer system manages, in real-time, the automation, communication, data acquisition, and control of the facility.

Two dynamic growth models, validated with on-line data from the facility, are developed. A monodisperse model is used to investigate the interesting dynamics which occur in the semi-batch reactor including pseudo-steady states, autoacceleration of the rate, and limiting conversions. A bidisperse model is used to study the suitability of the growth mechanism to influence relative growth via a local stability analysis and a time-varying output controllability analysis. The validation of this model proves that competitive growth experiments provide richer data than monodisperse experiments to distinguish between different radical absorption mechanisms.

A combined state estimator and controller, made up of a parameter adaptive steady state Kalman filter and a nonlinear shrinking horizon model predictive controller, is designed and implemented in the facility to control diameter ratio of the bidisperse system. The estimator estimates the system states, measured variables, controlled variable and two model parameters from frequent density measurements and infrequent particle size measurements. The controller incorporates these estimated states and the adapted parameters to predict the diameter ratio at the end of batch using the nonlinear bidisperse model. Monomer feed rate moves are calculated from an iterative optimization that minimizes deviations from a final diameter ratio set point. The ability of the framework to adequately realize final set points and reject disturbances for several semi-batch emulsion polymerizations is demonstrated.

3. Grafting Reactions in the Emulsion Polymerization of Vinyl Acetate Using Poly(Vinyl Alcohol) as Emulsifier

Guadalupe Magallanes

During the emulsion polymerization of vinyl acetate (VAc) using poly(vinyl alcohol) as stabilizer and potassium persulfate as initiator, the VAc reacts with PVA forming PVA - graft - PVAc. When the grafted polymer reaches a critical size it becomes water-insoluble and precipitates out from the aqueous phase to form polymer particles.

In order to monitor the grafting reactions, a separation method of the PVAc latex components was developed, consisting of the acetonitrile/hot water selective solubilization of the latex (not of the dried latex film). Fourier Transform Infrared (FTIR) spectroscopy and ^1H and ^{13}C Nuclear Magnetic Resonance (NMR) analyses of the isolated components showed that the PVAc homopolymer, linear water-soluble and grafted water-insoluble PVA were isolated. Once the confidence in the separation method was obtained, quantification of the grafted species was carried out by performing a mass balance after each selective solubilization process.

The kinetics behavior and the evolution of the number of particles with conversion were obtained. VAc emulsion polymerizations where the initiator concentration was varied showed that the VAc grafting in the aqueous phase ceased when the locus of polymerization becomes the polymer particles (constant number of particles). The total amount of grafted PVA decreased with the decrease in the initiator concentration, whereas the amount of grafted PVAc was independent of its concentration. The addition of a water-soluble chain transfer agent (CTA) increased the rate of polymerization, while the addition of a water-insoluble CTA did not affect it. Using either CTAs the amount of grafted PVAc was higher only at the initial conversions, while the amount of grafted PVA decreased at all conversions. A decrease in the molecular weight of the PVAc homopolymer and the water-soluble PVA was observed when using either CTAs. When a high molecular weight PVA with similar acetate content but higher degree of blockiness was used, the amounts of grafted PVAc and grafted PVA were lower. By increasing the degree of blockiness the rate of polymerization increases and the nucleation period is extended.

4. Evaluation of Dimethyl Meta-Isopropenyl Benzyl Isocyanate (TMI®) in Emulsion Polymerization

Samiuddin Mohammed

TMI® is a novel bifunctional monomer possessing an unsaturation and an isocyanate group. It can be incorporated into a polymer chain via copolymerization with conventional unsaturated monomers such as styrene, methyl methacrylate (MMA), and n-butyl acrylate (BA), in order to obtain polymers with pendant isocyanate groups. Crosslinking of these polymers can then be carried out through the isocyanate groups.

The performance of TMI as a comonomer in the emulsion terpolymerization with MMA and BA was studied. The isocyanate group of TMI was quite stable towards hydrolysis when the polymerization was carried out at 40°C using redox initiators. High concentrations of TMI were found to retard the polymerization kinetics, and lower the particle size. Several polymerization processes were developed to obtain high conversions at appreciable rates. The locus of the NCO groups in the latex particles could be controlled via seeded polymerization. NCO groups were concentrated at the particle surface by adding all the TMI during the second stage.

The mechanical properties of the TMI latex polymer films were investigated. External catalysts such as triethyl amine, when added prior to film formation, resulted in poor tensile properties as a result of premature crosslinking. When the films were cured after the completion of the film formation process, a significant improvement in the mechanical properties was observed. Tensile strength and modulus of the cured latex films were found to increase with TMI concentration. Latexes with NCO groups at the surface of the polymer particles exhibited the highest tensile strength and modulus. This was attributed to the development of a crosslinked network at the inter-particle boundaries as a result of interfacial crosslinking.

Single-pack latex systems which could be cured at room temperature were obtained by incorporating small amounts of methacrylic acid (MAA) in the TMI latex polymer. MAA acted as a catalyst to accelerate the moisture-curing reaction of the NCO groups at room temperature. These latexes exhibited the excellent shelf-stability of more than one year at room temperature.

5. A ^{13}C NMR Characterization Study of the Core/Shell Latex Particle Interphase and an Investigation of its Role in the Mechanical Behavior of Toughened PMMA

Veera Nelliappan

Toughening of brittle thermoplastics like poly(methyl methacrylate) (PMMA) can be achieved by incorporating particles which consist of radially alternating rubbery and glassy layers into the brittle matrix. Three layered core/shell latexes consisting of poly(divinylbenzene) (PDVB)/poly(butyl acrylate) (PBA)/poly(methyl methacrylate) (PMMA) were developed as toughening particles. The core/shell latex interphases, as well as the particle/matrix interphase have a considerable influence on the overall mechanical properties of the polymer composite. Two-layered PDVB/PBA and PBA/PMMA particles were synthesized for independent characterization and comparison with the three layered toughening particle.

Solid-state NMR was used to characterize the interphase of two layer PDVB/PBA and PBA/PMMA core/shell latex particles through measurement of spin-lattice relaxation times ([H]$T_1\rho$). The PDVB core latex particles were synthesized by miniemulsion polymerization and the stage II butyl acrylate was added semicontinuously. The thickness and the amount of the interfacial PBA has been calculated from the [H]$T_1\rho$ measurements by applying a model which was proposed for compatible blend systems. The thickness of the interphase of PDVB/PBA was calculated to be in the range of 5 to 7 nm.

A PMMA macromonomer was incorporated in the seed PBA latex using a miniemulsion process to compatibilize the seed polymer with the PMMA shell. Results from soap titration experiments and NMR relaxation studies revealed that the PMMA macromonomer predominantly partitions to the surface of the PBA latex. A PMMA shell was added to the uncompatibilized and compatibilized PBA seed latexes. The compatibilized latex had an interphase thickness in the range of 15 to 16 nm compared to the uncompatibilized core/shell latex which had a thickness of 10 to 11 nm.

Tensile and fracture properties of PMMA incorporating two-layer (PBA/PMMA with interphase thicknesses of 5 - 7 nm and 15 - 16 nm) or three-layer (PDVB/PBA/PMMA; PDVB/PBA interphase, 5 - 7 nm, and PBA/PMMA interphase, 15 - 16 nm) particles were compared. The fracture surface was examined with atomic force microscopy and scanning electron microscopy. It was found that composites prepared with three-layer particles had a higher fracture toughness compared to the two-layer particles, while those composites prepared with two-layer particles with a thicker interphase exhibited higher toughness values compared to ones with a thinner interphase thickness.

6. Structured Latex Particles For Modification of Polycarbonate

Rong Maria Hu

This work concentrates on synthesis and characterization of core/shell structured latex particles to be used as toughening agents in polycarbonate (PC). The novel concept of using an interpenetrating polymer network (IPN) particle as a core for both impact and damping controls was introduced.

Two kinds of rubbery cores, pure rubber (polymer A) and IPN rubber (polymer A + polymer B) were synthesized with the particle size ranging from 100 to 400 nm by emulsion polymerization and sequential emulsion polymerization techniques, respectively. The effect of crosslink densities of the polymer A particles on IPN morphology was studied. Different compositions of polymer B (T_g around 10°C) were selected to obtain different IPN morphologies, and consequently, different mechanical properties of the core/shell latex particles. A full coverage of the shell onto the core was synthesized by the semi-continuous emulsion polymerization technique. Different particle morphologies (e.g., IPN, core/shell, separate core/shell, multilayered core/shell, inverted core/shell) were synthesized to study the morphology effect on mechanical and damping properties. The particle size and morphology of structured latex particles were examined by electron microscopy. The glass transition temperatures of these polymers were determined by DSC and DMS. The degree of grafting of the shell polymer onto the core particles was measured by solvent extraction method. The damping properties were analyzed through the integration of both linear loss modulus and linear tan δ vs. temperature curves.

When using polymer A latex particles with high crosslinking density, IPN cores showed big phase separation, while a cellular-type morphology was obtained when using polymer A particles with low crosslinking density. By varying the composition of polymer B, a series of core/shell particles with IPN cores showed two and three glass transitions were synthesized, which could behave differently in toughening. About 80% SAN was grafted onto both P(Bd/S) and IPN cores. The IPN core/shell, separate core/shell, multilayered core/shell, and inverted synthesized core/shell polymers all showed higher damping than pure rubber core/shell polymers. The core/shell particles with IPN cores were the best dampers. It was also found that the inverted synthesized structured latex particles had higher damping property than normal synthesized rubbery core/glassy shell polymers.

EMULSION POLYMERS INSTITUTE
Lehigh University

Graduate Research Progress Reports
No. 46 July 1996

Emulsion Polymerization of Styrene in an Automated Reaction Calorimeter
(L. Varela de la Rosa)

Emulsion Copolymerization of Styrene and n-Butyl Acrylate in an Automated Reaction Calorimeter
(E. Özdeğer)

Towards an Understanding of the Role of Water-Soluble Oligomers in the Emulsion Polymerization of the Styrene/Butadiene/Acrylic Acid Termonomer System (X. Yuan)

Enhanced Droplet Nucleation in Miniemulsion Polymerization—A Kinetic and Mechanistic Study (P.J. Blythe)

Miniemulsion Copolymerization of Vinyl Acetate and Vinyl 2-Ethylhexanoate Monomers (E.L. Kitzmiller)

Copolymerization of Styrene and Butadiene Monomers via Miniemulsion
(D. Li)

Encapsulation of Inorganic Particles via Miniemulsion Polymerization
(B. Erdem)

The Role of the Polymerizable Surfactant Sodium Dodecyl Allyl Sulfosuccinate in the Emulsion Polymerization of Styrene
(J. Chu)

Grafting Reactions in the Emulsion Polymerization of Vinyl Acetate Using Poly(Vinyl Alcohol) as Emulsifier (G. Magallanes)

Grafting Reactions Occurring in the Emulsion Polymerization of Vinyl Acetate Using Poly(Vinyl Alcohol) as Emulsifier (B.M. Budhlall)

In-Situ Infrared Monitoring of Emulsion Polymerization Components
(D. Colombié)

Evaluation of Dimethyl Meta-Isopropenyl Benzyl Isocyanate (TMI®) in Emulsion Polymerization (S. Mohammed)

The Role of Compatibilizing Agents in the Development of Composite Latex Particle Morphology (P. Rajatapiti)

Suprastructured Latex Thermoplastics — A ^{13}C NMR Characterization Study (V. Nelliappan)

Structured Latex Particles for Modification of Polycarbonate
(R. Hu)

Micron-Size Structured Particles Via Dispersion Polymerization
(D. Wang)

Electrokinetic Lift Effects Associated with the Transport of Latex Particles in Capillary Hydrodynamic Fractionation (CHDF) (A.D. Hollingsworth)

Telechelic Polybutadiene: Synthesis, Characterization, and Crosslinking in Latex Films (J. Xu)

The Effect of Crosslinking on Latex Film Formation
(H. Mohd. Ghazaly)

Contribution to the International Polymer Colloids Group Newsletter

---

Alice P. Gast

Department of Chemical Engineering
Stanford University
Stanford, CA 94305-5025

The Gast research group is made up of seven Ph.D. students. Joanne Promislow, Eric Furst, Dean Wang, and Albert Lee are advised by Alice P. Gast, Mike Yatcilla and Szu-Wen Wang are jointly advised by Alice P. Gast and Channing R. Robertson, and Patrick Doyle is jointly advised by Alice Gast and Eric S. G. Shaqfeh. We are interested in the study of colloids and macromolecules, and the following pages contain abstracts from three recent research projects from members of the group.

STOCHASTIC SIMULATION OF THE RHEOLOGY OF FLEXIBLE, TETHERED CHAINS

Patrick S. Doyle, Eric S.G. Shaqfeh and Alice P. Gast

Department of Chemical Engineering, Stanford University, Stanford, California 94305

Abstract

As manufacturing and materials processing continue to emphasize reduction in product dimension, e.g. micromanufacturing and micromachining, the rheology of grafted or tethered films which are monomolecular in thickness has become of increasing concern. These tethered polymer layers modify the physical properties of the surface and have dramatically different behavior than free polymer films. Understanding these layers and the effective boundary conditions which can be applied to a bulk continuum when interacting with these films, requires knowledge of *molecular scale physics.* This includes how the polymers interact with a given external phase and their collective dynamics.

To understand these issues, we have developed a robust Brownian dynamics simulation for the shearing of tethered polymers which includes a self-consistent velocity profile in the tethered layer. The nonlocal rheology is formulated starting with a many-bead/rod model for a polymer with intra- and interpolymer interactions including excluded volume, hydrodynamic, Brownian and connectivity forces. With this formulation we then proceed with full simulations of dilute and semi-dilute polymer solutions tethered to a solid interface, *i.e.* polymer brushes. The formulation includes the correct ensemble-averaged equation for the mixture and thus the mean flow is solved self-consistently with the Brownian dynamics simulations. We examine both steady and oscillatory shear flow of confined polymer brushes. We find that under steady flow, the brushes are shear thinning in both normal forces and effective shear viscosity. During oscillatory flow, extreme shear thickening occurs when the ratio of the Weissenberg number to the dimensionless flow frequency $Wi/\omega \approx 3$. *Shear-induced diffusion* is shown to create this thickening. We find that the onset of shear thickening occurs when we are resonating with the collision rate of the beads which we predict using scaling arguments.

INVESTIGATION OF 2-DIMENSIONAL CRYSTALLIZATION OF STREPTAVIDIN AND CHOLERA TOXIN B

Szu-Wen Wang, Michael Yatcilla, Alice Gast, Roger Kornberg, and Channing Robertson

Department of Chemical Engineering, Department of Structural Biology
Stanford University, Stanford, California 94305

Abstract

Two-dimensional (2-D) protein crystallization has been employed to successfully determine 3-dimensional (3-D) structures of complex proteins that previously were not amenable to 3-D crystallization. Understanding the fundamental physical factors of 2-D crystallization can help one to grow higher fidelity crystals and solve the structures of proteins that have been difficult to obtain, which in turn can give insight into the biochemical mechanism of the protein. In addition, fundamental knowledge of protein ordering on surfaces is relevant to the relatively new and growing field of biosensors, especially for use in medical diagnosis devices. This project aims to gain a better understanding of how proteins and other biological macromolecules align themselves on an air-water interface, what the relevant factors and forces are, and other fundamental physical questions related to proteins in ordered arrays on surfaces.

Extensive work has been performed on the protein system streptavidin. Biotinylated lipids are spread in a monolayer on aqueous buffer, at an air-water interface. Streptavidin molecules are then injected into the aqueous solution. Lateral diffusion of proteins bound in the monolayer then allows the proteins to arrange themselves in an ordered array, creating 2-D crystals with distinct morphologies. The macroscopic morphology can be observed with a fluorescence microscope, while the lattice arrangement and individual proteins can be seen using transmission electron microscopy.

Distinct macroscopic morphologies have been observed with streptavidin crystals. Under conditions of pH > 6.0, dendritic X-shaped crystals are formed and give to C222 symmetry [Darst, et al., *Biophys. J.*, **59**, 387 (1991)]. When pH is lowered to 5.3-5.5, inverse S-shaped chiral morphologies are seen. Needle-like crystals observed at higher acidic conditions (pH < 5.0) correspond to reported P1 symmetry [Hemming, et al., *J. Mol. Biol.*, **246**, 308 (1995)]. Current work focuses on formation of the chiral structures at the intermediate pH range.

Future work includes investigating the effects of a homologous toxin protein impurity on cholera toxin subunit B, identifying the important molecular interactions for crystal growth, and using this information to model the dynamics of observed growth.

DENSITY FUNCTIONAL THEORIES OF CRYSTALLIZATION

Dean C. Wang and Alice P. Gast

Department of Chemical Engineering, Stanford University, Stanford, California 94305

Abstract

A fundamental understanding of the crystallization process is both of theoretical importance and also provides applications in such diverse areas as the fabrication of large crystals from the melt, the study of order-disorder transitions found in in colloidal systems, and the analysis of interactions in proteins which detemine their crystalline morphologies. We study the crystallization process via density functional theory (DFT).

The basic idea of DFT is that the structural and thermodynamic properties of the solid can be extrapolated from those of the equilibrium liquid. Following the weighted density approximation (WDA) formalism of Curtin and Ashcroft [Curtin and Ashcroft, *Phys. Rev. A* **32**, 2909 (1985)], we treat the solid as a liquid at a weighted, or coarse-grained, density. A less computationally intensive, and hence much more widely used, form of the WDA is the modified weighted density approximation (MWDA) of Denton and Ashcroft [Denton and Ashcroft, *Phys. Rev. A* **39**, 4701 (1989)].

The structural and thermodynamic properties of the liquid used as inputs in calculating the equilibrium solid properties are obtained via the Ornstein-Zernicke integral equation and its numerous closures. Closures we employ include the Martynov-Sarkisov closure [Martynov and Sarkisov, *Mol. Phys.* **49**, 1495 (1983)] and the Perturbative Hypernetted Chain (PHNC) integral equation closure [Kang and Ree, *J. Chem. Phys.* **103**, 3629 (1995)].

We model the liquid state as pairwise additive particles interacting through model potentials. Currently, hard sphere, power law (inverse nth power), and Lennard-Jones fluids are being studied. We also hope to study the Yukawa fluid, which is known to well describe many colloidal systems. While numerous researchers have determined that the hard sphere fluid yields excellent results under the WDA and MWDA when compared with computer simulation data for crystallization, softer potetnials or potentials with attractions fare more poorly. Hence, we wish to reformulate the WDA or MWDA so that it predicts more accurately the crystallization process for the model potentials under consideration.

Date: Thu, 05 Dec 1996 15:37:21 +0000
From: HELLY HEIJDEN VAN DER <helly@chem.tue.nl>
To: d.napper@chem.usyd.edu.au
Subject: IPCG contribution

** Proprietary **

This is the contribution of the Eindhoven group for the next IPCG Newsletter.
Could you please send a notification concerning receipt of this text?

ADVANCES IN CONTROLLING EMULSION (CO)POLYMERIZATION)

Anton L. German, Alex M. van Herk, and Bert Klumperman,
Laboratory of Polymer Chemistry, Eindhoven University of Technology,
P.O. Box 513, 5600 MB Eindhoven, The Netherlands

Introduction:

Polymerization in heterogeneous systems and dispersion polymers receive considerable and still increasing attention. It is obvious that environmental requirements lead to a strongly enhanced interest in solvent-free polymerization processes and solvent-free application of polymer products, for example waterborne paints and coatings. From the scientific point of view it is envisaged that polymerization in heterogeneous systems will offer unique opportunities of controlling heterogeneity, on (inter/intra)molecular scale as well as on dispersed particle (submicron/micron) scale. Therefore, we focus on studying a number of intrinsic possibilities offered by emulsion polymerization, including the pertaining kinetics.
In this presentation three important developments in emulsion polymerization will be highlighted, viz.: (1) compositional control in emulsion copolymerization, (2) vesicle bilayer polymerization, and (3) pulsed electron beam polymerization in latex particles.

Summary:

(1) Compositional Control in Emulsion Copolymerization

In general, the monomers used in copolymerization will possess different water solubilities. As a consequence, the monomer feed ratio in the latex particles will be different from the overall monomer feed ratio, and also depend on the monomer/water ratio (M/W).
When compared with copolymerization in homogeneous systems, this leads to a unique situation where the extent of composition drift and the occurrence of (pseudo)azeotropy, do not solely depend on the monomer reactivity ratios, but also on the (in principle adjustable) parameter M/W. Some emulsion copolymerization systems showing these features have been investigated1,2,3.
Although the effect of the molar mass distribution on the properties of polymer products is well recognized, the sometimes dramatic effects of the chemical composition distribution are certainly not, and are often neglected for convenience. It will be shown that emulsion copolymers of

styrene and methyl acrylate with the same average chemical composition but with different compositional distributions exhibit dramatic differences in mechanical properties, like fracture toughness, elongation at break and E-modulus4. Through better understanding of the kinetics and of the thermodynamic aspects of emulsion copolymerization it has become possible to control the composition drift and to prepare emulsion copolymers with either a narrow chemical composition distribution or a predefined compositional heterogeneity4,5.

(2) Vesicle Bilayer Polymerization

In emulsion polymerization systems the main focus has been on the micellar organization of surfactant molecules, whereas surprisingly enough vesicular structures received little or no attention. However, polymerization in vesicle bilayers in principle offers the possibility of preparing hollow latex particles, which have many challenging applications, for instance in controlled drug release systems6.

Typically twin-tailed surfactants like DODAB are being used to prepare a vesicle solution by sonication or extrusion. Under carefully controlled conditions, the vesicles can be swollen with monomer(s) till saturation. Next a conventional free radical initiator is added, leading to polymerization within the bilayer7,8. The resulting polymerized vesicles (av. diameter ca. 30 nm) are stable and contain high molar mass polymer (e.g. for polystyrene Mw=300,000).

It also has been shown8 that inorganic particles can be encapsulated selectively by the use of bilayer forming surfactants. The encapsulation procedure comprises bilayer adsorption, bilayer swelling and bilayer polymerization.

Depending on the reaction temperature vesicle bilayer polymerization takes place in an ordered liquid crystalline phase (below the phase transition temperature) or in a more disordered fluid phase (above the phase transition temperature). It is expected that these structural features will be reflected in the polymerization kinetics. Therefore, Pulsed Laser Polymerization (PLP) experiments are being performed to get more insight in the kinetics. First results indeed indicate a kinetic behaviour depending on temperature and vesicle size.

(3) Pulsed Electron Beam Polymerization in Latex Particles

In order to understand the kinetics and mechanism of emulsion polymerization, knowledge of the propagation rate coefficient (kp) and the local monomer concentration is of paramount importance. Several methods of obtaining kp have been reported and one of the more reliable techniques is Pulsed Laser Polymerization (PLP)9. In PLP radicals are generated through a photoinitiator, activated by a laser pulse. The time between pulses determines the growing time of a major number of chains because biradical termination mainly occurs just after the radical concentration has been increased through the subsequent laser pulses. Although PLP has been successfully used in (transparent) microemulsions10, in non-transparent systems, like in regular latexes, PLP is of limited use11,12.

This has led to an investigation13 into the possibilities of using high energy electrons, generated by a pulsed 3 MeV Van de Graaff accelerator as a source of initiating radicals. The 3 MeV electrons have a penetration depth of typically 1 cm in water without loss of intensity and independent of optical transparency.

The length of the chains terminated by laser light (PLP) or electron beam (PEBP) induced small radicals is given by the simple equation14:

$$LO,i = i * kp * [M] * t0 \qquad (1)$$

where: LO,i is the chain length (in monomeric units) of the polymer formed in the time between two pulses (can be obtained from the GPC trace), kp = the propagation rate coefficient, [M] the monomer concentration at the site of polymerization, t0 the time between two successive pulses, and i=1,2,3,.. . Once the value of kp is known, eq. 1 also can be used to obtain the monomer concentrations in microemulsion droplets or in latex particles12. The polymerization of styrene in latex particles has been studied by PEBP in order to obtain the monomer concentration in the particles13. Calculations show that the main source of initiating radicals is the aqueous phase13. In polystyrene latex particles with a diameter of 46 nm the monomer concentration was found to be 5.8 " 0.3 mol/dm3. The same value was found when using conventional methods (e.g. GLC), confirming that the kp-values obtained in homogeneous PLP (or PEBP) experiments are indeed valid in emulsion systems.

The PEBP method is similar to the previously introduced12 PLP method of obtaining monomer concentrations in the reacting latex particles. The PEBP method, however, is more flexible and opens the possibility of production on a larger scale of polymers with a specific molecular mass distribution.

References

1. G.H.J. van Doremaele, A.M. van Herk and A.L. German, Macromol. Symp, 35/36 (1990) 231
2. L.F.J. No#l, J.M.A.M. van Zon and A.L. German, J. Appl. Polym. Sci., 51 (1994) 2073
3. L.F.J. No#l, J.L. van Altveer, M.D.F. Timmermans and A.L. German, J. Polym. Sci., Part A: Polym. Chem., 32 (1994) 2223
4. H.A.S. Schoonbrood, H.M.G. Brouns, H.A. Thijssen, A.M. van Herk and A.L. German, Makromol. Symp., 92 (1995) 133
5. H.A.S. Schoonbrood, R.C.P.M. van Eijnatten, B. van den Reijen, A.M. van Herk and A.L. German, J. Polm. Sci., Polym. Chem. Ed., 34 (1996) 935
6. C.A. Finch, in 'Encapsulation and Controlled Release', edited by D.R. Karsa and R.A. Stephenson, Royal Society of Chemistry, Cambridge, 1-12 (1993)
7. J. Kurja, R.J.M. Nolte, I.A. Maxwell and A.L. German, Polymer, 34 (1993) 2045
8. H.F. Zirkzee, G.H. Rietjens, J. Kurja, A.L. German, P. Frederiks and M.C.A. Stuart, Submitted to Macromolecules, 1995
9. M. Buback, L.H. Garcia-Rubio, R.G. Gilbert, D.H. Napper, J. Guillot, A.E. Hamielec, D. Hill, K.F. O'Driscoll, O.F. Olaj, Jiarong Shen, D. Solomon, G. Moad, M. Stickler, M. Tirell and M.A. Winnik, J. Polym. Sci., Part C: Polym. Lett. Ed., 26 (1988) 293
10. S. Holdcraft and J.E. Guillet, J. Polm. Sci., Part A: Polym. Chem., 28

(1990) 1823
11. B. Manders, A.M. van Herk, A.L. German, J. Sarnecki, R. Schom@cker and J. Schweer, Makromol. Chem., Rapid Commun., 14 (1993) 693
12. J. Schweer, A.M. van Herk, R.J. Pijpers, B.G. Manders, and A.L. German, Makromol. Chem., Makromol. Symp., 92 (1995) 31
A.M. van Herk, H. de Brouwer, B.G. Manders, L.H. Luthjens, M.L. Hom and A. Hummel, Macromolecules, 29 (1996) 1027
O.F. Olaj, I. Bitai and F. Hinkelmann, Makromol. Chem., 188 (1987) 1689

Contribution to the IPCG Newsletter from

A. L. German
Eindhoven University of Technology,
Department of Polymer Chemistry and Technology
P.O.Box 513, 5600 MB Eindhoven, The Netherlands
tel. +31 40 2473600/fax. +31 40 2463966/e-mail: tgtkag@chem.tue.nl

LOCAL MONOMER CONCENTRATIONS IN EMULSION POLYMERIZATION

Anton L. German, Bart G Manders, Hennie F. Zirkzee, Bert Klumperman and Alex M. van Herk

Abstract: Knowledge of local monomer concentrations in the case of heterogeneous polymerizations is extremely important, since these local concentrations determine the kinetics of the reactions. In this paper two techniques to determine the local concentrations are reported. The first technique makes use of the well known pulsed initiation method, which is frequently used nowadays for the experimental determination of the propagation rate constant (kp). The second technique is applied for the determination of monomer concentrations in vesicle bilayer structures.

Molecular Mass Control in Methacrylic Copolymer Latexes Containing Glycidyl Methacrylate)

J.M.#Geurts, P.E Jacobs, J.G. Muijs, J.J.G.S. van Es, and A.L. German J. Appl. Polym. Sci. 1996, 61,
9-19.

Results are presented on the preparation and characterization of batch emulsion copolymers of butyl methacrylate and glycidyl methacrylate (GMA). The two main problems occurring during an emulsion copolymerization with GMA are partial hydrolysis of the epoxy groups and internal crosslinking of the latex particles formed. The influence of chain transfer agents (CTA) on the degree of crosslinking was investigated. Furthermore, the effect of reaction temperature and the addition of methacrylic acid on the sol/gel content of the polymer formed and on the rate of epoxy hydrolysis were investigated. It was found that lowering the reaction temperature did not increase the sol content; however, it significantly decreased the extent of hydrolysis. The addition

of a CTA (especially CBr4) increased the sol content of the polymer, and good control over the molecular mass was achieved. The addition of methacrylic acid showed that this monomer can be used without any compli#cations with respect to the control of the sol content of the polymer formed.

Contribution to the IPCG Newsletter from
the Sydney University Polymer Centre
Reporter: Bob Gilbert
Chemistry School, Sydney University, NSW 2006, Australia.

The following abstracts from various members of the SUPC summarize current research directions.

ESR Detection of Species in the Free-radical Polymerisation of Styrene. MP Tonge, A Kajiwara, M Kamachi, RG Gilbert. Polymer, submitted.

> Very high-resolution electron spin resonance (ESR) studies of the bulk free-radical polymerisation of styrene showed several species in addition to the poly(styryl) propagating radical. Such species have an unknown effect on the kinetics of the polymerisation process, and are unlikely to be detectable by other experimental techniques. The general implications for free-radical polymerisations are discussed, including possible actions as chain transfer agents and effect on measurements of the propagation rate coefficient by pulsed-laser polymerisation, as well as the experimental conditions so as to avoid the formation of these species.

Critically evaluated rate coefficients for free-radical polymerization, 2. Propagation rate coefficients for methyl methacrylate. Sabine Beuermann, M Buback, TP. Davis, RG Gilbert, RA Hutchinson, OF Olaj, GT Russell, J Schweer, AM van Herk. Macromol. Chem. Phys., submitted.

> Pulsed-laser polymerization (PLP) in conjunction with molar mass distribution (MMD) measurement is the method of choice for determining the propagation rate coefficient k_p in free-radical polymerizations. The authors, members of the IUPAC Working Party on *Modeling of kinetics and processes of polymerization*, collate results from using PLP-MMD to determine k_p as a function of temperature T for bulk free-radical polymerization of methyl methacrylate at low conversions and ambient pressure. Despite coming from several different laboratories, the values of k_p are in excellent agreement and obey consistency checks. These values are therefore recommended as constituting a benchmark data set, one that is best fitted by
>
> $$k_p = 10^{6.427}\ \mathrm{L{\cdot}mol^{-1}{\cdot}s^{-1}}\ \exp\left(\frac{-22{,}36\ \mathrm{kJ{\cdot}mol^{-1}}}{R{\cdot}T}\right)$$
>
> The 95% joint confidence interval for these Arrhenius parameters is also given. In so doing, we describe the most appropriate statistical methods for fitting $k_p(T)$ data and then obtaining a joint confidence interval for the fitted Arrhenius parameters. As well, we outline factors which impose slight limitations on the accuracy of the PLP-MMD technique for determining k_p, factors which may apply even when this technique is functioning well. At the same time we discuss how such systematic errors in k_p can be minimized.

Propagation rate coefficient of vinyl neo-decanoate by pulsed laser polymerization. R. Balic, R.G. Gilbert, M.D. Zammit, T.P. Davis and C.M. Miller, Macromolecules, in press (MA961384+).

> The propagation rate coefficient (k_p) for vinyl *neo*-decanoate has been measured by pulsed-laser polymerization (PLP) over the range –21 to +21 °C. The Mark-Houwink-Sakaruda constants required for GPC analysis were obtained using size-exclusion chromatography with an on-line viscosity detector. The data, which satisfy various

consistency tests for PLP (invariance of k_p to laser pulse frequency, etc.), fit the relation k_p (dm^3 mol^{-1} s^{-1}) = $10^{7.45}$ exp(−22.5 kJ mol^{-1}/RT); the joint confidence region for these Arrhenius parameters is also given. These Arrhenius parameters are similar to those for vinyl acetate [$10^{7.16}$ exp(−20.7 kJ mol^{-1}/RT)]; the small differences between these Arrhenius parameters are however statistically significant at the 95% confidence limit. The vinyl *neo*-decanoate used is actually a mixture of isomers: CH_2=$CHOCOCR_1R_2CH_3$, where the total number of carbons in R_1 and R_2 is 7. Theory suggests that the k_p values for all these isomers should be very similar and polymerization of the mixture can be treated as a homopolymerization with a k_p equal to the average k_p.

Exit in the emulsion polymerization of vinyl acetate. H. De Bruyn, R.G.Gilbert and M.J. Ballard. Macromolecules, in press.

The following model is proposed to explain the independence of polymerization rate on monomer concentration which is often observed in the emulsion polymerization of vinyl acetate: that radical loss is by transfer to a monomeric species which is very slow to propagate and whose radical activity is lost by exit and termination, either in the aqueous phase or when it enters a particle containing a growing radical. Since the transfer step is rate-determining, the rate of this process is proportional to monomer concentration, which cancels the dependence on monomer concentration in the overall polymerization rate expression; this model also predicts that the radical loss rate coefficient should be either $k_{tr}C_P$ or $2k_{tr}C_P$, depending on which is the actual fate of the desorbed radical (where k_{tr} is the rate coefficient for transfer to monomer and C_P is the concentration of monomer in the particles). Experimental radical loss rates, determined directly by γ-radiolysis relaxation studies, are quantitatively in accord with the hypothesis.

Mechanisms for radical entry and exit: – Aqueous-phase influences on polymerization. R.G. Gilbert. Chapter in *Polymeric Dispersions. Principles and Applications*, ed. J.M. Asua, Kluwer Academic, 1997, 1-16.

In most emulsion polymerizations, entry of radicals from the aqueous phase (e.g., arising from persulfate initiator) is the start of radical activity resulting in long chains. Whether or not a radical arising from initiator succeeds in initiating a long chain inside a particle depends on competing aqueous-phase fates, such as termination and (if particle formation is still occurring) forming a new precursor particle. In *ionically-stabilized* systems, the rate-determining steps for entry are propagation in the aqueous phase to a degree of polymerization (z) at which the species becomes surface active (e.g., for persulfate initiator and styrene monomer, the species is of the form $^{\bullet}M_3SO_4^-$, where M is a monomer unit), aqueous-phase propagation, and aqueous-phase termination. The actual entry step, whereby a z-meric radical becomes attached irreversibly to a particle (so that it can propagate to a long chain), is not rate-determining. However, when the particle is *sterically stabilized*, it appears that irreversible entry of a z-mer is so slow as to be rate-determining (e.g., because of the existence of an extended "hairy" layer around the particle wherein diffusion takes place very slowly). While models for the value of z exist which reproduce those inferred experimentally for ionically-stabilized particles, models for initiator efficiencies in polymerically-stabilized systems are lacking.

Exit (desorption) of radical activity is important for relatively water-soluble monomers such as vinyl acetate. Moreover, it is kinetically important even for hydrophobic monomers such as styrene, if the particle is sufficiently small. This can be understood in terms of the mechanism for exit: a monomeric radical is formed within the particle by transfer (either to monomer or to chain-transfer agent); if the particle is sufficiently small, this radical may desorb into the aqueous phase and diffuse away from the particle before it undergoes propagation (which would result in a species sufficiently insoluble as to be unable to desorb to any significant extent). The rate coefficient for exit is thus a function of the transfer constant, the diffusion coefficient and solubility in the aqueous phase, and the rate coefficient for propagation of the monomeric species. An expression yielding the value of the exit rate coefficient in terms of these various parameters gives acceptable accord with experiment for systems with ionic stabilizer. For polymerically-stabilized latexes, exit rate coefficients are drastically reduced below those expected from this expression, again consistent with slow diffusion in an extended viscous hairy layer.

The experimental data for entry and exit rate coefficients on which these inferences are based can be obtained from combining two independent types of measurements. (1) In a system wherein radical loss is dominated by exit, polymerization in a seeded system is initiated by γ rays, and the system removed from the radiation source after an approximate steady state has been achieved. Monitoring the relaxation rate in the system in the absence of external radical generation then yields the exit rate coefficient, *provided* that account is taken of the fate of exited radicals in the aqueous phase; means of taking this into account have been deduced. (2) The entry rate coefficient can be obtained by observing the steady-state polymerization rate in a seeded system with the desired initiator in a system where termination is not rate-determining (a "zero-one" system), together with a knowledge of the exit rate coefficient for that system (from γ relaxation). It is important in each case to take account of "background thermal" entry, a poorly-understood but often significant effect which may arise, e.g., from residual peroxide radicals in or on the particle.

Particle size distributions. E.M. Coen and R.G. Gilbert. Chapter in *Polymeric Dispersions. Principles and Applications*, ed. J.M. Asua, Kluwer Academic, Dordrecht, 1997.

Particle size, and particle size distribution, are involved in a number of properties of a polymer latex, such as its viscoelastic behavior. Various techniques can be used to measure *average* particle size (such as photon-correlation spectroscopy), while particle size *distributions* can be measured (laboriously) by calibrated electron microscopy, or much more conveniently by carefully-calibrated capillary hydrodynamic fractionation (CHDF). Unfortunately, general means of rapid *in situ* measurement of particle size in industrial reactors have yet to be developed.

Prediction of a particle size distribution can be separated into the case for Interval 1 (i.e., during particle formation) and subsequent evolution in the absence of new particle formation (Intervals 2 and 3). Given the rate coefficients for entry, exit and termination (including the dependence of the termination rate coefficient on the lengths of the two chains involved, and of all rate coefficients on particle size), the PSD in Intervals 2 and 3 can be readily computed by numerical solution of the appropriate evolution equation. For cases where these rate coefficients have been established independently, such calculations give good accord with measured PSDs. Moreover, appropriate comparison between theory and experimental PSDs can be used to infer information about the size dependence of the entry rate coefficient, especially in competitive growth experiments; however, it is essential in such cases to take careful account of the fate of exited radicals: exit is most rapid from small particles, and if all exited radicals re-enter, this can give a major component to the rate of entry into large particles, since larger particles are more likely to capture desorbed radicals from the aqueous phase.

Prediction of the PSD in Interval 1 is much more complex, since account must be taken of the complexities of nucleation kinetics. The most general treatment is one which considers the formation of precursor particles (which in this context are defined as particles which are colloidally unstable) both by surface-active (z-meric) radicals becoming micelles, and by longer radicals reaching a critical degree of polymerization j_{crit} whereby they undergo homogeneous nucleation. Other events which must be considered is these radicals also entering pre-existing particles, aqueous-phase termination, and coagulation of precursor particles. The full size dependence of all these rate parameters must also be considered, since, for example, capture by pre-existing particles is more likely when these particles are large. Nucleation ceases (or secondary nucleation starts!) when all new radicals terminate in the aqueous phase or enter pre-existing particles rather than forming new ones. The equations describing these events can be readily solved (to do this properly requires fully calculating the PSD), but alas contain significant parameters whose values are uncertain, such as those describing coagulation of precursor particles. While physically reasonable parameter values can be found which can reproduce experiment (eg., the dependence of the particle number on initiator and surfactant concentrations, and the PSD during Interval 1), such models are not yet reliably predictive.

Polymerization at high conversion. D. Kukulj and R.G. Gilbert. Chapter in*Polymeric Dispersions. Principles and Applications*, ed. J.M. Asua, Kluwer Academic, Dordrecht, 1997.

Emulsion polymerization at high conversion is relatively poorly understood, yet is of considerable technical importance: for example, in removal of residual monomer, in achieving maximum plant productivity, and control and understanding of effects such as peculiarities in molecular weight distributions, branching, etc., in the last few percent of a polymerization process. Several effects are considered in this context.

1. Monomer partitioning between aqueous and particle phases at very high conversion becomes important both because this controls the overall polymerization rate and also (through the entry mechanism discussed elsewhere) because it controls initiator efficiency (in the absence of "chasers"). While the so-called Vanzo equation has been used in many cases to quantify this partitioning, new work shows that this relation is inapplicable at very high conversion (or rather, that it can only be fitted to the data with unphysical parameter values, such as a negative Flory-Huggins χ). Replacing the Vanzo equation, semi-empirical fits must be used. The effect of very low aqueous-phase monomer concentration at high conversion seems always to result in a dramatically lowered initiator efficiency, even for monomers and initiators which are 100% efficient at lower conversions.

2. If the initiator is charged, then the entering species is probably tethered to the particle surface ("surface-anchoring"). Except at very high conversions, the ends of such anchored chains see much of the interior of the particle by reaction-diffusion, and moreover, transfer is a relatively frequent event which leads to a short chain which migrates throughout the particle before undergoing further propagation. At very high conversion, the situation is different: both propagation and transfer are greatly reduced because of the low monomer concentration, and another entering radical may terminate the anchored chain before it undergoes significant propagation. This can result in an increased concentration of relatively short chains (say, of molecular weight 10^4–10^5) in a shell at high conversion, an inference which is consistent with observed high-conversion molecular weight distribution data as well as a decrease in $\bar{n}$ at low monomer concentration. The effect is seen in both glassy (MMA) and rubbery (BMA) systems.

* The following publications have appeared since the previous Newsletter:

Determination of kinetic parameters for propagation in free-radical polymerizations: an assessment of ab initio procedures. J.P.A. Heuts, R.G. Gilbert and L. Radom. J. Phys. Chem., **100**, 18997 - 19006 (1996).

Critically-evaluated propagation rate coefficients in free radical polymerizations. I. Styrene and methyl methacrylate. R.G. Gilbert. Pure & Appl. Chem., **68**, 1491-4 (1996).

Effects of poly(acrylic acid) electrosteric stabilizer on entry and exit in emulsion polymerization. E.M. Coen, R.A. Lyons and R.G. Gilbert, Macromolecules, **29**, 5128-35 (1996).

Transfer constants from complete molecular weight distributions. D.I. Christie, R.G. Gilbert, Macromol. Chem. Phys., **197**, 403-12 (1996).

Pulsed-laser polymerization measurements of the propagation rate coefficient for butyl acrylate. R.A. Lyons, J. Hutovic, M.C. Piton, D.I. Christie, P.A. Clay, B.G. Manders, S.H. Kable and R.G Gilbert. Macromolecules, **29**, 1918-27 (1996).

A priori prediction of propagation rate coefficients in free radical polymerizations: propagation of ethylene. J.P.A. Heuts, R.G. Gilbert and L. Radom. Macromolecules, **28**, 8771-81 (1995).

JOURNAL OF COLLOID AND INTERFACE SCIENCE 178, 442–445 (1996)
ARTICLE NO. 0139

Surface Structure of Natural Rubber Latex Particles from Electrophoretic Mobility Data

C. C. HO,*,[1] T. KONDO,† N. MURAMATSU,† AND H. OHSHIMA†

*Department of Chemistry, University of Malaya, 59100 Kuala Lumpur, Malaysia, and †Faculty of Pharmaceutical Sciences, Science University of Tokyo, Shinjuku-ku, Tokyo 162, Japan

Received February 21, 1995; accepted September 11, 1995

Fresh natural rubber latex particles are stabilized by adsorbed proteins and phospholipids while those for high-ammonia latex concentrate are stabilized mainly by adsorbed long-chain fatty acid soaps, the hydrolysis products of phospholipids. The structure of this surface layer surrounding the latex particles is analyzed using the electrophoresis model of Ohshima and Kondo. Good agreement between theoretical and observed electrophoretic mobility was found, except at very low ionic strength. The results were consistent with a model of an uncharged bared polyisoprene latex particle coated by a charged mixed layer of long-chain fatty acid soaps, proteins, and polypeptides of finite thickness in matured latex concentrate. This surface layer is ion-penetrable and its resistance to liquid flow changes with time on prolonged hydrolysis.

Key Words: natural rubber latex; electrophoretic mobility; latex particle surface layer structure.

Presented at

INTERNATIONAL RUBBER CONFERENCE - IRC '96
17 - 21 June 1996, G-Mex Symposium Centre, Manchester, UK

Surface free energies and surface morphologies of natural and modified natural rubber latex films

C.C. Ho and M.C. Khew
Department of Chemistry, University of Malaya,
59100, Kuala Lumpur, Malaysia.

Abstract

Surface free energies of latex dipped films of natural rubber (NR) and modified natural rubbers, namely low protein natural rubber (DPNR), and oil-extended natural rubber (ONR) were determined by the contact angle method. The dispersive and polar components of the free energies were evaluated by various known equations. The surface free energy and its components depend on the equations used and also on the type and nature of the additive(s) incorporated into the rubber during the modification process. For each type of latex film, the Harmonic-mean method gave the highest polar component compared with those from the Geometric-mean method and Fowkes' method. This trend is the same for each type of latex film. However, the magnitude of these components were different for different types of latex films. Comparison with synthetic rubbers especially polyisoprene rubber (IR) were made.

Effect of leaching on surface free energy of natural rubber film was also investigated. The polarity of unwashed NR was higher than that of the leached ones, being ~0.5 and ~0.15 respectively. The non-rubber constituents of NR latex, especially proteins, are usually exuded from the rubber matrix on drying during film formation. The present results show clearly these polar materials are not compatible with the rubber molecules. They accumulated at the rubber surface through exudation and rendered the film surface relatively hydrophilic. The above conclusion was confirmed by the morphology and surface roughness study of the latex fims using atomic force microscopy (AFM). The implication of this on the processing and application of rubber dipped goods is discussed.

POLYMERIC MATERIALS ENCYCLOPEDIA

Editor-in-Chief
JOSEPH C. SALAMONE
Professor Emeritus
University of Massachusetts, Lowell

VOLUME
6
M–O

CRC Press
Boca Raton New York London Tokyo

NATURAL RUBBER LATEX (Polymeric Flocculant for Tin Tailings Slurries)

C. C. Ho* and K. C. Lee
Department of Chemistry
University of Malaya

E. B. Yeap
Department of Geology
University of Malaya

Dewatering is the science of separating water from solids. In any dewatering process, two aspects are important: the total amount of removable water and speed. The dewatering of tin tailings slurry, confined to so-called ex-mining ponds, has never been satisfactory. Like most other mining slurries, the main difficulty lies not in clarifying the supernatant water but in removing water from the soft, settled clays. This can be traced to the fact that the tin tailings (consisting mainly of clay minerals of colloidal dimension) left behind by tin mining are generally polydisperse in size and multimineralic.[1] These fine, highly charged clay particles form a stable colloidal dispersion. After a long time the slow, self-settling characteristics of the dispersed solids result in a soft sediment (some as low as only 20% solids), with some haze probably persisting above it. Owing to its high water content, the soft sediment is thus non-load-bearing and unacceptable for most engineering purposes. The current practice of surcharging the soft slurry with sand after pumping off the pond water and then draining the entrapped water of the soft slurry by vertical drains is unsatisfactory, both in terms of the quality of the reclaimed land and cost.

---

*Author to whom correspondence should be addressed.

0-8493-2470-X/96/$0.00+$.50

INTERNATIONAL POLYMER COLLOIDS GROUP NEWSLETTER

Contribution
from

Norio Ise[1], Kensaku Ito[2], Toshiki Konishi[1], Eiji Yamahara[1],
B.V.R. Tata[1], and Junpei Yamanaka[3]

[1] Central Laboratory, Rengo Co.,Ltd., Ohhiraki, Fukushima, Osaka 553,
[2]Department of Chemical and Biochemical Engineering,
Toyama University, Toyama 930,
and
[3]Polymer Phasing Project, ERATO, Research Development Corporation of Japan,
15 Morimoto-cho, Shimogamo, Sakyo-ku, Kyoto 606, Japan

(Reporter: Norio Ise)

....

BVR Tata is currently at Central Laboratory, Rengo Co., Ltd. by the Visiting Scientists Program of the Company. His permanent address is Indira Gandhi Centre for Atomic Research, Kalpakkam, Tamil Nadu, India.

....

Structural Inhomogeneity in Dilute Dispersions of Poly(Chlorostyrene-styrene sulfonate) Particles

Tata-Yamahara-Rajamani-Ise (publication in preparation) synthesized poly-(chlorostyrene-styrene sulfonate) particles by emulsion copolymerization technique and carried out a concurrent analysis of the dispersion structure at low volume fractions (< 0.06) in Fourier space by using ultra-small-angle X-ray scattering (USAXS) and in the real space by confocal laser scanning microscope (CLSM). The dispersions were purified by dialysis, ultrafiltration and ion-exchange. By curve fitting of the USAXS curves of salt-added dispersions with the form factor of an isolated sphere, the diameter of the particles was determined to be 1800 A ± 120 A. The analytical charge and effective charge densities were determined by conductometric titration and conductivity measurements to be 7.0 ± 0.2 and 0.25 ± 0.02 μ C/cm^2, respectively. Their constancy was confirmed by the repeated measurements over the period of USAXS and CLSM measurements. The background salt concentration in the purified dispersions was estimated to be 1.5 μ M from conductivity measurements. The USAXS measurements were carried out on dispersions introduced into a quartz capillary using a Bonse-Hart camera with Ge crystals (Konishi et al. Phys. Rev. B51, 3914 (1995); J. Am. Chem. Soc. 117, 8422 (1995)). Fig. 1 shows the desmeared scattering intensity $I(Q)$ as a function of scattering wave vector Q. All samples exhibited a first peak and a split second peak riding over the form factor $P(Q)$, which suggested a glass-like ordering for such dilute dispersions. The first peak appeared at higher Q values than those expected from the homogeneous particle distribution, implying the interparticle spacing in the ordered structure (D_{exp}) being smaller than the average spacing (D_0), as was often observed by us to be the case for various colloidal particles and macroions. This fact shows the presence of attraction between particles and also indicates that a significant fraction of the dispersion volume must be free from particles, namely voids.

Whether the voids exist actually or not was investigated by confocal laser scanning microscope. The dispersions were introduced into a quartz cylindrical cell of 10 mm diameter and 20 mm height. Using an inverted type CLSM (Carl Zeiss), the dispersions were studied in the presence of ion-exchange resin particles in nylon mesh bags hanged from the top. The top of the cell was sealed with airtight caps and the temperature was regulated at 24° C. The sample was confirmed to be homogeneous initially (< 8 hours). After two days small voids were seen, which were stable only for a few minutes. After 10 days, large voids were observed deep inside the suspensions, as shown in Fig. 2. They were very stable for several days and were found to reappear within 16 hours after shaking. It was confirmed that the particles around the voids moved so slowly that they could be traced for several seconds and averaging of the image frame over several seconds sharpened the image. This suggests that the particles around the voids was amorphous (glass-like), confirming the glass-like ordering observed by USAXS. Thus there is a good correlation between the USAXS and CLSM results.

Constant volume Monte Carlo simulation were performed using the Sogami potential $U_s(r)$ [J. Chem. Phys. 81, 6320 (1984)], which contains both the long-range attractive and short-range repulsive tails and has the form $U_s(r) = B[(A/r) - \kappa]\exp(-\kappa r)$ with $A = 2 + \kappa d \coth(\kappa d/2)$, $B = 2[eZ \sinh(\kappa d/2)/\kappa d]^2/\varepsilon$, $\kappa^2 = 4\pi e^2(n_pZ + C_s)/(\varepsilon k_BT)$, Ze is the particle charge, d the particle diameter, C_s the salt concentration, T the temperature, ε the dielectric constant and k_B the Boltzmann constant The position of the potential minimum R_m is given as $R_m = A + [A(A+4)]^{1/2}/2\kappa$ and its depth by $U_m =$

$U(R_m)$. After reaching equilibrium the pair correlation function, $g(r)$, was calculated using particle coordinates and is shown in Fig. 3. Note that $g(r)$ shows a first peak and a split second peak suggesting the glass-like order. Further we observe the first peak position to be at smaller distance than D_0 which confirms again reduction in the interparticle distance. The corresponding projection of the coordinates in the MC cell (Fig 3 (b)) shows voids.

It should be noted that the simulations with an effective pair-potential having a long-range attractive term could account for the USAXS and CLSM observations. On the other hand, they could not be reproduced when the DLVO potential was used.

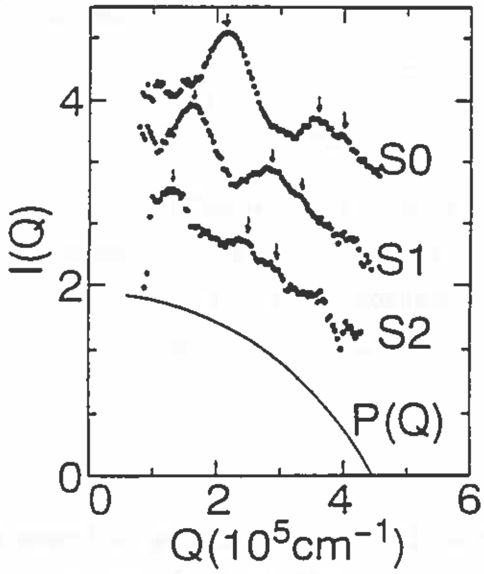


Fig. 1. Scattered intensity $I(Q)$ vs Q at particle concentrations of 19.5, 8, and 4 x 10^{12} cm^{-3}) from the top. The curves were shifted vertically for the sake of clarity. The vertical arrows represent the positions of first and split second peaks. The continuous curve is the theoretical form factor for $d = 1800 \pm 120$ A.

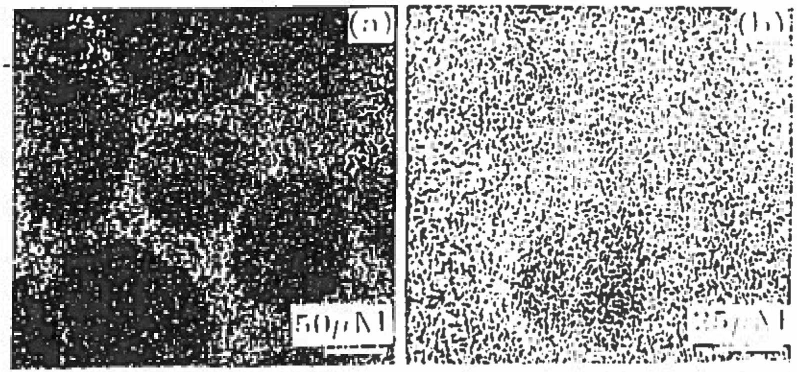


Fig. 2. CLSM micrographs with a magnification of 20x/0.75 (a) at $n_p = 2 \times 10^{12}\,cm^{-3}$ at 43 μ m from the oversleep and (b) at $n_p = 8 \times 10^{12} cm^{-3}$ and 60 μ m.

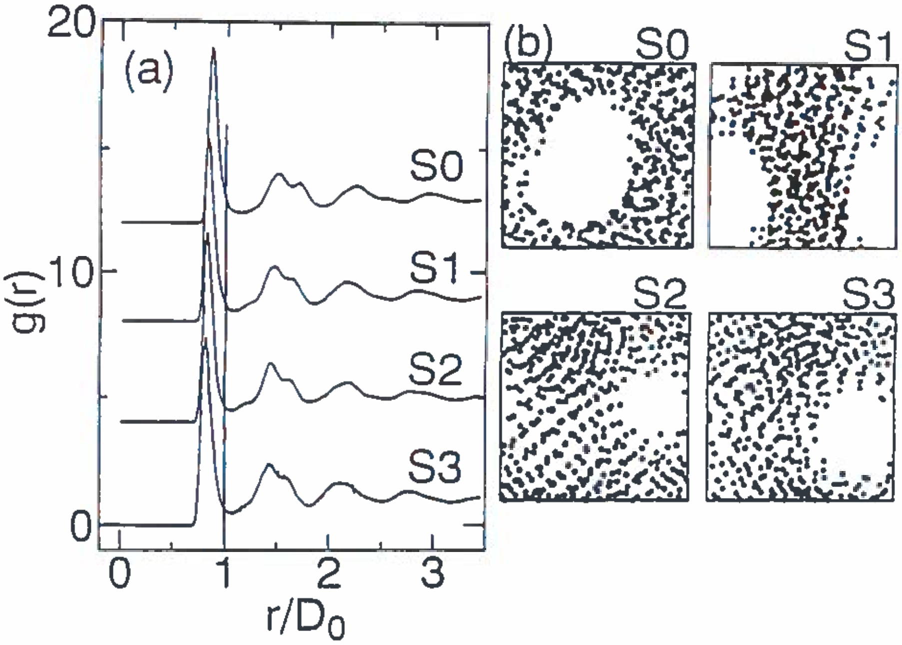


Fig. 3. (a) *g(r)* Vs *r/D₀* at n_p= 19.5, 8, 4, and 2 x10^{12} cm^{-3} from the top. The vertical line represents the average particle spacing *D₀* obtained from n_p. (b)Projection of the particle coordinates (normalized to the unit of *D₀*) in the MC cell at n_p= 19.5 x 10^{12} (S0), 8 x 10^{12} (S1), 4 x 10^{12} (S2), and 2 x 10^{12} cm^{-3} (S3).

Re-Entrant Order-Disorder Transition in Aqueous Dilute Dispersions of Ionic Colloidal Silica Particles

Yamanaka et al. studied the "phase" diagram of colloidal silica particles, KE-P10W and Cataloid SI-80P , (net charge density of the H-type particles $\sigma_{e,H}$ = 0.08 and 0.26 μ C/cm^2, respectively and d = (0.12 ± 0.01) and (0.10 ± 0.01) μ m). The analytical charge density σ_a ,which was determined by conductance measurements, was varied by adding NaOH as described in a previous paper (J. Yamanaka et al. Phys. Rev. E. in press). The "phase" diagram was constructed by observing iridescence due to formation of the ordered structure as a function of σ_a and is shown in Fig.4. The salt concentration C_s was determined from the sum of concentrations of coexisting NaOH and hydronium ions in the water used.

At σ_a = 0.1 μ C/cm^2, ordering did not take place even at C_s = 2 μ M. On the other hand, at σ_a = 0.2 μ C/cm^2 ordered structures were formed in a few minutes. The order-disorder transition point shifted towards higher C_s with increasing σ_a as expected. With further increase in σ_a a plateau region appeared, after which C_s at the transition point became smaller. Thus, there exist lower and upper limits of σ_a for the transition at given C_s's. To our knowledge, this is the first observation of the "re-entrant" transition in terms of the charge density.

The USAXS profiles at rather low charge densities for KE-P10W were already described in a previous paper (J.Yamanaka et al. Phys. Rev. E 53, R4314 (1996)).

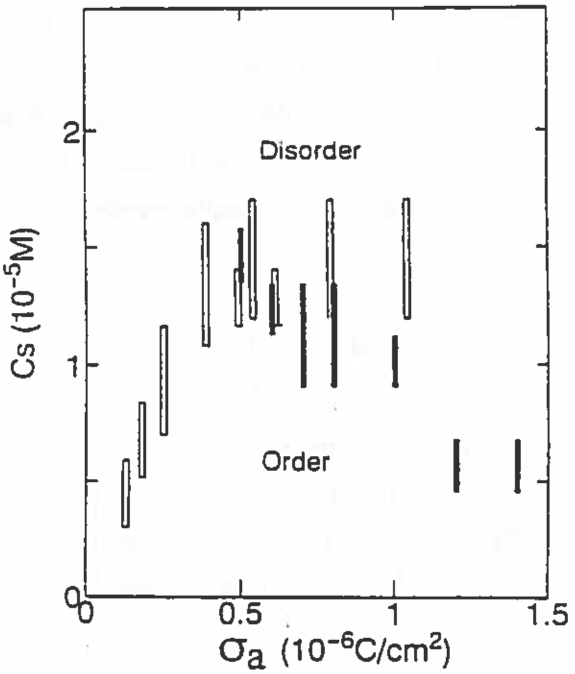


Fig. 4. "Phase" diagram for order-disorder transition in colloidal silica dispersions at room temperature at 3 vol % and at various salt concentrations and analytical charge densities. Open symbols:KE-P10W. Filled symbols: SI-80P.

Two-Dimensional Ultra-Small-Angle X-ray Scattering from a Colloidal Single Crystal

A two-dimensional ultra-small-angle X-ray diffractometer was constructed and described in IPCG Newsletter 27, No. 1, (1996). A detailed study was carried out for a "single" crystal of KE-P10W silica particles at a concentration of 2.5 vol %. Since the 2D-USAXS apparatus is equipped with a mechanism of rotating the sample as in 3-circle diffractometers used in the wide-angle measurements, we can directly measure the intensity of scattered X-ray $I(Q)$ at each scattering vector $\boldsymbol{Q}$ with the components written by

$$\boldsymbol{Q} = (Q \cos \chi \cos \phi,\ Q \cos \chi \sin \phi,\ Q \sin \chi)$$

where Q is the magnitude of the scattering vector. Fig. 5 shows contour plots of the 2D-USAXS profiles against the rotation angles χ and ϕ of the sample capillary. The Q

values were 2.33, 3.26, and 4.02 x 10^{-3} A^{-1} for Fig. 5 (a), (b), and (c), respectively, which were obtained at scattering angles of 118, 165 and 203 sec of arc, respectively. Further measurements were done by changing the direction of the scattering vector while fixing its magnitude. The intensity was dependent on ϕ and χ, indicating that the structure is oriented.

The scattering vector was calculated from θ, ϕ, and χ. To determine the crystal structure we followed the procedure proposed by Busing and Levy (W.R. Busing and H. A. Levy, Acta Cryst. 22, 457 (1967)). We used a 3 x 3 matrix, matrix UB, to relate the scattering vector at the diffraction peak with the Miller indices *h,k,* and *l* of the diffraction planes of an expected colloidal single crystal as follows:

$$\begin{pmatrix} q_x \\ q_y \\ q_z \end{pmatrix} = \mathrm{UB} \times \begin{pmatrix} h \\ k \\ l \end{pmatrix}$$

Consequently we determined the matrix UB as

$$\mathrm{UB} = \begin{pmatrix} 1.21 & 1.11 & -0.07 \\ -0.59 & 0.73 & 1.35 \\ 0.93 & -0.98 & -0.93 \end{pmatrix} \times 10^{-3}\ \mathrm{A}^{-1}$$

This implies that a "single" crystal of a bcc symmetry was formed in the dispersion (2.5 vol%) with a lattice constant of 3800 A and the [$1\bar{1}1$] direction is parallel to the capillary axis. The crystal planes corresponding to the observed diffraction peaks are shown by the Miller indices in Fig. 5.

Conversely, by assuming a bcc single crystal with the lattice constant and the direction found above, we estimated the peak positions for various planes by using the above equations and the results are indicated by circles. The agreement between observed and calculated positions is noteworthy. Besides 22 peaks observed and confirmed by the calculation, there are several diffraction peaks that could not be reproduced by the calculation. This suggests that a small number of crystallites of unconfirmed symmetry and orientation were formed in addition to the single crystal. However, because of their relatively low intensities, and also in light of the fact that most of the observed peaks could be reproduced by the calculation in terms of the single crystal, we decided not to give further serious attention to these crystallites.

It is to be noted that the information discussed above confirms that derived earlier by using the 1D-USAXS for the same silica systems (T. Konishi et al. Phys. Rev. B 51, 3914 (1995)). In short, the orientation observed requires the (110) plane of the bcc structure to be parallel to the glass wall. The fact, that the most densely packed plane of negatively charged particles in the bcc structure is "in contact" with likewise negatively charged glass surface, is consistent with previous microscopic observation and also with recent observation of the positive adsorption of ionic latex particles or surfactant micelles near like-charged interface (R. Thomas et al. J. Phys. Chem. 97, 13907 (1993); K. Ito et al. J. Am. Chem. Soc. 117, 5005 (1995)), though it contradicts with the standard double layer interaction theory.

Further study is being conducted on the peak intensity and peak width.

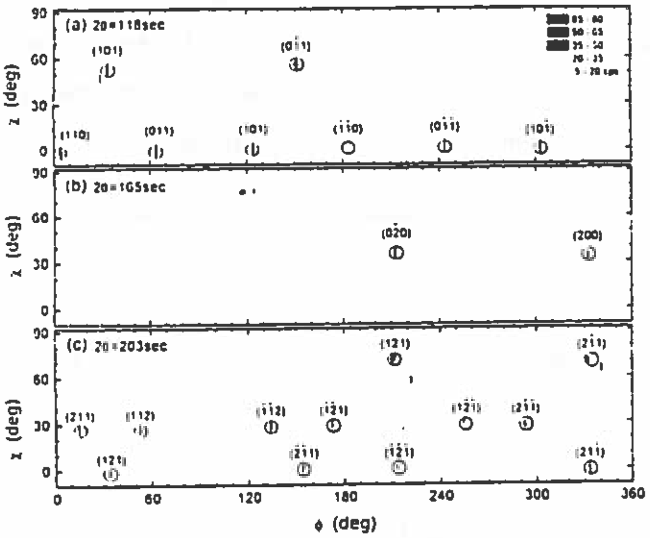


Fig. 5. Contour plots of the 2D-USAXS intensities against χ and ϕ for colloidal dispersion in water (2.5 vol%). (a) 2 θ =118, (b) 165, and (c) 203 sec. The circles indicate the calculated positions of the diffraction peaks for a bcc lattice with a lattice constant of 3800 A and with [1$\bar{1}$1] being parallel to the capillary axis. The diffraction peaks were assigned by the method described in the text to the corresponding diffraction planes indicated by Miller indices.

Positive Adsorption of Negatively Charged Latex Particles Near Like-Charged and Non-Charged Interfaces

Ito et al. further studied on the positive adsorption of latex particles near like-charged interface by using CLSM (partly, Proc. Japan Acad. 72B, 62 (1996) and partly publication in preparation). (1) They studied the particle distribution in H_2O-D_2O mixtures of various densities and confirmed that the particle sedimentation is not the cause of the observed positive adsorption.

(2) they synthesized latex spheres having varying amounts of styrene sulfonate (a comonomer) and determined the particle numbers in the region of 5 - 25 μm from the glass surface ($N_{interface}$) and those in the region of 100 - 120 μm (N_{bulk}). The latter was confirmed to agree with that expected as the bulk value from the particle concentration, particle diameter and focal volume. According to Fig. 6 the positive adsorption was enhanced with increasing particle charge number. The standard explanation for this observation is that the particles were pushed toward the interface by widely accepted repulsive interaction inside the dispersion. If this interpretation were correct, the positive adsorption must take place even toward uncharged interface. (This is not the case as will be demonstrated below). Furthermore, if this interpretation were valid, such an effect must have been considered in the standard double layer interaction theory. This has not been the case, either, however.

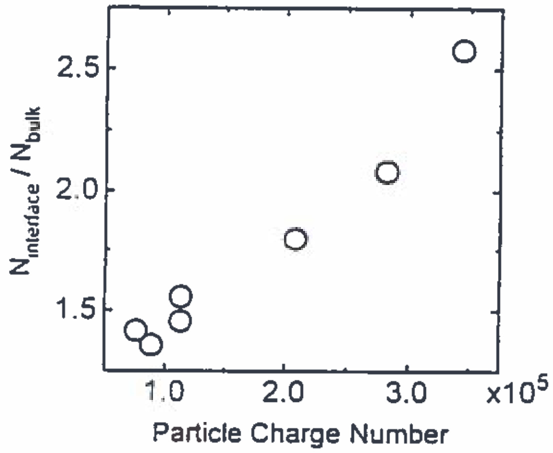


Fig. 6. Positive adsorption of anionic polymer latex particles near glass surface at various charge number of particles.

(3) To show that the adsorption is caused by an electrostatic effect between the interface and particles, not by the interparticle repulsion, Ito et al. modified the glass surface by polymerizing p-styrenesulfonate (PSS) or acrylamide (PAA) to reactive end groups of a silane coupling agent bound to Si-OH groups on the glass surface. The ζ potentials of PSS-modified glass was -94 mV while that of the untreated glass was -70 mV at 10^{-4}M NaCl solution. That of the PAA-treated sample was -4 mV whereas the untreated glass showed -24 mV at 10^{-2} M NaCl solution. The CLSM results are shown in Fig. 7. Clearly, the positive adsorption was more enhanced for PSS-modified glass surface than for the untreated one. No adsorption took place on the PAA-modified glass.

Obviously, the positive adsorption becomes more pronounced with increasing charge number of the interface.

(4) It has often been pointed out that the degree of dissociation of the weak acid group on the glass surface (-SiOH) was lowered due to approach of the particles so that the positive adsorption resulted. Although the change in the degree of dissociation is not established experimentally, the fact that positive adsorption occurred for the PSS-modified glass and the styrene-styrene sulfonate copolymer particles shows that the above interpretation is not acceptable.

(5) Another factor which we have often come across is the possible effects of cations such as Na^+ coming out from the glass. These ions form a positive atmosphere, which might contribute to the observed adsorption. This assertion can be shown to be irrelevant because the adsorption was also observed for a quartz plate, from which only a negligible amount of cations would be released. Further experiments using a Nafion-coated polyethylene surface show also positive adsorption, confirming the irrelevancy of the assertion, since no cations comes out from polyethylene and only sulfonate groups exist on the surface.

We thus believe that the charged plates attract like-charged particles through the intermediary of counterions and the attracted particles pull on the other particles, resulting a very long-range attraction (typically, 100 μm).

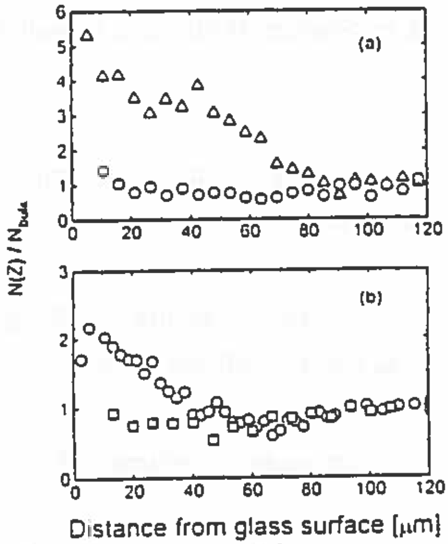


Fig. 7. Positive adsorption of latex particles near modified glass surfaces. Latex concentration: 0.08 vol %. (a) PSS-modified (△, $\zeta = -94$ mV)) and untreated (○, $\zeta = -70$ mV) glasses. (b) PAA-modified (□, $\zeta = -4$ mV) and untreated (○, $\zeta = -24$ mV) glasses.

Publication between May, 1996 and October, 1996

(1)J. Yamanaka, T. Koga, N. Ise, and T. Hashimoto, Control of Crystallization of Ionic Silica Particles in Aqueous Dispersions by Sodium Hydroxide, *Phys. Rev. E.* 53, R4314 (1996).

(2)N. Ise, Long-Range Electrostatic Attraction Between Macroions Mediated by Oppositely Charged Counterions: Experimental Supports, Past and Present. *Ber. Bunsenges. Phys. Chem.* 100, 841 (1996).

(3)T. Konishi, E. Yamahara, and N. Ise, Characterization of Colloidal Silica Particles by Ultra-Small-Angle X-ray Scattering, *Langmuir* 12, 2608 (1996).

(4)J. Yamanaka and N. Ise, Comment on "Shear Modulus Titration in Crystalline Colloidal Suspension", *J. Colloid Interface Sci.* 179, 324 (1996).

(5)T. Furuta, E. Yamahara, T. Konishi, and N. Ise, Ordering in Aqueous Cellulose Hydrolysate Dispersions: An Ultra-Small-Angle X-ray Scattering Study, *Langmuir* in press.

(6)J. Yamanaka, Y. Hayashi, N. Ise, and T. Yamaguchi, Control of Surface Charge Density of Colloidal Silica by Sodium Hydroxide in Salt-free and Low Salt Dispersions, *Phys. Rev. E* in press.

(7)B.V.R. Tata and N. Ise, Homogeneous to Inhomogeneous Transition in Charged Colloids, *Phys. Rev. B* 54, 6050 (1996).

(8)K. Ito, T. Muramoto, and N. Ise, Gathering of Charged Colloid Particles Near Like Charged Entities, *Proc. Japan Acad.* 72B, 62 (1996).

(9)N. Ise, Commentary on Commentary, *Hyoumen* 34, 189 (1996) (in Japanese).

(10) N. Ise, K. Ito, H. Matsuoka, and H. Yoshida, Colloidal Dispersions Studied by Microscopy and X-ray Scattering, in "Ordering and Phase Transitions in Charged Colloids" ed. A. K. Arora and B. V. R. Tata, VCH Publishers, New York, 1996.

Contribution to the International Polymer Colloids Group Newsletter

by

Haruma Kawaguchi

Department of Applied Chemistry, Keio University
3-14-1 Hiysohi, Yokohama 223 Japan
TEL: +81-45-563-1141 ext.3456 FAX: +81-45-562-7625
e-mail: haruma@applc.keio.ac.jp

Colloidal Properties of Microspheres Having Thermosensitive Layers

Poly(N-isopropyl acrylamide) (PNIPAM) has its lower critical solution temperature (LCST) at 32°C. PNIPAM microgels and microspheres having PNIPAM shell layers change their size and other colloidal properties discontinuously near the LCST although the discontinuity depends on the structure of PNIPAM phase. In this study, two kind of core-shell microspheres shown in Figure 1 were prepared and the relation between the shell structure and colloidal properties was discussed.

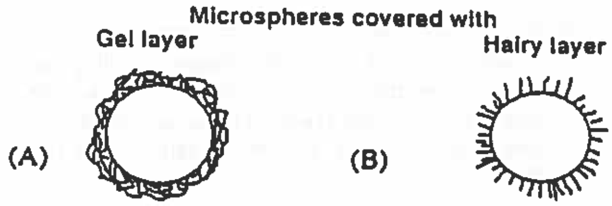


Figure 1 Microspheres having crosslinked (A) and hairy (B) PNIPAM shells

Preparation of Microspheres Having Crosslinked (A) and Hairy (B) PNIPAM shells

For the preparation of microspheres A, first, styrene (St) and NIPAM were copolymerized in an emulsifier-free aqueous medium. Monodisperse microspheres were obtained but their hydrodynamic size little depended on temperature. To give sharp thermosensitivity to the microspheres, seeded polymerization of NIPAM and methylenebisacrylamide was carried out using the above-mentioned microspheres as a seed. The microspheres were purified by repetitive centrifugation-decantation-redispersion.

Microspheres B were prepared with the following procedure; St-acrylamide copolymer latex was prepared by soap-free emulsion copolymerization and partially hydrolyzed in order to convert the latex particles to carboxylated ones. PNIPAM having amine groups was prepared by polymerizing NIPAM in the presence of an amine group-carrying chain transfer reagent. Then the PNIPAM was bound to carboxylated particles.

This paper has been presented at

International Satellite Workshop on
Nano-Particles-Metals, Semiconductors and Polymers

held at Yamaguchi, Japan on December 7, 1996.

Colloidal Properties of Microspheres Having Crosslinked PNIPAM Shell

Transition between hydrophobic hydration and dehydration of PNIPAM through its LCST causes expansion - collapse of PNIPAM phase. Expansion and collapse, which corresponds to swelling and deswelling, of PNIPAM in the shell of core-shell particles can be confirmed from the change of hydrodynamic size of the microspheres at different temperatures. Hydrodynamic diameter of the microspheres was measured by photon correlation spectroscopy and a result is shown in Figure 2A [1]. The extent of swelling is also determined from the density of ionic groups (n in Ohshima's equation (Eq. 1) for electrophoresis of soft particles [2]) in the shell of particles. Temperature dependence of n of particles having crosslinked PNIPAM shell was similar to that of hydrodynamic size and discontinuous around the LCST of PNIPAM

Swollen particle becomes soft and shrunken one becomes hard. The softness of particle can be estimated from the lambda value which is a function of the viscosity and frictional coefficient of shell layer (Eq. 3). Temperature dependence of softness of PNIPAM shell is shown in Figure 2C.

$$\mu = \frac{\varepsilon_r \varepsilon_0}{\eta} \frac{\psi_0 / \kappa_m + \psi_{DON} / \lambda}{1/\kappa_m + 1/\lambda} + \frac{zeN}{\eta \lambda^2} \qquad \text{(Eq. 1)}$$

$$\kappa = \kappa (1 + (zN/2vn)^2)^{1/4} \qquad \text{(Eq. 2)}$$

$$\lambda = (\gamma/\eta)^{1/2} \qquad \text{(Eq. 3)}$$

where η is the viscosity, γ the frictional coefficient of the hydrogel layer, ε_T the relative permittivity of the solution, ε_0 the permittivity of a vacuum, φ_{DON} the Donnan potential of the hydrogel layer, φ_0 the potential at the boundary between the hydrogel layer and the surrounding solution and, κ the Debye-Huckel parameter, and zeN the density of the fixed charges in the hydrogel layer.

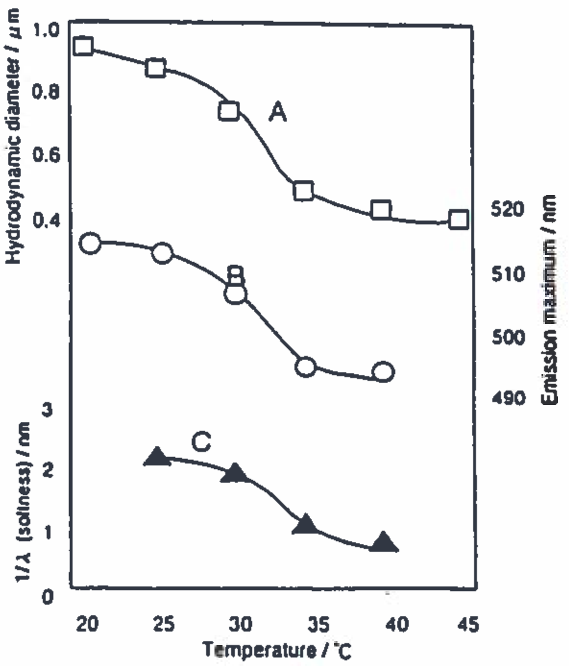


Figure 2 Temperature dependence of hydrodynamic size (A), hydrophilicity (B) and softness (C) of microspheres having crosslinked shell

Transition of PNIPAM also resulted in the change of hydrophilicity / hydrophobicity in the PNIPAM shell regions. Hydrophilicity / hydrophobicity was assessed by emission spectra of a hydrophobic probe such as 8-anilinonaphthalene-1-sulphonic acid, magnesium salt (ANS). The emission maximum of ANS vs. temperature is shown in Figure 2B. Protein adsorption is a measure of hydrophilicity of surfaces. Amount of IgG adsorption was measured as a function of temperature. The results shown in Figure 3 indicate that the surface of Pst particle is highly hydrophilic regardless of temperature but the hydrophilicity / hydrophobicity of the surface of PNIPAM particle changed with temperature. The change was continuous. Perhaps surrounding water does not allow disconinuous change in hydrophilicity around the LCST of PNIPAM.

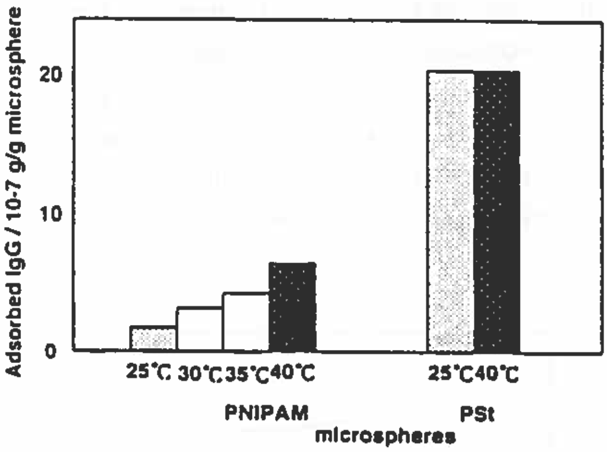


Figure 3 Adsorption of IgG on PNIPAM and PSt particles at different temperatures

Microspheres Having PNIPAM Shell as Enzyme Carriers

Two types of microspheres shown in Figure 1 were used as enzyme carriers. Trypsin was bound to crosslinked PNIPAM shell or bound to the end of PNIPAM hair. Immobilization of enzyme brought about an increase in the LCST of the hybrid PNIPAM by 3 to 7°C depending on the amount of immobilization. Benzoyl-DL-arginine-beta-naphthylamide(BANA) and alfa-casein

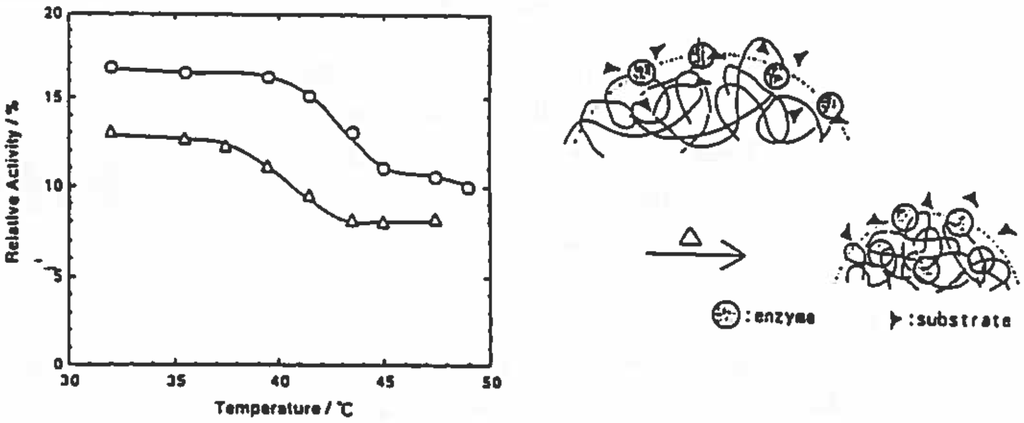
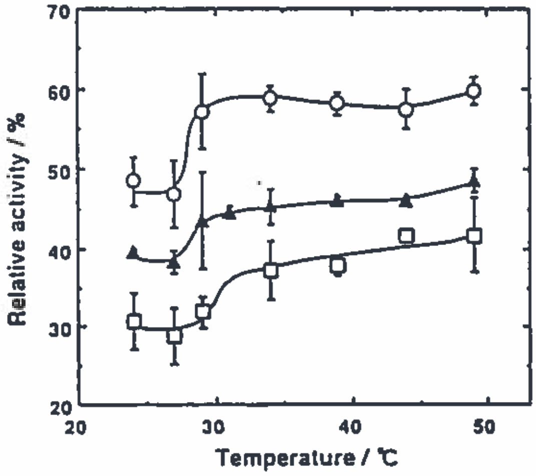


Figure 4 Enzymatic activity of trypsin immobilized in crosslinked PNIPAM shell

were used as the substrates for immobilized trypsin. The activity of immobilized enzyme is a relative one comparing with that of free enzyme.

The enzymatic activity of trypsin immobilized in crosslinked PNIPAM shell decreased above the LCST as shown in Figure 4 [3]. This was attributed to a decrease in the diffusion of substrate and / or entrapment of enzyme in the PNIPAM network. When trypsin was immobilized via a hydrophilic spacer, the activity lost its temperature dependence.

The temperature dependence of enzymatic activity in trypsin-carrying hairy PNIPAM system was quitely different from that of the above-mentioned gel shell system as shown in Figure 5 [4]. The increase in the activity above 30℃ (LCST of non-enzyme-conjugated PNIPAM) is attributed to an increase in the accessibility of substrate to enzyme due to the preferential collapse of non-enzyme-conjugated PNIPAM which exposes the enzyme to aqueous phase as illustrated in Figure 5.



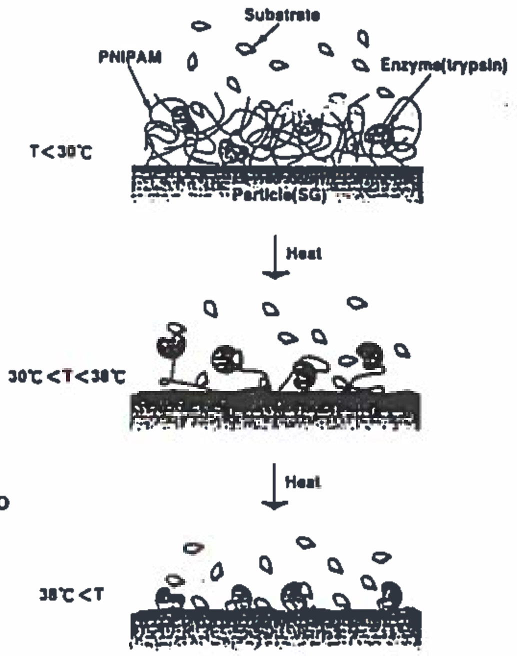


Figure 5 Enzymatic activity of trypsin immobilized to the chain end of PNIPAM hair on particles (Three curves are for three trypsin-carrying latex systems with different densities of immobilized trypsin)

References

1) H.Kawaguchi, Functions of monodisperse, thermosensitive hydrogel microspheres. in "Biomedical Functions and Biotechnology of Natural and Applied Polymers" ed. by M.Yalpani, ATL Press (1996) pp. 157 - 168
2) H.Ohshima, T.Kondo, J. Colloid Interface Sci., 130, 281 (1989)
3) T.Shiroya, N.Tamura, M.Yasui, K.Fujimoto, H.Kawaguchi, Colloids Surfaces B: Biointerfaces, 4, 267 (1995)
4) M.Yasui, T.Shiroya, K.Fujimoto, H.Kawaguchi, ibid, accepted for publication.

Recent Publications by H.Kawaguchi, et al.

○ H.Kawaguchi, Functions of monodisperse, thermosensitive hydrogel microspheres. in "Biomedical Functions and Biotechnology of Natural and Artificial Polymers" ed. by M. Yalpani, ATL Press (1996) pp. 157-168

○ H.Torii, K.Fujimoto, H.Kawaguchi, Chemical properties of water-soluble, nonionic azo compounds as initiators for emulsion polymerization. J. Polymer Sci., Polym. Chem. Ed., 34, 1237-1243 (1996)

○ Y.Kamijo, K.Fujimoto, H.Kawaguchi, Y.Yuguchi, H.Urakawa, K.Kajiwara, Preparation and structual characterization of hydrogel microspheres. Polym. J., 28, 309-316 (1996)

○ H.Kawaguchi, K.Fujimoto, Y.Nakazawa, M.Sakagawa, Y.Ariyoshi, M.Shidara, H.Okazaki, Y.Ebisawa, Modificatin and functionalization of hydrogel microspheres. Colloids Surfaces A: Physicochem. Eng. Aspects, 109, 147-154 (1996)

○ T.Wada, H.Watanabe, H.Kawaguchi, and H.Handa, DNA Affinity Chromatography. in "Methods in Enzymology. Vol.254. Oncogene Techniques" ed. by Peter K.Vogt, Academic Press (1995) pp. 595-605

INTERNATIONAL POLYMER COLLOIDS GROUP NEWSLETTER

Contribution from the Department of Chemical Engineering,
Yonsei University, 134, Shinchon-dong, Sudaemoon-ku, Seoul 120-749, Korea

Reported by Jung-Hyun(Jay) Kim

Current researches accomplished in our laboratory include: (1) Synthesis and characterization of resorcinol/formaldehyde wet gel particles by emulsion-gel process, (2) Preparation of very small and high surface charged latex particle using alkali-soluble random copolymer, (3) Molecular weight distribution of free radical bulk terpolymerization of α-Methyl Styrene/Styrene/Acrylic Acid in CSTR : Experimental analysis and model simulation, (4) Effects of surface charge on grafting efficiency of acryl-modified water-based polyurethane dispersion.

Abstracts of published and accepted contributions include : (1) Structural morphology developments in the interfacial phase of heterocoagulated composite particles : dynamic mechanical measurements, (2) Synthesis of resorcinol/formaldehyde organic aerogels by low temperature supercritical drying process, (3) Adsorption of BSA on highly carboxylated microspheres-quantitative effects of surface functional groups and interaction forces, (4) Process for the preparation of conducting polymer composites (I) : effect of the porosity on the conductivity, (5) Process for the preparation of conducting polymer composites (II) : effect of polymerization parameters on conductivity.

Synthesis and Characterization of Resorcinol/Formaldehyde Wet Gel Particles by Emulsion-Gel Process

Hae-Joon Lee, Jae-Hwa Song, and Jung-Hyun Kim

Aerogels are unusual porous materials because of their unique microstructure consisting of pores and particles which are in the nanometer size range. They have unique properties such as high porosity, large surface area, low density and low thermal conductivity. Numerous applications have been investigated including thermal insulation, support of catalysts, microfilters, adsorbents, etc. The Resorcinol/ Formaldehyde aerogel monoliths has demonstrated that the thermal conductivity components are correlated with the bulk density and the underlying aerogel structure as determined by the Resorcinol/Catalyst mole ratio.

RF-aerogel microspheres are potentially attractive for the formation of new low density composites. These microspheres can be packed as loose powders or bonded together with a polymer binder to achieve thermal conductivities that are only slightly higher than their monolithic counterparts. Resorcinol and formaldehyde were mixed in a 1:2 molar ratio, distilled water was used as a diluent to control the overall reactant concentration, and sodium carbonate was added as a base catalyst. After stirring to form a homogeneous solution, the mixture was poured into glass bottle, sealed and cured at elevated temperature. For solutions containing 5wt% reactants, the sol-gel polymerization was carried out for 5h at 80℃. An inverse emulsion polymerization was used to produce gel particles that we refer to as microspheres. In a glass reaction kettle, 1l of cyclohexane(or toluene, xylene) was heated to 70℃. Approximately 250ml of the RF solution was slowly added to the cyclohexane with agitation. The RF solution was dispersed into spherical droplets throughout the cyclohexane. After the inverse emulsion had been heated for 24-48 h, the agitation was stopped and the spherical gel particle allowed to settle. Cyclohexane was decanted from the reaction kettle and replaced with acetone. The particle size controlled by emulsification conditions. Their size depend upon the agitation rate, the amount of surfactant and the type of oil.

REFERENCES

1. Pekala, R. W., *J. Mater. Sci.*, **24**, 3221 (1989).
2. Hümmer, E., Lu, X., Rettelbach, Th., and Fricke, J., *J. Non-Cryst. Solids*, **145**, 211 (1992).
3. Lu, X., Caps, R., Fricke, J., Alviso, C. T., and Pekala, R. W., *J. Non-Cryst. Solids*,**188**, 226 (1995).

Preparation of Very Small and High Surface Charged Latex Particle Using Alkali-Soluble Random Copolymer

Doug-Youn Lee and Jung-Hyun Kim

Alkali-soluble random copolymer(ASR), poly(styrene/alpha-methylstyrene/acrylic acid) [Mn: 4,300, acid number: 190], was used as a polymeric emulsifier in the emulsion polymerization of styrene(St) and methyl methacrylate(MMA) respectively. The formation of aggregates in aqueous solution and the effects of neutralization degree of ASR in the emulsion polymerization were investigated.

ASR could form aggregates like micelles and the size and solubilization ability of the aggregates were strongly dependent on the degree of neutralization and ionic strength. By increasing degree of neutralization of ASR to 100%, the size and solubilization ability of the aggregates decreases. The excess alkali over the 100% neutralization of ASR results in the more effective aggregation of the ASR chains. The PS and PMMA latexes prepared using ASR showed very small particle size[ca. 40nm] and high surface charge due to significant chain transfer reaction of ASR. The PS latexes showed monodispersed particle size distribution. However, the particle size distribution of PMMA latexes became broader as the neutralization of ASR increased. The effect of water solubility of the monomer and the neutralization degree of ASR on particle formation mechanism was the main factor for explaining the particle size distribution. The efficiency of ASR aggregate will differ for different degree of neutralization of ASR and will be the factor determining the particle nucleation mechanism and the breadth of the particle size distribution in batch polymerization.

REFERENCES

1. Ping-Lin Kuo et al, *J. of Polymer Sci.*, Part A: Polm. Chem., 31, 99 (1993).
2. Ping-Lin Kuo et al, *J. of Applied Polymer Sci.*, 47, 1295 (1993).
3. K. Wang, in "Water-Soluble Polymers," ed. by Butler & Zhang, ACS Symp. Ser. 467, 218 (1991).
4. Myers, Surfactant Science and Technology, VCH Publishers, 81 (1988).
5. S. Dune, in Emulsion Polymerization, ed. by Irja Piirma, Academic Press, 221 (1982).

Molecular Weight Distribution of Free Radical Bulk Terpolymerization of α-Methyl Styrene/Styrene/Acrylic Acid in CSTR: Experimental Analysis and Model Simulation

Byoung-Jo Lee, Doug-Youn Lee, and Jung-Hyun Kim

The free radical bulk terpolymerization of α-methyl styrene/styrene/acrylic acid in a continuous stirred tank reactor(CSTR) was studied theoretically and experimentally over ranges of temperature, residence time and initiator concentrations. Molecular weight and molecular weight distributions of synthesized polymers were measured using a gel permeation chromatography.

The main purpose of the present work is to examine the possibility of synthesizing such α-methyl styrene/styrene/acrylic acid terpolymer with the low molecular weight and narrow molecular weight distribution and estimate the influence of process variables on the molecular weight distribution. The mathematical model of molecular weight distribution in CSTR was built using the 'instantaneous property method' and Arrhenius relationships for the reaction rate parameters. Two different models were established to predict the molecular weight distribution of the terpolymer based on simple and complex kinetics. The chain transfer phenomena was considered in the complex kinetics model. The effects of the other process variables were included in the mathematical models.

The molecular weights of the products decreased as the reaction temperature, the residence time, and initiator concentration increased. The complex kinetics model showed better agreement with the molecular weight distribution of the terpolymer product in CSTR than the simple kinetics model. The agreement between the experimental and calculated molecular weight distribution suggested that the 'instantaneous property method' was good technique to investigate the molecular weight distribution of terpolymer in CSTR.

REFERENCES

1. Hidetaka Tobita, *Macromolecules*, **28**, 5119 (1995).
2. L.K. Kostanski and A.E. Hamielec, *POLYMER*, **35**, 4168 (1994).
3. Hidetaka Tobita and Archie E. Hamielec, *POLYMER*, **32**, 2641 (1991).
4. J.P. Congalidis, J.R. Richards and W.H. Ray, *AIChE Journal*, **35**, 891 (1989).

Effects of Surface Charge on Grafting Efficiency of Acryl-modified Water-based Polyurethane Dispersions

Il-Hyuk Kim and Jung-Hyun Kim

Water-based polyurethane(PU) dispersions have received considerable attention in the past few decades due to their successful applications in coatings and adhesives. A water-based PU dispersions are binary colloidal systems in which PU particles are dispersed in a continuous water phase. Generally, the water-based PU dispersion can be produced by incorporating hydrophilic groups into the main polymer chains.

Monodispersed PU particles were prepared by neutralization emulsification method. The grafting efficiency of the reaction of PU and acryl-monomer with different surface charge was investigate. PU dispersions were prepared by polyaddition of isophorone diisocyanate(IPDI) to poly(propylene glycol)(PPG), dimethylolpropionic acid(DMPA), and n-methyl-2-pyrrolidone(NMP), followed by neutralization of pendant COOH groups with triethylamine(TEA). Methyl methacrylate(MMA) and hydroxy ethyl acrylate(HEA) were used as acrylic monomer. Ammonium persulfate(APS), Sodium lauryl sulfate(SLS), and Triton-X405 were used. Buffer was used to control the surface charge during the polymerization of acrylic monomers. Grafting efficiency was investigated according to the degree of neutralization by changing mole ratio of TEA to DMPA. The results showed that the grafting efficiency of HEA monomer was higher than that of MMA monomer. In the case of polymerization of MMA, the grafting efficiency decreased as much as dissociated -COOH, -OH goups. In the case of HEA, however, the grafting efficiency increased.

REFERENCES

1. T. R. Earnest and W. J. Macknight, *J. Polym. Sci.* Macromol. Rev., **16**, 41 (1981).
2. D. Dieterich, W. Kerberle, and H. Witt, *Angew. Chem. Int. Ed.*, **9**, 40 (1970).
3. R. E. Tirpak and P. H. Makusch, *J. Coatings Technol.*, **58**, 738 (1986).
4. D. Dieterich, *Prog. Org. Coatings*, **9**, 281 (1981).
5. P. H. Markush, U. S. Patent 4, 408, 008 (1981).

Structural Morphology Developments in the Interfacial Phase of Heterocoagulated Composite Particles : Dynamic Mechanical Measurements

- *Polymer Gels and Networks, accepted* (1996)

Young-Jun Park, Hyun-Jae Ha, and Jung-Hyun Kim

ABSTRACT The dynamic mechanical properties of polymeric composites composed of poly(methyl methacrylate) continuous-phase and various inclusion types of heterocoagulated composite particles were investigated in order to relate them to the morphology of shell region of composite particles. Using heterocoagulation process, large particles were encapsulated with various types of small particles ; (1) conventional linear type polymer particles, (2) cross-linked polymer particles, (3) reactive polymer particles capable of forming crosslinked structure, whereby the interfacial properties of the composite become modified. These composite particles were subsequently annealed to form continuous shell region and then mixed with matrix particles. It showed that chain diffusion movement of the small particles having different chain characteristics influences on the network formation being formed at the interfacial shell region. The ability of maintaining interfacial domain structure depends on the degree of network formation.

Synthesis of Resorcinol/Formaldehyde Organic Aerogels by Low Temperature Supercritical Drying Process

– *Korean J. Material Research, accepted* (1996)

Jae-Hwa Song, Hae-Joon Lee, and Jung-Hyun Kim

ABSTRACT Organic aerogel, with large inner surface(600 ~ 1000m^2/g) and ultrafine pore structure(≤100nm), was prepared by sol-gel process. The aerogel was prepared by condensation polymerization of resorcinol and formaldehyde in an aqueous media followed solvent extraction using supercritical drying process without changing its structure. The

effects of the reaction conditions, such as the amount of solids content (2~5%), on the final properties of aerogel were investigated. Initial reaction conditions were found to be important factor to the properties of aerogels, especially surface area and pore size. Also, in order to investigate the thermal properties of aerogel, surface characteristics was analyzed in the range of 100~300℃. As temperature rose, the pore size was increased and the surface area was reduced.

Adsorption of BSA on Highly Carboxylated Microspheres-Quantitative Effects of Surface Functional Groups and Interaction Forces

- *J. Colloid and interface Sci.*, *177*, p613-620 (1996)

Jeong-Yeol Yoon, Ham-Yong Park, Jung-Hyun Kim, and Woo-Sik Kim

ABSTRACT In order to elucidate the relations between the amount of surface functional groups and interaction forces, BSA adsorption experiments were performed, using highly carboxylated PS/PMMA microspheres as well as conventional ones. Two kinds of interaction forces were considered in this study, hydrogen bonding and hydrophobic interactions, while ionic interactions were assumed to be small or constant. Hydrophobic interactions were dominant in the low N_c (number density of surface carboxyl groups) region, below 1 carboxyl group nm^{-2}, and were relatively sensitive to pH, while hydrogen bonding was dominant in the high N_c region, above 2 carboxyl group nm^{-2}, irrespective of pH. The transition region between these two interaction forces was 1-2 carboxyl groups nm^{-2} on the surface of a microsphere. When comparing the two extremes of hydrophobic interaction and hydrogen bonding, the latter was stronger, which was different from earlier studies. It can be explained that the conventional carboxylated microspheres do not have enough carboxyl groups on their surfaces. Adsorption constant K diminished as N_c increased, which means that the affinity itself is reduced by hydrogen bonding. Adsorbed layer thickness calculated from the C_m (adsorbed amount in equilibrium) were 4.66-7.08 nm; this means that the BSA molecules exist between the side-on and end-on mode.

Process for the Preparation of Conducting Polymer Composites (I) : Effect of the Porosity on the Conductivity

- *J. Korean Ind. & Eng. Chemistry*, 7, 2, p393-400 (1996)

Suk-Hye Son, Young-Jun Park, and Jung-Hyun Kim

ABSTRACT The conducting polymer composites were prepared by imbibing the porous particle with an $FeCl_3$ oxidant solution, drying the imbibed porous particle, and imbibing again with pyrrole solution for polymerization to take place in the pore. The conductivity of the porous composite particles, was higher than that of nonporous particles. Also, the conductivity of composite was increased with increasing specific surface pore volume and area of the host porous particles since the degree of formation of conducting polymer in the pore increased.

Process for the Preparation of Conducting Polymer Composites (II) : Effect of Polymerization Parameters on Conductivity

- *J. Korean Ind. & Eng. Chemistry, accepted* (1996)

Suk-Hye Son, Young-Jun Pak, and Jung-Hyun Kim

ABSTRACT The conducting polymer composites were prepared by imbibing the porous particle with the $FeCl_3$ oxidant solution, drying the imbibed porous particle, and imbibing again with pyrrole solution for polymerization to take place in the pore of porous particles. The effect of synthesis conditions on the conductivity of composite polymers were investigated. It was found that the conductivity of composite polymers was dependant on the concentration of pyrrole monomer, nature of the oxidants and solvents used for the oxidant and pyrrole, which influence the degree of penetration/distribution of polyprrole in the composite and reaction of dopant with pyrrole.

LEIDEN COLLOID AND INTERFACE PHYSICS GROUP

The staff members of the Leiden Colloid and Interface Group are

- Prof. dr. D. Bedeaux
- Dr. ing. G.J.M. Koper
- Dr. E.M. Blokhuis

Furthermore, there is a varying number of post-docs, graduate (PhD) students and undergraduate students.

Research topics:

- *Polymers and Polyelectrolytes*
    - **Proton binding to complex materials,** Koper
- *Microemulsions and Dispersions*
    - **Aggregation and phase behaviour of droplet phase microemulsions,** Smeets, Sager, Koper, Bedeaux
    - **Dendrimer surfactants,** Sager, Koper, Bedeaux
    - **Dielectric and elecro-optical properties of "living polymers",** Cirkel, Cavaco, Koper
    - **Thermodynamics of small systems,** Koper
- *Statistical Mechanics of Surfaces*
    - **Phase behaviour of the water/AOT/oil system,** Sager, Blokhuis, Koper
    - **Optical properties of particles at surfaces,** van der Zeeuw, Koper, Bedeaux
    - **Statistical thermodynamics of interfaces,** Groenewold, Blokhuis, Bedeaux
    - **Irreversible thermodynamics of surfaces,** Fujitani, Bedeaux
    - **Wetting phenomena of simple and complex fluid interfaces,** Blokhuis, Bedeaux
    - **Rheology of the polymer-air interface,** Sagis, Bedeaux

Proton binding to complex materials

Koper

aim: to develop a method to systematically describe the binding properties of complex materials such as polyelectrolytes, proteins, humics, etc. for protons and other small ions. This research is performed in close collaboration with Borkovec of the ETH in Zürich.

progress: we have performed potentiometric titration experiments on dilute aqueous poly(propylene imine) dendrimers. The obtained curves compare well with those predicted by our Ising model description using parameters taken from data on simple molecules. In collaboration with the Laboratory of Organic Chemistry of the Technical University Eindhoven (van Genderen and Meijer) we have also performed natural abundance ^{15}N-NMR titrations on these molecules. These curves also compare well with the model predictions, albeit with different parameters as is expected because of the high concentrations required for the NMR-experiments.

plans: In collaboration with BASF in Ludwigshafen (Horn) we will perform potentiometric titration of various branched polyelectrolytes and compare those to our model predictions.

Aggregation and phase behaviour of droplet phase microemulsions

Smeets, Sager, Koper, Bedeaux

aim: To obtain a better understanding of aggregation processes in microemulsions. The aggregation behaviour of e.g. AOT water-in-oil microemulsion droplets has been investigated quite intensively by a variety of methods over the last decade. Nevertheless there is still no clear physical picture available and the driving force for aggregation remains unknown. We address droplet aggregation in the same framework as the (temperature) evolution of phases occurring in ternary mixtures of surfactant, water and oil; namely by looking at the changes of the properties of the interfacial film separating water and oil domains. For this purpose we systematically modify the interfacial film, by e.g. changing the oil, addition of SDS and salt, and compare the onset of aggregation with changes in the overall phase behaviour, e.g. shifts in the upper phase boundary of the ater-in-oil microemulsion phase.

progress: we obtained a set of data for the system water/(AOT/SDS)/iso-octane using mainly viscometry to investigate droplet aggregation, while preliminary SANS and SAXS measurements have been carried out at Risø (Roskilde, Denmark) and DESY (Hamburg, Germany). Addition of the more hydrophilic SDS to an interfacial AOT film leads to changes in the spontaneous curvature in the way that the interface will be less curved towards the oil. Both the upper phase boundary as well as the aggregation onset are shifted linearly to lower temperatures as the SDS-concentration is increased.

plans: we wish to complete the SDS data set by dielectric permittivity and conductivity measurements. The aim is here to find the link between droplet clustering and the strong increase in the conductivity observed in water-in-oil microemulsions. SAXS measurements are planned to look at the structural changes in the water-in-oil microemulsions as a function of temperature for different oils and addition of SDS.

Dendrimer surfactants

Sager, Koper, Bedeaux

aim: dendrimer surfactants, consisting of a polystyrene chain and a dendrimer "head", are a very interesting class of new surfactants since they present a link between ordinary surfactants and block co-polymers. They posess the size of a block co-polymer but the geometrical shape of an ordinary surfactant. A further advantage is the possibility to change the geometry of the head-group by binding different generations of the dendrimer to the polystyrene chain. This is work is performed in collaboration with Elissen-Román and Meijer (TU, Eindhoven).

progress: so far we have looked at solutions of the low-generation dendrimer surfactants in oil and determined a preliminary phase diagram. Freeze-fracture TEM and dynamic light scattering experiments have been carried out to confirm earlier measurements by Joosten (DSM Research, Geleen). So far it is not clear whether they do form reversed micelles in the oil or whether liquid crystalline phases form before micellisation occurs.

plans: for further investigations vapor pressure osmometry measurements are planned at Leiden.

Dielectric and elecro-optical properties of "living polymers"

Cirkel, Cavaco, Koper

aim: Lecithin dissolved in an apolar solvent with minute amounts of water forms giant wormlike micelles whose properties are very similar to those of equilibrium polymers (living polymers). The complication of the dynamics of these systems consists of the additional time scale related to the breakage and recreation of the polymers. We study the dynamics of these dispersions with two complementary techniques: dielectric spectroscopy and electro-optic birefringence.

progress: having developed a method to account for electrode polarization in dielectric spectroscopy, we performed a systematic analysis of the dielectric response of lecithin microemulsions, thereby varying lecithin concentration and water to lecithin ratio. The preliminary results indicate a strong correlation with viscometric data from our collaborators at the Institut für Polymere at the ETH in Zürich (Cavaco and Schurtenberger). Both sets of experimental data seem to indicate, in contrast to the present consensus, that branching of the polymers is an important process.

plans: to complement the dielectric spectroscopy analysis with a systematic electro optic birefringence analysis to further investigate the influence of branching. The recently developed instrument for electro-optic light scattering will be used to obtain more structural information on the system. Furthermore the effect of electric field on the polymer size distribution will be investigated.
Based on our current knowledge of the water/lecithin/oil system, we proposed to investigate *organogels as electrorheological fluids* for the SON/STW program *Supramolecular Chemistry & Technology*.

Thermodynamics of small systems

Koper

aim: to establish thermodynamic relations for systems containing small entities such as droplet phase microemulsions and nucleating systems. This work is performed in close collaboration with Reiss of the UCLA.

progress: we have studied the Kelvin relation, e.g. an equilibrium between a two-component drop in which the solute is involatile and the vapor of the solvent component. Using the theory of the thermodynamic potential we verify that regimes of both stable and unstable equilibrium exist. This also allowed us to study the fluctuations in drop size and derive the critical-like behaviour that occurs at the boundary between the stable and the unstable regime.
We studied the constant pressure ensemble and the volume scale that must be introduced in order to represent the corresponding partition function as a dimensionless integral. Also the close connection between the constant pressure ensemble and Einstein fluctuation theory is analyzed.

plans: the constant pressure ensemble is widely used in numerical simulations. We will try to demonstrate the importance of the volume scale involved for these necessarily small systems.

Phase behaviour of the water/AOT/oil system

Sager, Blokhuis, Koper

aim: a special feature in the phase diagram of e.g. water/AOT/decane is the appearance of a two-phase region, with a critical point facing the oil-surfactant side of the Gibbs triangle, in which two oil-continuous droplet phases of nearly the same radius are in equilibrium with each other. The transition from a one-phase water-in-oil microemulsion into these two coexisting droplet phases has been intensively investigated by mainly SAXS or SANS measurements and has been described in the literature in terms of a liquid/gas transition. However, the full phase diagram, evolution of the phases with temperature, has not yet been determined and understood. This work is performed in close collaboration with Strey (MPI, Göttingen).

progress: we determined the temperature evolution of the phases located at the oil corner of the Gibbs triangle for the water/decane/AOT system. If one starts with a solution of reversed micelles in the oil (AOT/decane side) and adds water, the evolution of phases appearing with increasing temperature changes with the amount of water added. At lower water content one observes at high temperatures a phase transition from the water-in-oil droplet phase, L_2, into two oil-continuous droplet phases, L_2'' concentrated in droplets and L_2' dilute in droplets. With increasing water content the transition is shifted to lower temperatures and at a certain water content a lamellar phase, L_α, appears at higher temperatures leading to the following phase sequence as a function of temperature: $L_2 \rightarrow L_2'' + L_2' \rightarrow L_\alpha + L_2'' + L_2' \rightarrow L_\alpha + L_2'$. On increasing the water content further the coexistence region ot the $L_2'' + L_2'$ becomes smaller in temperature and finally disappears leading to the transition $L_2 \rightarrow L_\alpha + L_2'$. At high water content a water-continuous droplet phase shows up at high temperatures. In this case one observes the following sequence as temperature is increased: $L_2 \rightarrow L_\alpha + L_2' \rightarrow L_\alpha + L_1 + L_2' \rightarrow L_1 + L_2'$. A similar phase evolution has been observed by Penders and Strey on the water side of the Gibbs triangle for a nonionic surfactant upon addition of a long chain alcohol. In their case the phase evolution can be explained by changes in the natural curvature and the rigidity of the interfacial surfactant film. On addition of alcohol the interfacial film becomes more hydrophobic since a certain amount of the alcohol will go into the interface and therefore less curved towards water and the rigidity increases. As a result the cloud point temperature comes down with increasing amount of alcohol until bilayer phases, $L_\alpha + L_3$, start to form leading to a quite complicated phase diagram.

plans: in order to show the full analogy between the nonionic surfactant system on the water side upon addition of alcohol with the AOT system on the oil side upon addition of water, more phase diagram studies are planned for different amounts of added salt. Upon addition of water the electrostatics of the AOT head groups changes leading to a change in the natural curvature, less curved towards oil, and an increase in the rigidity constant. We expect to find the L_α phase also in the case of AOT if a small amount of salt is added.

Optical properties of particles at surfaces

van der Zeeuw, Koper, Bedeaux

aim: to compare the predictions of optical theories for optically rough thin films with experimental results obtained by means of scanning angle reflectometry. Films consisting of latex particles, in the size range from 50 to 500 nm, are used as model system. This work is performed in close collaboration with the Institut Charles Sadron in Strasbourg (Mann and Schaaf).

progress: the effect of size polydispersity on the reflectivity of latex particles adsorbed on glass surfaces has been investigated both experimentally and theoretically. The main result is that size polydispersity does not affect the particle size as inferred from experimental reflectivity curves whereas the surface coverage is affected. This led us to conclude that scanning angle reflectometry is a suitable technique for particle sizing.
Also in collaboration with the Institut Charles Sadron in Strasbourg, we have studied structural changes in antigen-antibody layers adsorbed on silica surfaces. With this system we have been able, as far as we know *for the first time*, to obtain information on the *structure* of the layer: the layer is more dense away from the silica surface. This demonstrates the added value of scanning angle reflectometry versus (fixed angle) ellipsometry.

plans: the size range attainable with latex particles is limited and therefore we shall turn our attention to smaller particles: dendrimers. Through a collaboration with DSM Research (Geleen) a considerable size range of poly(propylene imine) dendrimers is at our disposition. After extensive characterization we shall investigate dendrimer films adsorbed on glass surfaces.

Statistical thermodynamics of interfaces
Groenewold, Blokhuis, Bedeaux

aim: to establish thermodynamic relations for systems involving curved interfaces,

progress: the surface free energy of electrolyte solutions near curved interfaces has been calculated along the lines of a similar calculation performed by Onsager and Samaras for flat interfaces. The results may be used to gain more insight in microemulsions involving nonionic surfactants.

plans: to calculated the free energy of confinement of electrolyte solutions.

Irreversible thermodynamics of surfaces
Fujitani, Bedeaux

aim: to gain understanding of mass, energy, and charge transport along and through a surface between phases using non-equilibrium thermodynamics. This work is performed in close collaboration with Kjelstrup (NTNH, Trondheim).

progress: subjects analyzed in detail were the occurrence of temperature jumps across electrode surfaces, the "overpotential" as a surface singularity of the electric field as well as the application to alluminum electrolysis cells.

plans: future work will focus on e.g. thermal osmosis, mass and charge transport through membranes and the analysis of the contribution of the electrode surfacess to the emf of a cell.

Wetting phenomena of simple and complex fluid interfaces

Blokhuis, Bedeaux

aim: theoretical investigation of wetting phenomena of simple and complex fluid interfaces.

progress: attention has focussed on the following topics: structure of the three phase region near the wetting transition, in collaboration with Widom, Perkovic, Han and Tessler (Cornell University); three phase region between amphiphilic layers; bending energy of amphiphilic layers; formation of wetting layers; influence of the intermolecular potential on the surface tension, in collaboration with Zollweg (Cornell University) and Holcomb (NIST, Boulder); influence of gravity on the shape of a liquid droplet on a solid substrate.

plans: in the near future attention will focus on the following three topics: description of wetting of vesicles on a solid substrate, the influence of the intermolecular potential on the structure and tension of a fluid interface near a wetting transition, in collaboration with van Giessen (Cornell University), and the incorporation of the bending energy in the description of a fluctuating interface.

Rheology of the polymer-air interface

Sagis, Bedeaux

aim: In continuum mechanics a phase interface is usually represented as a two-dimensional surface, or dividing surface, that is sensibly coincident with the phase interface. The material behavior of the phase interfaces can be characterized by associating excess rheological parameters with these interfaces. In the "Newtonian limit" the behavior can be characterized by the surface shear viscosity and a surface dilatational viscosity. For interfaces that exhibit viscoelastic behavior, additional parameters like for example a surface elasticity have to be taken into account. The rheological properties of a phase interface can have an appreciable influence on a system. They can effect the dampening of turbulence near a free surface. The surface dilatational viscosity and surface elasticity have been shown to be important parameters in the thinning of thin liquid films. There is evidence that the surface rheology is also an important factor in surface instabilities in polymer processing. Very little work has been done to develop theories for the calculation of surface viscosities. The existing work limits itself to the calculation of viscosity profiles in narrow pores, using an extension of the Green-Kubo formalism for linear transport coefficients.

The objective of this research is to develop a theory for the calculation of the surface shear viscosity for a planar liquid-vapor interface. First, the liquid-vapor interface of a pure Lennard-Jones fluid will be considered (because of its simplicity). Subsequently the theory will be extended to the liquid polymer-air interface.

progress: We have developed a theory for the calculation of the surface shear viscosity of a planar liquid-vapor interface. The theory is an extension of the generalized hydrodynamics formalism, originally developed for the calculation of linear transport coefficients in isotropic bulk fluids. We have derived an expression for the surface shear viscosity in terms of the first four moments of the autocorrelation function of the transverse parallel velocity. We have calculated the specific form of these moments for a planar liquid-vapor interface, for a simple fluid.

plans: The theory is currently being used to calculate the surface shear viscosity of the liquid-vapor interface in a Lennard-Jones fluid. The results of these simulations will be published in a forthcoming article. An extension of the theory to the liquid polymer-air interface is being prepared.

CONTRIBUTION FROM THE DOW CHEMICAL COMPANY

The following paper was presented at the IUPAC Macro Seoul '96 in Korea in October, 1996 and will be published in IUPAC Symposium Series - "Macromolecular Symposia".

THE THERMAL BEHAVIORS OF LATEXES: WET LATEX Tg'S

Do Ik Lee*, Lynn C. Walker, Charles S. Kan
Emulsion Polymers Research, The Dow Chemical Company,
Midland, Michigan 48674, U.S.A.

Abstract: The thermal behaviors of latexes were studied by using MicroCal MC-2 Scanning Calorimeter which is a differential scanning micro-calorimeter capable of handling fluids under pressure. The MC-2 unit was found to be uniquely capable of measuring not only the glass transition temperatures (Tg's) of wet latexes, but also the extent of annealing (enthalpy relaxation) that has a profound impact on the deformability of latex particles and, in turn, the film formation of latexes. The effects of polar monomers, the neutralization of carboxylated latexes, and coalescing agents on the wet latex Tg's were also studied.

INTRODUCTION

Most applications of latexes require film formation. For this reason, the mechanisms for latex film formation (1-8) have been extensively studied. For the measurement of the minimum film formation temperatures (MFFT's) of latexes, a minimum film formation temperature apparatus consisted of a temperature gradient plate and a cover with air flow is widely used. For correlation, a differential scanning calorimeter (DSC) is concurrently used to determine the glass transition temperatures (Tg's) of dry latex polymers, and a dynamic mechanical spectrometer (DMS) is also used to measure both the Tg's and viscoelastic properties of dry latex polymers. Although these measurements such as Tg, G' (storage shear modulus), G" (loss or viscous shear modulus), and tan δ (G"/G') are correlated with the MFFT's of latexes, it was thought that the Tg's of wet latexes would be better correlated with their MFFT's. In other words, the film formation of latexes was thought to be more directly related to their wet latex Tg's rather than to their dry polymer Tg's during the film formation. Scatena, Sanmartin, and Zilio-Grandi (9) investigated the effect of water on the Tg of a bulk-prepared polyvinyl acetate by using a Perkin-Elmer DSC and found that its Tg decreased at a rate of 6° C/% water up to 4% water content. Recently, Heymans and Daniel (10) studied the Tg's and MFFT's of a series of vinyl alcanoate (VeoVa 9 and VeoVa 10)-vinyl acetate copolymer latexes by using a Perkin-Elmer DSC and found that their MFFT's were better correlated with their wet latex Tg's than with their dry polymer Tg's. In the present study, we have used MicroCal's MC-2 Scanning Calorimeter (11), a differential scanning micro-calorimeter capable of handling fluids under pressure, to study the thermal behaviors of latexes, especially to determine the Tg's of wet latexes. We have found that the MC-2 micro-calorimeter is indeed very capable of measuring the Tg's of wet latexes. In addition, we have been able to measure the extent of annealing of latex polymer particles as a function of time, the effect of the neutralization of carboxylated latexes on their wet latex Tg's, the effect of coalescing agents on the wet latex Tg's, etc. This paper reports our studies on the thermal behaviors of latexes made by using the MicroCal MC-2 Scanning Calorimeter.

EXPERIMENTAL

Figure 1 shows a schematic drawing of the MicroCal MC-2 Scanning Calorimeter. The MC-2 utilizes two cells, sample and reference, of 1.2 ml machined from tantalum. The cells are permanently located in close proximity in the geometric center of an adiabatic shield. Both cells are carefully matched for mass and volume and supported by capillary tubes extending to the top of the instrument. The cells are totally filled with dilute solution, without head space. Nitrogen gas pressure, 15 to 60 psig, is maintained on a common header external to the calorimeter. This design allows experimental data to be measured above the normal boiling point of the solvent. When a temperature induced process takes place in the sample cell, a temperature difference is detected via a 100 junction wire-wound thermopile that provides an electrical signal to an amplifier and control unit which in turn modulates power into the sample cell to minimize the off-balance signal. The calorimeter thus records the difference in electric power, which is directly proportional to the difference in the heat capacity, between the sample and water-filled reference cell. These devices are ideally suited to measurements of the apparent specific heat (ΔCp) of a system as a function of temperature. For measurements, all latex samples were diluted to 4-8% solids. All scans were run at 0.5° C/min.

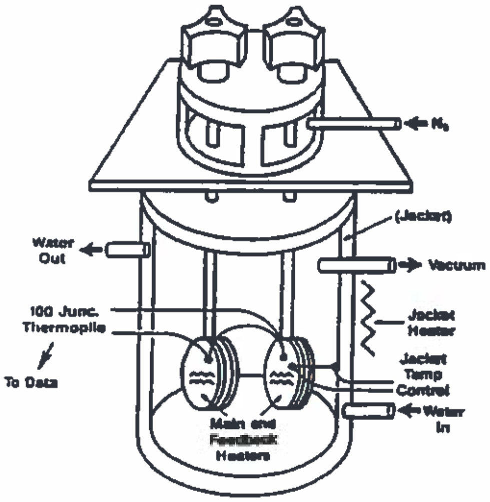


Figure 1. Schematic of MicroCal MC-2 Scanning Calorimeter (11)

RESULTS AND DISCUSSION

Wet and Dry Latex Tg's and MFFT's of a Polyvinyl Acetate (PVAc) Latex - PVAc latexes are well known to form continuous films at room temperature in spite of the fact that their dry latex polymer Tg's are well above room temperature. These unique film-forming behaviors of PVAc latexes have been understood in terms of water plasticization currently referred to as hydroplasticization. For this reason, we have decided to determine the wet Tg of a PVAc latex by using the MC-2 differential scanning micro-calorimeter and then, to compare its wet latex Tg with its dry polymer Tg measured by a DuPont DSC 2100. Figures 2 and 3 show a MC-2 scan for a PVAc latex and a DuPont DSC scan for a dry PVAc latex polymer, respectively. A large endotherm near the transition temperature shown in Figure 2 is due to the annealing of latex polymer particles (enthalpy relaxation) which will be discussed later. As shown in Figures 2 and 3, the wet and dry polymer Tg's of a PVAc latex are 13.1° C and 29.3° C, respectively. As expected, its wet latex Tg is lower than room temperature. The MFFT of this particular PVAc latex was found to be 21° C. It is interesting to note that its MFFT was higher than its wet latex Tg. This finding is not surprising because the MFFT's of hydrophobic latexes such as styrene-butadiene (S/B) latexes are a little higher than their dry latex polymer Tg's.

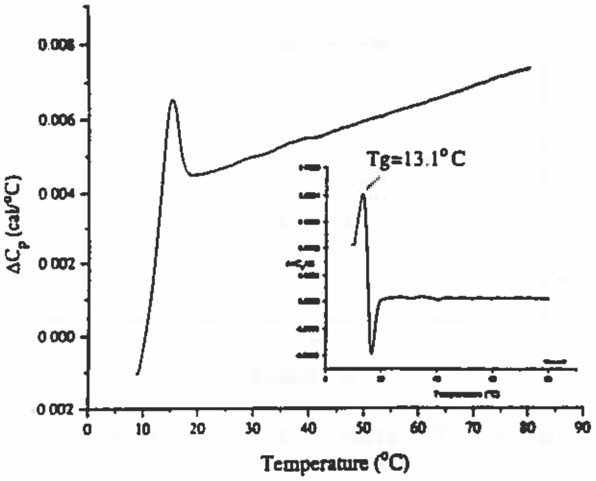


Figure 2. MC-2 scan for a PVAc Latex

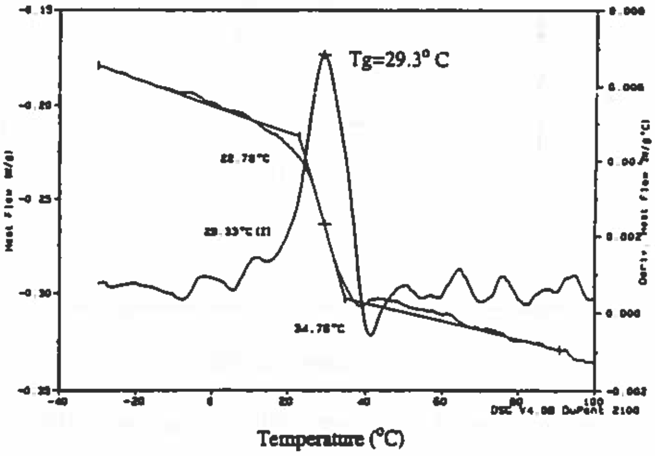


Figure 3. DSC scan for a dry PVAc Polymer

The Effects of Polar Monomers and Neutralization on Wet Latex Tg's - Table 1 shows the effect of monomer polarity on the wet latex Tg's of various latexes containing different polar monomers and their dry and wet latex Tg differences. Table 1 clearly shows that polar monomers depress wet latex Tg's and increase the dry and wet latex Tg differences. Figure 4 shows the effect of the neutralization of a carboxylated acrylic latex on its wet latex Tg. The ionization of carboxylic groups by neutralization lowers the wet latex Tg because of the greater water plasticization.

The Effect of Coalescing Agents on Wet Latex Tg's - Figure 5 shows the effect of a coalescing agent on the wet latex Tg's. It has been found that the MC-2 is especially suited to studies on the thermal behaviors of latex blends and the competitive plasticization of blend latexes, as shown in Figure 5. Table 2 shows the effect of a coalescing agent, Texanol*, on the wet Tg's of acrylic and styrene-acrylate latexes. Texanol is slightly more efficient for styrene-acrylate latexes.

Table 1. Dry latex polymer Tg's by DSC, wet latex Tg's by MC-2, and dry and wet Tg differences (ΔTg's) of latexes containing different polar monomers

Latex composition	DSC Tg, °C	MC-2 Tg, °C	ΔTg, °C	Comments
54MMA/42BA/4AA	34	17	17	BA & 4 AA
54MMA/42EA/4AA	47	25	22	EA & 4 AA
57MMA/42EA/1AA	44	29	15	EA & 1 AA
54S/42BA/4AA	37	31	6	S
44S/10MMA/42BA/4AA	29	20	9	S/MMA
34S/20MMA/42BA/4AA	30	19	11	S/MMA
24S/30MMA/42BA/4AA	28	18	10	S/MMA
14S/40MMA/42BA/4AA	31	17	14	S/MMA
54MMA/42BA/4AA	37	17	17	MMA

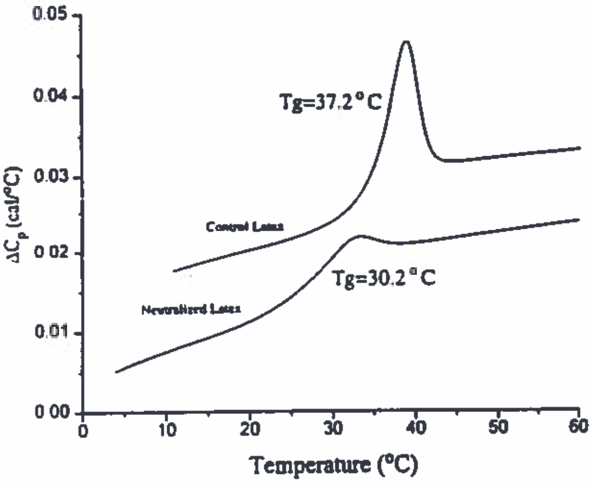


Figure 4. The effect of neutralization on wet latex Tg

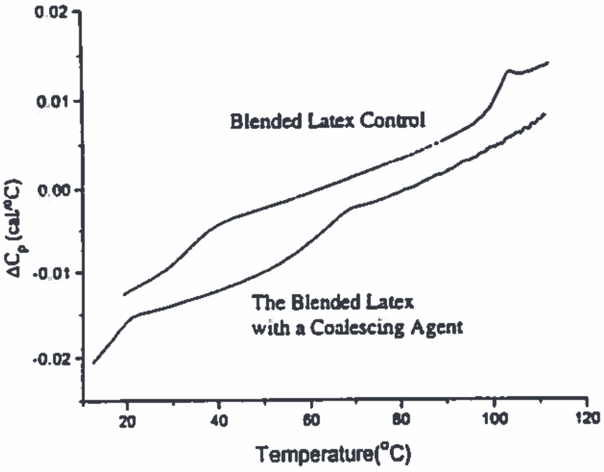


Figure 5. The effect of a coalescing Agent

Table 2. The effect of Texanol* on wet latex Tg's: MC-2 Tg's, ΔTg's and ΔTg's/% coalescent

Latex composition	Texanol level, %	MC-2 Tg, °C	ΔTg, °C	ΔTg/% coalescent
54MMA/42EA/4AA	0	25	0	0
	1.93	21	4	1.84
	3.89	17	8	2.16
	5.14	14	11	2.14
				Av. 2.05
49S/47EA/4AA	0	40	0	0
	1.96	35	5	2.55
	3.83	31	9	2.35
	6.77	25	15	2.16
				Av. 2.35

Texanol*: 2,2,4-Trimethylpentane-1,3-diol, isobutyric ester

The Effect of Annealing on Wet Latex Tg's and MFFT's - Figure 6 shows the first, 2nd, 3rd, 4th and 5th MC-2 scans for a styrene-butadiene (S/B) latex. The first scan was made on a fresh sample which had been aged for a long time. Thus, this scan represented the thermal behavior of a fully annealed latex sample. It is interesting to note that it shows a large endotherm near its transition temperature. This endothermic behavior was found to be caused by annealing (enthalpy relaxation) (12). The subsequent scans were made on the same sample right after the first scan cycle. These subsequent scans do not show any endothermic behaviors, suggesting that annealing is time- and temperature-dependent. The Tg's of the first and subsequent scans were determined to be 39.0° C and 33.2° C, respectively. It was also found that pre-heating latexes above their Tg's prior to film formation lowered their MFFT's by 4 to 6° C, that is, the MFFT's of fully relaxed, annealed latexes were 4 to 6° C higher than those of their pre-heated, then quickly quenched counterparts. Figure 7 shows the effect of time on the extent of annealing for a carboxylated acrylic latex. The extent of annealing is known to be dependent on both annealing temperature and time (12).

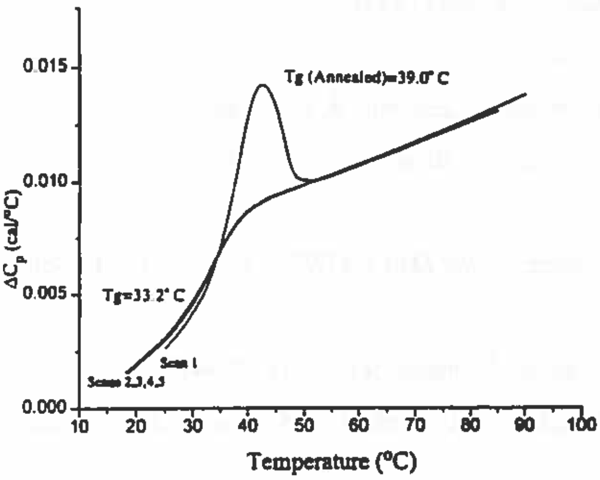


Figure 6. The effect of annealing on the thermal behavior of a styrene-butadiene (S/B) latex

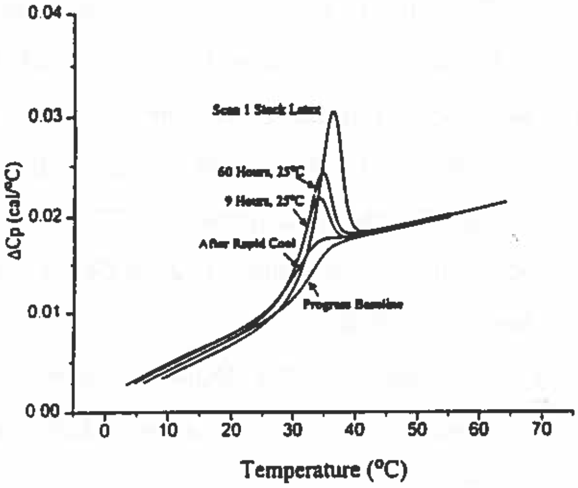


Figure 7. The extent of annealing vs. time for a carboxylated acrylic latex

CONCLUSION

MicroCal MC-2 Scanning Calorimeter has been found to be an excellent differential scanning micro-calorimeter for studying the thermal behaviors of latexes, especially the measurement of wet latex Tg's. The effects of polar monomers, the neutralization of carboxylated latexes, and coalescing agents on wet latex Tg's have been studied. The MC-2 is ideally suited to studying the extent of wet latex annealing by measuring the magnitude of endotherms as a function of both time and temperature. It has been also found that pre-heating latexes above their Tg's would lower the wet latex Tg's and MFFT's. This finding has a significant impact on the use of hard latexes as either film forming binders or non-film forming latexes for a variety of applications.

ACKNOWLEDGMENTS

One of the authors (DIL) would like to thank Dr. Ralph Czerepinski for consultations. Also, the authors would like to thank Mary Chen for some of the experimental data reported in this study.

REFERENCES

(1) R.E. Dillon, L.A. Matheson, E.B. Bradford, *J. Colloid Sci.* **6**, 108 (1951)

(2) G.L. Brown, *J. Polym. Sci.* **22**, 423 (1956)

(3) G. Mason, *Br. Polym. J.* **5**, 101 (1973)

(4) K. Kendall, J.C. Padget, *Int. J. Adhesion and Adhesives* **2**, 149 (1982)

(5) S.T. Eckersley, A. Rudin, *J. Coat. Tech.* **62**, 89 (1990)

(6) M.C. Goh, D. Juhue, O.-M.Leung, Y. Wang, M.A. Winnik, *Langmuir* **9**, 1319 (1993)

(7) P.R. Sperry, B.S. Snyder, M.L. O'dowd, P.M. Lesko, *Langmuir* **10**, 2619 (1994)

(8) F. Lin, D.J. Meier, *Langmuir* **11**, 2726 (1995)

(9) M. Scatena, P. Sanmartin, F. Zilio-Grandi, *Proceedings of the IXth FATIPEC Congress*, Brussels, Sec. 3, 68 (1968)

(10) D.M.C. Heymans, M.F. Daniel, *Polymers for Advanced Technologies* **6**, 291 (1994)

(11) MicroCal, Inc., 22 Industrial Drive East, Northampton, MA 01060, U.S.A., Tel: 413-586-7720; Fax: 413-586-0149

(12) S.E.B. Petrie, *J. Polym. Sci. Part A-2*, **10**, 1255 (1972)

CONTRIBUTION TO THE INTERNATIONAL POLYMER COLLOIDS GROUP NEWSLETTER

Surface Conduction on Latices and other Colloids

J. Lyklema
(work in collaboration with A. van der Linde, M. Minor and A. van der Wal)

Wageningen Agricultural University
Department of Physical and Colloid Chemistry
P.O. Box 38
6700 EK Wageningen

In our previous communication (IPCG, Vol. 27, nr. 1, June 1996) we reported on the relation between the conductivity of latex plugs, K(plug), and the bulk conductivity K^L, if the latter is changed by changing nature and concentration of the electrolyte. A linear relation was found, from the intercept of which the surface conductivity K^σ could be evaluated.

K^σ consists of a diffuse part ($K^{\sigma d}$, described by the Bikerman equation) and a non-diffuse part, $K^{\sigma i}$, accounting for tangential mobility of counterions in the stagnant layer. Because of the hydrodynamic stagnancy, no electro-osmosis takes place and hence simply

$$K^{\sigma i} = \sigma_i^i u_i^i \qquad [1]$$

if σ_i^i is the surface charge density of the counterions in this layer and u_i^i the lateral mobility of these ions. For more than one type of counterion [1] has to be replaced by a sum. As σ_i^i is experimentally accessible (from subtraction of the electrokinetic charge σ^{ek} from the surface charge σ^o, the latter obtainable via titration), [1] in principle offers the possibility of computing the mobility in the inner layer. Intuitively one would expect the ratio u_i^i / u_i^L, where u_i^L is the limiting mobility in bulk, is lower than unity.

Table.

System	Sign of the surface charge	Counterion	u_i^i / u_i^L	Ref.
SiO_2 (Stöber)	–	K^+	0.96	1
α-Fe_2O_3 (haematite)	+	Cl^-	0.70	1
polystyrene latex	–	H^+, Li^+, Na^+, K^+	0.85	2
ibid. + adsorbed PEO	–	H^+	0.60	2
bacterial surfaces	–	Na^+	0.2-0.5, depending on species	3

1. Kijlstra (cited in FICS II, ch. 4).
2. Minor-v.d. Linde (1996)
3. Minor-v.d. Wal (1995)

Our collected experience confirms this. See the collection in the table. Details of the analysis may differ somewhat between the various systems. Generally speaking, the hydrodynamic stagnancy of the adjoining fluid does not drastically impair the mobilities of counterions. This observation is directly relevant for the interpretation of the slip process. It is also noted that the ratio u_i^i / u_i^L is, at least for our latex, independent of the nature of the counterion. It is also conform to our expectation that hairy layers force the counterions to follow a more tortuous path: see the effect of PEO.

We intend to continue this line of research and publish elsewhere about it.

THE UNIVERSITY OF SYDNEY
POLYMER COLLOIDS GROUP
REPORTER: DH NAPPER

K:/3b2/jobs/rapid/r96_130.3d
Datum: 19. 09. 1996 Busse

Macromol. Rapid Commun. 17, *0000–0000 (1996)* 1

Experimental discrimination between competing nucleation theories in microemulsion polymerizations

*Dong Ryul Kim, Donald H. Napper**

School of Chemistry, The University of Sydney, Sydney, NSW 2006, Australia

(Received: July 2, 1996; revised manuscript of August 1, 1996)

SUMMARY:

The particle nucleation processes involved in the microemulsion polymerizations of styrene and methyl methacrylate have been investigated using pyrene fluorescence intensity measurements as a function of conversion. Very distinctive differences were observed between the results for the two different monomers. The styrene fluorescence results were consistent with nucleation occurring within the microemulsion droplets, followed by the subsequent heterocoagulation of the nucleated particles with remaining droplets. The very different methyl methacrylate data were consistent with a homogeneous nucleation mechanism.

Langmuir **1996**, *12*, 3139–3142 3139

Studies of the Validity of the Dye Leaching Method for Investigating Particle Nucleation Mechanisms in Emulsion Polymerizations

Dong Ryul Kim and Donald H. Napper*

School of Chemistry, University of Sydney, Sydney, New South Wales 2006, Australia

Received November 14, 1995. In Final Form: March 18, 1996⊗

It has been proposed that the addition of a tracer dye to a styrene emulsion polymerization system prior to the commencement of polymerization can cast light on the mechanism of latex particle nucleation. It was argued that the dye would be able to be leached out of the resulting latex by dialysis if a micellar mechanism were operative whereas leaching would be precluded if the particles were nucleated by a coagulative mechanism. Experiments to test this proposed method have been reported previously by Pashley and co-workers: they showed that leaching occurred with an oil soluble initiator, thus suggesting a micellar nucleation mechanism, but was not observed if the water soluble persulfate anions were used as the initiator, implying a coagulative nucleation mechanism. It is shown here that the interpretation of such experiments, performed in unbuffered systems, was vitiated by large changes in pH, such as occurs with persulfate anions as the initiator. It was found that, irrespective of the chemical nature of the initiator, dye could be leached from high pH latexes (pH > 8.0) but could not be leached from low pH latexes. Identical results were obtained whether or not the dye was added to the emulsion system prior to the commencement of polymerization or postadded after the latex had been formed. Moreover, the leaching of the dye from a high pH latex could be halted by lowering the pH. The results suggest that considerable caution must be exercised in deducing nucleation mechanisms using the dye leaching method.

21 June 1996

ELSEVIER

Chemical Physics Letters 256 (1996) 51–56

CHEMICAL
PHYSICS
LETTERS

Volume phase transitions of poly(N-isopropylacrylamide) latex particles in mixed water-N,N-dimethylformamide solutions

Peng Wei Zhu, Donald H. Napper *

School of Chemistry, The University of Sydney, Sydney, NSW 2006, Australia

Received 27 December 1995; in final form revised 9 April 1996

Abstract

Volume phase transitions of poly(N-isopropylacrylamide) (PNIPAM) latex particles in mixed water–N,N-dimethylformamide (DMF) solutions were studied at different temperatures and crosslink densities using dynamic light scattering. A collapse-swelling behaviour was observed on the addition of N,N-dimethylformamide to an aqueous dispersion medium. The degree of swelling was found to be dependent on the temperature and crosslink density. The transition between the collapsed state and the swollen state was continuous. The cononsolvency of water and DMF for PNIPAM latex particles has been interpreted in terms of the changes in the interactions between their components.

ELSEVIER

Colloids and Surfaces
A: Physicochemical and Engineering Aspects 113 (1996) 145–153

COLLOIDS
AND
SURFACES A

Interfacial coil-to-globule transitions: the effects of molecular weight

Peng Wei Zhu, Donald H Napper *

School of Chemistry, The University of Sydney, Sydney NSW 2006, Australia

Received 23 October 1995; accepted 9 January 1996

Abstract

The coil-to-globule transitions of fractionated poly(*N*-isopropylacrylamide) chains attached to electrosterically stabilized polystyrene latex particles were studied for molecular weights ranging from 3×10^5 to 2×10^6. The shapes of the transitions proved to be a sensitive function of the polymer molecular weight: the component of the transition that occurred under better than θ-solvency conditions increased significantly (from 30 to 80%) as the molecular weight was decreased by an order of magnitude; concomitantly, the component that occurred under worse than θ-solvency conditions was substantially decreased. Studies carried out with ^{13}C NMR supported the hypothesis that these two types of transitions were phenomenologically different. The transitions in worse than θ-solvents can be attributed to the strong attractive binary interactions that characterize worse than θ-solvents, whereas the transitions in better than θ-solvents arose from the weaker attractive many-body interactions, i.e. *n*-clustering. Simple scaling law considerations imply that the component of the coil-to-globule transitions arising from *n*-clusters should decrease with increasing molecular weight of the interfacial polymer, in conformity with the experimental data.

Keywords: Coil-to-globule transitions; *n*-Cluster effects; Interfacial chains; Molecular weight; Poly(*N*-isopropylacrylamide); Polystyrene latex

JOURNAL OF COLLOID AND INTERFACE SCIENCE 177, 343–352 (1996)
ARTICLE NO. 0042

Coil-to-Globule Type Transitions and Swelling of Poly(N-isopropylacrylamide) and Poly(acrylamide) at Latex Interfaces in Alcohol–Water Mixtures

PENG WEI ZHU AND DONALD H. NAPPER[1]

School of Chemistry, The University of Sydney, Sydney, N.S.W. 2006, Australia

Received March 31, 1995; accepted June 7, 1995

The coil-to-globule type transition and swelling of poly(N-isopropylacrylamide) chains at latex interfaces in mixed dispersion media were studied. A combined collapse–swelling behavior was observed on the addition of lower alcohols (methanol, ethanol, or 2-propanol) to an aqueous dispersion medium. The PNIPAM chains collapsed to a minimum size in the water-rich region and then reswelled on further addition of the alcohol. Both collapse and reswelling were reversible. The collapse of the higher molecular weight PNIPAM chains with narrower polydispersity was found to proceed almost to completion and to be relatively sharp prior to the attainment of θ conditions. It was found that the minimum size of the collapsed chains was dependent upon both the number of carbon atoms in the alcohol and the temperature studied. The volume fraction of alcohol corresponding to this minimum size was also dependent upon the number of carbon atoms in the alcohol but was essentially independent of the temperature of the dispersion medium. The experimental observations have been explained by the variations in the hydrophobic interactions and the hydration of the polymer chains. The results suggest that the collapse of interfacial PNIPAM chains in the alcohol–water mixed media occurs as a consequence of the effects of alcohols on the environment of the PNIPAM chains, whereas the chain swelling results from the direct interaction of the alcohol molecules with the hydrophobic groups in the PNIPAM macromolecules. The attractive hydrophobic interactions in PNIPAM layers are believed to play an important role in promoting the chain collapse after the interactions between the PNIPAM chains and the alcohols are diminished. The validity of this interpretation was supported by similar studies on poly(acrylamide). © 1996 Academic Press, Inc.

Contribution to Polymer Colloids Group Newsletter

by

M. Nomura, H. Tobita and K. Suzuki
Department of Materials Science and Engineering,
Fukui University, Fukui, Japan.

News on Polymer Colloids in Japan:

The 9th Polymeric Microsphere Symposium was held in Tsukuba in November 11-13, 1996. In this symposium, 71 papers were presented. The preprint, although written in Japanese, is available by direct request to Nomura. Next symposium is to be held in November 1998 in Fukui. The 7th IKETANI CONFERENCE on "International Symposium on Advanced Technology of Fine Particles" is to be held in October 14-17, 1997 in Yokohama, Japan. The chairman is Professor H. Kawaguchi of Keio University. Those who are interested in presenting paper in this symposium should write to Professor H. Kawaguchi.

Recent Research Activity on Polymer Colloids in Fukui University

(1) Thermodynamic Correlation of Partial and Saturation Swelling of Styrene-Acrylonitrile Copolymer Particles by Styrene and Acrylonitrile Monomers

X. Liu, M. Nomura* and K. Fujita, Department of Materials Science and Engineering, Fukui University, Fukui, Japan, *J. Appl. Polym. Sci.*, in press.

Synopsis: The possibility of thermodynamic correlation of partial and saturation swelling of styrene-acrylonitrile (SAN) copolymer particles by styrene (St) and acrylonitrile (AN) monomers is investigated. The unknown Flory-Huggins interaction parameters involved in the thermodynamic swelling equations are estimated by fitting the equations to the experimentally observed monomer concentrations. It is shown that the concentration of each monomer in SAN copolymer particles predicted by using the thermodynamic swelling equations with the parameters and constants estimated in this study agrees fairly well with that observed experimentally over a wide range of experimental conditions. The validity and utility of the parameters and constants estimated from saturation swelling are also demonstrated by showing that the experimental results for partial swelling of SAN copolymer particles by AN monomer dissolved in the aqueous phase agree with those predicted by the thermodynamic equation for partial swelling.

(2) Saturation Swelling of ABS Latex Particles by St and AN Monomer Mixtures

X. Liu, M. Nomura*, Y-H. Liu, K. Ishitani and K. Fujita
Department of Materials Science and Engineering, Fukui University, Fukui, Japan,
Ind. Eng. Chem., Res., to be published in honor of Professor Hamielec, in press

Synopsis: In order to explain the experimentally observed saturation swelling of ABS latex particles by a styrene (St) and acrylonitrile (AN) monomer mixture, a two-phase swelling model is proposed based on the assumption that in ABS latex particles, poly(styrene-*co*-acrylonitrile) (SAN) domains are randomly dispersed in a continuous polybutadiene (PB) matrix, and that thermodynamic equilibrium for both styrene and acrylonitrile monomers is attained among the SAN domain, PB matrix and monomer droplet phases, respectively. It is shown that the observed saturation concentrations of St and AN monomers in ABS latex particles consisting of different weight ratios of PB/SAN agree very well with those predicted by this model.

Contribution to the IPCG Newsletter December, 1996

Masayoshi Okubo
Department of Chemical Science and Engineering, Faculty of Engineering,
Kobe University, Kobe 657, Japan
Phone 81-78-803-1142, Fax 81-78-803-1169
e-mail: okubo@appchem.chme.kobe-u.ac.jp

Publications (1996) continue

(6) Production of core-shell composite polymer particles utilizing the stepwise heterocoaguration method

M. Okubo, Y. Lu

Colloids Surfases A: Phisicochem. Eng Aspects, **109**, 49-53 (1996)

Core-shell composite polymer particles, in which the polymer composing the core was more hydrophilic than that composing the shell, were produced as follows. First, by the stepwise heterocoagulation, which we suggested in 1990, of small cationic "hydrophobic" polymer particles (SP) onto a large anionic "hydrophilic" polymer particle, composite particles having uneven surfaces were produced and then they were treated at higher temperature than the glass transition temperature (Tg) of SP.

(7) Formation mechanism of anomalous "golf ball-like" composite polymer particles by seeded emulsion polymerization

M. Okubo, Y. Murakami, T. Fujiwara

Colloid Polym. Sci., **274**, 520-524 (1996)

Recently, the authors found that anomalous polystyrene/polybutyl acrylate composite particles, whose surfaces had many dents, were produced by emulsifier-free seeded emulsion polymerization of butyl acrylate with polystyrene seed particles. Such a particle was named a "golf ball-like" particle. In this article, the morphology and the formation mechanism of the golf ball-like composite polymer particles were studied.

(8) Preparation of nanoparticles by "dissolution" of submicron-sized ionized styrene-methacrylic acid copolymer particles in nonionic emulsifier solution

M.Okubo, R. Sugiura, N. Fukami, A.Ito

Colloid Polym. Sci., , in press

(9) **Micron-sized monodispersed polymer particles produced by seeded polymerization for the dispersion of high swelling of polymer particles with a large amount of monomer**

T. Yamashita, M. Okubo

Colloid Polym. Sci., , , in press

(10) **Preparation of temperature-sensitive polymer particles having different lower critical solution temperatures**

M. Okubo, H. Ahmad, M. Komura

Colloid Polym. Sci., , , in press

(11) **Production of micron-sized monodispersed composite polymer particles by seeded polymerization utilizing the dynamic swelling method**

M. Okubo, T. Yamashita, T. Suzuki, T. Shimizu

Colloid Polym. Sci., , , in press

Contribution to the IPCG Newsletter December, 1996

Tsuneo Okubo
Department of Applied Chemistry and Graduate School of Material Science,
Gifu University, Gifu, 501-11, Japan
Phone +81-58-293-2620, Fax +81-58-230-1893,
e-mail: okubotsu@apchem.gifu-u.ac.jp

On January 1996 T. Okubo moved from Kyoto to the ***Gifu University*** as full professorship. On april 1st, Associate Professor Akira Tsuchida(from Kyoto University) and Research Technician Kazuo Takezawa(from Tokyo Science University) joined our group. Main activity of our group is 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. This October microgravity experiments on the colloidal crystallization was made using TR-5A rocket. Absorption and/or adsorption pnemomena of colloidal spheres, viscosity of colloidal gases, liquids and crystals, surface tension of synthetic and biological polyelectrolytes, and other physico-chemical properties of macroions have been studied.

Publications(1996)

(1)"**Electrically Induced Shear Waves in Colloidal Crystals** ", M. Stoimenova, Vassil Dimitrov and T. Okubo, *J. Colloid Interface Sci.*, in press(1996).

The static light scattering method is used for the detection of acoustic waves induced in colloidal crystals and liquids by low frequency electric pulses. The method is sensitive to both density and shear modes and can be applied for the study of the liquid-crystalline phase transitions. At low fields the variations of light scattering intensity follow both amplitude and the phase variations of the wave motion and enable the determination of resonance parameters, hence of viscoelastic parameters of the colloidal system.

(2)"**Static and Dynamic Light-scattering of Colloidal Gases, Liquids and Crystals**", T. Okubo, K. Kiriyama, N. Nemoto and H. Hashimoto *Coll.Polymer Sci.*, **274**, 93-104(1996).

Static and dynamic light-scattering measurements are made for colloidal-crystals, -liquids and -gases of silica spheres, 103 nm in diameter, in the exhaustively deionized suspension and in the presence of sodium chloride. Sharp peaks in the scattering curve are observed, for the first time, for the colloidal crystals in very diluted aqueous suspension. The product of the effective diffusion coefficient and the scattered light intensity is found constant over the whole range of the scattering angle measured for the colloidal crystals and liquids. Three and two dynamic processes have been extracted separately from time profiles of autocorrelation function of colloidal crystals and liquids, respectively from Marquadt histogram analysis. Decay curves of colloidal gases are characterized by a single translational diffusion coefficient, D_0. D_0 of the gases is always lower than the calculation from the Stokes-Einstein equation with the true diameter of spheres, and increases as ionic concentration increases.

These experimental results emphasize the important role of the expanded electrical double layers on the diffusive properties in the colloidal crystals, liquids and gases.

(3)"**Colloidal Single Crystals of Silica Spheres in the Presence of Simple- and Poly-electrolytes, and Ionic Detergents**", T. Okubo, H. Fujita, K. Kiriyama and H. Yamaoka, *Coll.Polymer Sci.*, **274**, 73-80(1996).

Colloidal single crystals of silica spheres(103 nm in diameter) are formed in the presence of various kinds of salts, (1)simple electrolytes,i.e., sodium chloride, calcium chloride and lanthanum chloride, (2)polyelectrolytes such as 3-6 type ionen polymer(polybrene^{R}), poly-N-ethylpyridinium bromide, a copolymer of N-benzyl pyridinium chloride and N-hexadecyl pyridinium bromide, and sodium polyethylene sulfonate, and (3)cationic and anionic detergents, hexadecyltrimethylammonium bromide and sodium dodecylsulfate. Shape and size of their single crystals, phase diagram, and the relationship between the two parameters among the critical concentration of melting, conductance and pH of the crystal-like suspensions have been studied. Colloidal single crystals of *positively charged spheres* have been formed in this study by the method of the charge reversal of spheres through the strong adsorption of cationic polyelectrolytes onto the anionic silica spheres.

(4)"**Phase Diagram of Alloy Crystal in the Exhaustively Deionized Suspensions of Binary Mixtures of Colloidal Spheres**", T.Okubo and H.Fujita, *Colloid Polymer Sci.*, **274**, 368-374(1996).

Phase diagrams of liquid-like, alloy crystal-like and amorphous solid-like(AS) structures have been obtained for the exhaustively deionized aqueous suspensions of the binary mixtures of polystyrene or silica spheres. Diameter, polydipersity index(standard deviation of diameter divided by the mean diameter) and size ratio of the binary spheres(diameter of small sphere divided by that of large one) range from 85 to 136 nm, 0.07 to 0.26 and 0.76 to 0.93, respectively. Close-up color photographs of the alloy crystals are taken and the crystal structure has been analysed from reflection spectroscopy. Most of the alloy crystals are *substitutional solid-solution*(sss) type and body-centered cubic lattice structure. Formation of the alloy crystals is attributed to the important role of the expanded electrical double layers in the deionized condition and increase toward unity in the effective size ratio, which is the effective diameter of small sphere including double layer divided by that of large sphere. AS structure is formed at the rather high concentrations of two spheres, where the thickness of the electrical double layer is thin and the effective size ratio is comparatively small.

(5)"**Importance of the Electrical Double Layers in Structural and Diffusional Properties of Deionized Colloidal Suspension**", T. Okubo, *Colloids Surfaces*, **109**, 77-88(1996).

An important role of the electrical double layers in the structural, rheological, and diffusional properties of colloidal suspensions especially in the deionized state has been discussed. Formation of the giant colloidal single crystals, which are colored brilliantly and most beautiful, is due to the electrostatic intersphere *repulsion* and to the highly expanded electrical double layers surrounding colloidal spheres. Phase diagram, rigidity and viscosity of the colloidal crystals are nicely explained with the contribution of the electrical double layers. The translational and rotational diffusion coefficients of colloidal particles are quite sensitive to the ionic concentration of the suspension, which is also beautifully explained with the thinning of the electrical double layers with increasing ionic concentration. Furthermore, diffusive modes in the colloidal crystals and liquids analyzed by dynamic light scattering measurements are consistent with the important contribution of the electrical double layers.

(6)"**Static and Dynamic Light-scattering of Colloidal Crystals of Monodispersed Polystyrene Spheres**", T. Okubo and K. Kiriyama, *Ber.Bunsenges.Phys.Chem.* , **100**, 849-856(1996).

Static and dynamic light-scattering measurements are made for colloidal-crystals, -liquids and -gases of monodispersed polystyrene spheres, 109 nm in diameter, in the exhaustively deionized suspension and in the presence of sodium chloride. Sharp peaks in the scattering curve are observed for the colloidal crystals in very diluted aqueous suspension. The product of the effective diffusion coefficient and the scattered light intensity is found constant over the whole range of the scattering angle measured for the colloidal crystals. Three and two dynamic processes have been extracted separately from time profiles of autocorrelation functions of colloidal crystals and liquids, respectively from the non-negative least square analysis. Decay curves of colloidal gases are characterized by a single translational diffusion coefficient, D_0. D_0 of the gases at low ionic concentrations is lower than the calculation(D_c) from the Stokes-Einstein equation with the true diameter of spheres, and increases and reaches D_c as ionic concentration increases. These experimental results emphasize the important role of the expanded electrical double layers on the diffusive properties in the colloidal crystals, liquids and gases.

(7)"**Electro-optic Effects in Colloidal Crystals** ", T. Okubo and M. Stoimenova, ACS Book, "Polymers for Advanced Optical Applications", Am.Chem.Soc., in press.

Colloidal single crystals of giant size(3 to 8 mm) have been observed in exhaustively deionized and highly diluted suspensions of monodisperse polystyrene and silica spheres. Kinetics of crystal growth is discussed briefly. Size of the single crystals increases sharply as sphere volume fraction decreases, and the crystal is largest at sphere concentration slightly higher than the critical concentration of melting. Dynamic aspects in the visco-elastic properties of colloidal crystals have been also discussed. g-factor, which indicate the magnitude of thermal motion, in colloidal crystals, range from 0.03 to 0.1, and are close in value to those of stable crystals of metals and proteins. Static and dynamic light-scattering measurements have been made for many kinds of colloiudal crystals. Three and two dynamic processes are extracted separately from time profiles od autocorrelation function of colloida crystals and liquids, respectively. Electro-optic effects of colloidal crystals are studied both by using the electric light-scattering technique and by reflection spectroscopy in a.c. electric fields. Two electro-optic relaxations are obtained and their relation to electrically-induced acoustic modes is demonstrated. Phase difference and higher order harmonics are clearly observed at low frequencies. The oscillating decay of the effects observed in a narrow low frequency range demonstarets their relation to undamped shear waves of the crystall lattice.

(8)"**Structural and Dynamic Properties in the Complex Fluids of Colloidal Crystals, Liquids and Gases**", T. Okubo and K.Kiriyama, J.Mol.Liquids, in press.

Static(SLS) and dynamic light-scattering(DLS) measurements are made for colloidal-crystals, -liquids and -gases of silica spheres, 110 nm in diameter, which are typical examples of the complex fluids. Very sharp peaks are observed in the light-scattering curves. At the peak scattering vectors in the scattering intensity(I), very small values of the effective diffusion coefficient(D_{eff}) are evaluated. Product of I and D_{eff} is roughly constant for the colloidal crystals, liquids and gases over the scattering angles measured. The structure factor, $S(q)$ are evaluated from the $I(q)$ observed and the particle structure factor, $P(q)$. The nearest-neighboured interparticle distances of colloidal crystals and liquids estimated from the peaks in the $S(q)$ curves, l_{obs} agree excellently with the effective diameters of spheres(d_{eff}) including the electrical double layers in the effective hard-sphere model and also with the mean intersphere distances, l_0 calculated from the sphere concentration(l_{obs} ª d_{eff} ª l_0). Three and two dynamic processes have been extracted separately from time profiles of autocorrelation function of colloidal crystals and liquids, respectively from the non-negative least square analysis. Hydrodynamic diameters of spheres in the crystal-like and liquid-like suspensions can not be evaluated from DLS measurements. Decay curves of colloidal gases are characterized by a single translational diffusion coefficient. The latter is always lower than the calculation from the Stokes-Einstein equation using true diameter of spheres and increases as ionic concentration increases. These experimental results emphasize the importance of the expanded electrical double layers and the electrostatic intersphere repulsion on the structural and dynamic properties of the colloidal crystals, liquids and gases.

(9)"**Growth of Colloidal Crystals under Low-Gravity**(Japanese)", M.Ishikawa, H.Nakamura, S.Kamei, T.Okubo, T.Morita, K.Kawasaki and Y.Kono, *J.Microgravity Appl.Soc.Japan*, **13**, 149-157(1996).

Colloidal crystals are known as a particle system which forms ordered arrays in deionized water. Colloidal crystals offer an important oppotunity to study the dynamics of crystallization. In atomic or molecular fluids, the rate of attachment of particles to a growing interface is the order of picoseconds, whereas in a colloidal system it corresponds to the rate of diffusion of particles in the order of several ten milliseconds. This slows growth rates significantly and allows detailed mechanism of nucleation and growth of crystals to be studied on a convenient timescale. We aimed to clarify the effects of microgravity on nucleation and growth processes using colloidal crystals as a model material. Using reflection spectrum method, lattice constants Do were determined based on the Bragg reflection. The intensity measurements of Bragg reflections were executed to evaluate the appearance of small nuclie during the crystal growth under low-gravity. Light scattering methods were also applied to low-gravity experiments. Low-angle light scattering method and dynamic light scattering method were used to measure the size of grown crystallites and to evaluate diffusion coefficients of latex particles during the formation of colloidal crystals, respectively. Low-gravity experiments were executed during parabolic flights of MU-300 rear-jet airplane.

(10)"**Colloidal Crystals, Polymeric**", T.Okubo, *Polymeric Materials Encyclopedia,* J.C.Salamone(ed), CRC Press, Boca Raton, **2C**, 1290-1298(1996).

Preparation, crystal structure, single crystls and crystal growth, phase equilibria, viscometric, elastic & dynamic properties, external field effect and applications are reviewed on the polymeric colloidal crystals.

Contribution to IPCG Newsletter from Laboratoire de Chimie et Procédés de Polymérisation (LCPP-CNRS) (*) and Unité Mixte CNRS-BioMérieux (UMR 103) - LYON-(France)
(submitted by J. Guillot, A. Guyot and C. Pichot)

(*)New adress : LCPP-CNRS/C.P.E. Bât. 308 F. B.P. 2077. 43, Avenue du 11 Novembre 1918. 69616. Villeurbanne CEDEX. . Fax : (33) 4 72.43.17.68

A) Capture of oligoradicals in emulsion polymerization, Catherine Marestin, Jérôme Claverie, Alain Guyot
A slightly crosslinked polystyrene seed latex has been derivatized in order to attach living nitroxide radicals. It results a permanent ESR signal. When engaged in the radical emulsion polymerization of methylmethacrylate, the decrease of that ESR signal can be used as measure of the capture of the oligo radicals. Of course the polymerization yield in these conditions is practically nul.

B) Reactive surfactants in emulsion polymerization, Brigitte Muller, Olivier Sindt, Alain Guyot, Alain Goux
Some new reactive surfactants have been engaged in styrene emulsion polymerization.
Among then

1. A very simple hemiester of maleic anhydride
2. The latter further reacted with polyethylene oxide-monomethyl ether.
3. That POE-monomethyl ether has been engaged as initiator of the ring opening anionic polymerization of ε coprolactone, as well as butylene oxide. The resulting bloc copolymer was either killed with VBC, or, after hydrolysis reacted with maleic anhydride and also TMI (ε methylstyrene isocyanate derivative).

Publications on this topic have been submitted

- J. Applied Polymer Sci. "Styrene emulsion polymerization in the presence of a maleate functional surfactant" by Alain Goux and Alain Guyot.

- J. Colloid and Polym. Sci. "Reactive surfactants in heterophase polymerization Part I Synthesis of functionalized poly(ethylene oxide)-b-poly(butylene oxide) and their use as surfmer, inisurf and transurf in heterophase polymerization by E. Schipper, T. Hamaide, P. Lacroix-Desmazes, O. Sindt, B. Muller, A. Guyot, M. Van der Euden, F. Vidal, J. Van Es, A. German, A. Montaya Goni, D.C. Sherington, H. Schoonbrood, J. Asua and M. Sjoberg.

C) Dispersion polymerization
The following publication have been or published or submitted.
Reactive surfactants in heterophase polymerization

Part II. Maleate based polyethylene oxide macromonomers as steric stabilizer precursor in the dispersion polymerization of styrene in ethanol-water media by P. Lacroix-Desmazes and A. Guyot, Macromolecules 1996 29 4508

Part III. Polyethylene oxide macromonomers and polymerizable surfactants (surfmer) as stabilizer in styrene dispersion polymerizationby P. Lacroix-Desmazes and A. Guyot, Polymer Bulletin 1996 37 183

Part IV. Dispersion polymerization of styrene and methylmethacrylate particles formation and prediction of final size by P. Lacroix-Desmazes and A. Guyot, Colloid Polymer Sci. 1996 274 .....

D) High solid multisized emulsion copolymerization

The following publication have been submitted.
Colloid Polymer Sci. : Characterization of particles size and size distribution of multisized polymer latices by centrifuge quasi elastic light scattaring by F. Chu, C. Graillat, J. Guillot and A. Guyot

Both in Colloid Polymer Sci. : Rheology of concentrated multisized Poly (St/BA/MMA) latices by F. Chu, J. Guillot and A. Guyot

E) Copolymerisation of α-methyl styrene/MMA on polystyrene and polybutadiene seeds.

Fabrice Martinet(PhD) and Jean Guillot

A fundamental investigation of batch emulsion α–methylstyrene(αMS)/MMA at various feed compositions and temperatures has definitely shown a huge radical desorption mechanism ($\tilde{n} \cong 0.05 - 0.1$). The same values of $\tilde{n}$ were also observed in seeded copolymerisations on PS and Pbutadiene seeds, at different Monomer/seed ratios. Experimental data showed a marked effect of MMA water solubility on kinetics (rate of polymrisation) and copolymer characteristics. Molecular weights distribution, glass transition behaviour and grafting efficiency are investigated.

Copolymerisation of αMS with styrene(S) (Ramon Castellanos ans Jean Guillot) was also studied, in batch, at various temperatures and feed compositions. No significant radical desorption was observed and $\tilde{n} \cong 0.5$. As with MMA kinetics and moleculatr weights are drastically decreased with increasing temeprature and αMS contents, owing to the competition beween propagation and depropagation.

In emulsion, a general feature is that αMS leads to very tiny particles. The glass transition of αMS copolymers with S or MMA are increased, but not as much as expected from the high Tg of PαMS (270°C), for increasing αMS content lowers, too, the molecular weights and, as a consequence, lowers the macromolecules Tg's(chain-end effect). For both systems, the copolymer Tg's pass through a maximum value wich is close to 120°C for S and close to 145°C for MMA, in connection too with reactivity ratios and other parametres.

At the same time, modelling and simulation computer programme have been improved quite satisfatorilly for both a better basic knowledge and further process and copolymer quality control. These works will be soon published.

F) Emulsion vinyl acetate(VAc) / butyl acrylate(BA) copolymerisations.

Christian Graillat, Timothy McKenna and Jean Guillot.

Emulsion vinyl acetate / butyl acrylate copolymerisations have been done at various temperatures, monomer feed compositions and polymerisation processes (batch, semicontinuous, multi-stage, seeded), in the presence or not of chain transfer agents(CTA), in order to improve the basic knowledge and quantify the inter-connections beetween the main parameters influencing the

copolymerisation and the copolymer properties. The softwares developed take into account monomer partitioning, radical desorption, gel effect, diffusion limitations for heavy CTA, which lower a lot their efficiency in emulsion processes. Multi-stage copolymerisations allow to get large and quite complex composition drifts and molecular weight distributions, sometimes required for specific applications. The kinetics and copolymer properties control are quite sensitive to temperature changes and, above all, to monomer and CTA addition policies. However, it is possible to keep within the desired range the Tg's as well as the molecular weight distribution.
The reactor has been equipped with accurate thermal sensors for on-line estimation of the heat balance, in order to get this way an on-line conversion sensor, after calibration of this reactor. The results are promising and the simulation software is now working on-line. The work is in progress with two postgraduate students (process control).

G) Modelling of glass transition of mixtures of random copolymers of very different molecular weights. Christian Graillat and Jean Guillot.

This work is originated by the observation that often when small molecular weight homopolymers or copolymers of the same nature are generated in a polymerisation along with much larger macromolecules, the expected plastisizing effect is not the general rule. On the contrary, broadened thermogrammes (DSC, e.g.) are observed, but with no significant lowering of the higher Tg's. The same behaviour is also observed with artificial polymer mixtures of small and large molar masses prepared in a solvent and then dried up. A modelling of the effect of the molecular weight distribution(MWD) on Tg's was developed assuming that terminal dyads of the polymer and copolymer chains have a much larger mobility than the inner ones (chain-end effect). As a matter of fact, in low molecular mass polymer, the number of such terminal dyads is larger than entanglements and can be easily computed. Computer softwates were completed with this MWD effect on individual macromolecules Tg's. Applied to αMS/MMA or αMS/S solution, bulk and emulsion copolymers wherein depropagation can generates complex MWD, this very simple approach gives a good quantitative account of experimental data on the change in Tg's with αMS contents and polymerisation temperature. In particular it explains quite clearly the maximum Tg's values experimentally observed.
The agreement was also good with artificial mixtures of homopolymers of VAc of very different masses (8000 and 100 000) ; i.e. a spreading towards lower temperatures and not a simple shift. However, with other (co)polymer systems, it seems that plastisizing can occur ; what should then be connected with polymer compatibility. Indeed, good thermodynamic interactions are normally required for plastisization.

H) Development of sensors for emulsion Process Control. Density and Ultrasound velocity sensors. Marie Laure Nesti(PhD), D. Tembou Nzudie and Jean Guillot.

As already mentionned, heat balance could be a reliable on-line conversion sensor in solution, bulk and emulsion (co)polymerisation ; but it could eventually required some corrections from time to time off-line gravimetry data. Other on-line available sensors have been tested such as a combined density and ultrasound velocity sensor, proposed by Anton Paar. This sensor (DPRSPR 417) was used for the on-line monitoring of the conversion of semi batch terpolymerisation butyl acrylate/styrene/methacrylic acid at high solid content (≥ 50 %). The conversion is calculated from the density and sound velocity combined measurements, with relations including temperature and composition effects. The validity of this on-line estimation of the conversion has been confirmed in a good agreement with gravimetry data.

A publication has been submitted to J. Appl. Polym. Sci. :
« Combined sensor for online conversion monitoring in emulsion polymerisation at high solid content » . M.L. Nesti, D. Tembou Nzudie, J. Guillot.

Other sensors are also tested in collaboration, such as near infrared sensors.

I) Emulsion copolymerisation in continuous reactors. Jean Guillot, Timothy McKenna, Gerald Neyret, JérômeTorres
Investigation of emulsion (co)polymerisation in continuous reactors has been started with postgraduate students, in two CSTR reactors, first on polystyrene homopolymerisation. The main objective is to understand the copolymerisation kinetics, the nucleation and the copolymer property control in such reactors. Kinetics, particle size and distribution, molecular weight distribution as well as glass transition are systematically investigated and connected with experimental parameters such as feed rates(monomer, emulsifier, initiator, CTA), residence times, temperature.

Adsorption of Oligonucleotides onto cationic latex particles precoated with a nonionic surfactant (Triton X405), F. Ganachaud, A. Elaïssari, C. Pichot A. Laayoun, Ph. Cros (UMR 103)

A sudy has been performed on the adsorption of single stranded oligonucleotide (dT35) both onto bare aminated polystyrene latex particles and onto the same latex precoated with a nonionic surfactant (TritonX405). The adsorption behavior of ODN has been correlated to the electrophoretic mobility of the adsorbent by examining the influence of pH and ionic strength on the maximum amount adsorbed. The ODN adsorption was rapid onto cationic bare latex in comparison with the precoated one. The maximum adsorbed amount of Triton was in the range 5.5 mg/m2, the highest value being typical of a loosely packed monolayer. The surfactant desorption was investigated as a function of washing steps using the serum replacement technique. It was found that the residual adsorbed amount of Triton was around 1 mg/m^2. The maximum adsorbed amount of oligonucleotide was in the range 0-0.9 mg/m^2 depending on the adsorbent and experimental conditions. The adsorption isotherms of ODN on the bare and precoated latex particles, indicated that there is no surfactant effect on the adsorption affinity constant. The influence of pH showed that the adsorption on both latexes decreases with decreasing the cationic charge on the latex surface as already reported. However, the effect of ionic strength on the ODN adsorption was found to depend upon the nature of latex surface. Accordingly, a correlation has been found between the maximum amount adsorbed and the zeta potential of latex particles at zero coverage. This study showed that the adsorbed nionic surfactant on the latex particles reduces the non-specific adsorption of oligonucleotides at basic pH, therefore, the covalent grafting can be performed and optimized.

Covalent coupling of oligonucleotides on well defined amino containing particles
F. Ganachaud, Th. Delair, A. Elaïssari and C. Pichot (UMR 103)

The covalent coupling and the adsorption of activated oligonucleotide, i.e. a poly(thymine) 35 bases , on an aminated latex are currently investigated. First, desorption of adsorbed oligonucleotide has shown that in basic media, at a high ionic strength, and in the presenc e of a non ionic surfactant, it was possible to desorb roughly the overall quantity of adsorbed molecules. A preactivation step of the oligonucleotide is necessary to allow the molecule to be bound on the latex surface. Activation with diisothiocyanate (DITC) has shown encouraging results, especially when the activation is performed less than 40 minutes in order to avoid hydrolysis reaction. Then, coupling reactions have been performed as a function of the medium, varying pH, ionic strength, temperature, etc. Although the adsorption is dependent upon these parameters, the covalent coupling, i.e. the amount still bound after desorption, is set quite constant. However, this quantity is also affected according to the presence or not of a surfactant or not at the particle surface.

Recent papers (UMR 103):

I-Emulsifier-free emulsion copolymerization of styrene with two different amino-containing cationic monomers:
2) Surface and colloid properties
F. Cornier , F.Ganachaud , A. Elaissari, C. Pichot
(accepted to J. Applied Polym. Sci)

Abstract: The colloidal and surface properties of copolymer latex particles prepared by batch emulsifier-free emulsion polymerization of styrene with two different amino containing monomer (Amino Ethyl Methacrylate Hydrochloride (AEMH) and Vinyl Benzyl Amine Hydrochloride (VBAH)) and 2,2'-azobis(2amidinopropane) dihydrochloride(V50) were investigated. The final particle size was found to decrease with increasing the functional monomer concentration. Different titration methods were used to quantify the surface amino (brought by the initiator) and amidino groups (originated from the initiator) on the latex particles. The same behavior was observed on both type of latexes : with increasing the functional monomer concentration caused the surface amino groups density to increase from 0 to a plateau value at 8.2 µC/cm^2, whereas the surface amidino groups density decreased from 18.5 to 2 µC/cm^2. These results were confirmed otherwise by electrophoretic measurements and they corroborated those obtained in a previous kinetical study (Part1) concerning the role of functional monomers as transfer agent.

II -Adsorption of single stranded DNA fragments onto cationic aminated latex particlesF. Ganachaud, A. Elaissari, C. Pichot, A. Laayoun, P. Cros
(accepted to Langmuir)

Abstract: In this study, the adsorption behaviour of single-stranded oligodeoxyribonucleotides (ODN) onto well-characterized polymer latex particles has been investigated. At first, the case of polythymidylic acid (poly dT) was thoroughly examined as a function of pH and ionic strength in the presence cationic polystyrene colloids prepared by emulsifier-free copolymerization of styrene and vinyl benzylamine hydrochloride. Due to the the polyelectrolyte character of the oligodeoxyribonucleotides (which are negatively charged) and the positive ones of the particles, strong adsorption was clearly emphasized together with a high affinity; a decrease in the adsorption was observed upon raising the pH. This corroborated that electrostatic forces play a major role in the adsorption process, however the contribution of hydrophobic forces was also evidenced using the various adsorption isotherms at various pHs, and extrapolating these results to zero surface charge density (s=0) and to zero zeta-potential (z=0) of the latex particles. Moreover, the effect of poly(dT) chain length on the maximum adsorbed amount on the latex particles was also investigated, providing information on the state of conformation of the ODN at the particle surface; it was suggested that the ODN adsorbs in a flat conformation; Such a behavior can be extended regardless

of ODN nature so long as the support was oppositely charged. Finally, it was attempted to predict the adsorption behavior of single-stranded ODN using the general approach of Hesslink for polyelectrolytes.

III- Conformation study of oligonucleotides covalently bound to polystyrene latex particles by fluoresc ence energy transfer

M.T. Charreyre, O. Tcerkasskaya, M.A. Winnik, A. Hiver, T. Delair, P. Cros, C . Pichot, B. Mandrand

(submitted to Langmuir)

Abstract: Steady-state fluorescence energy transfer experiments were carried out to probe the conformation of single-stranded DNA oligomers covalently bound to the surface of polystyrene latex microspheres. These oligonucleotides can adopt various conformations, from an adsorbed conformation on the latex particle surface to a brush conformation. To study this system, a donor of energy transfer (fluorescein) was covalently attached to the free ends of the oligonucleotides, and an acceptor of energy transfer (tetramethylrhodamine) was covalently bound to the latex surface. The extent of resonance energy transfer was found to be more effective at low pH and low ionic strength, reflecting a shorter distance between the free ends of the oligonucleotides and the latex particle surface. In contrast, the oligonucleotides move away from the surface at basic pH or high ionic strength, becoming more accessible for hybridization with complementary DNA strands, and exhibiting less energy transfer. The addition of surfactant, or the presence of a large number of grafted oligonucleotides per latex particle, also promotes a brush conformation.

IV- Quantification of specific immunological reactions by atomic force microscopy

Agnès Perrin, Véronique Lanet, Alain Theretz (UMR 103)

(in press, Langmuir)

Abstract: The aim of this work is to demonstrate the ability of the Atomic Force Microscopy (AFM) to detect and to quantify specific immunological reactions between antibodies and antigens, with a view to creating a very sensitive biosensor. A monolayer of anti-ferritin antibodies was adsorbed onto alkyl silane modified silicon oxyde substrates, which were characterized by X-ray Photoelectron Spectroscopy (XPS) and contact angle measurements. The sensitivity limit for antibody detection was quantified by RIA, and compared to that obtained by Enzyme Linked Immuno Sorbent Assay (ELISA), and by AFM after antibody binding with colloidal gold labelled conjugates. In this latter case, substrates modification after reaction was checked by measuring the surface roughness (R_{rms}) variations. AFM was found to be more sensitive than RIA, with a detection limit of $0.3x10^{-3}$ ng of antibodies per mm^2. Then, the biosensor performance was investigated using ferritin solutions of various concentrations : the antibody/antigen reaction was quantified by directly detecting the antigen, and measuring surface roughness modifications. Results were compared to sandwich immunoassay techniques. Up to now, AFM has detected a minimum ferritin concentration of 0.06 µg/ml.

V- Preparation of conjugates betweem oligonucleotides and N-vinylpyrrolidone/ N-acryloxysuccinimide copolymers and applications in nucleic acid assays to improve sensitivity

M.N. Erout, A. Troesch, C. Pichot, P. Cros

(Bioconjugate chemistry, 7, n° 5, 568, (1996)

Polymer Colloid Group Newsletter
Contribution from the University of Akron by I. Piirma

AIBN as Initiator in Emulsion Polymerization of PMS, St and MMA
Progress Report: Zheng Fang

The mechanisms of p-methyl styrene(PMS), methyl methacrylate(MMA), styrene(St), and PMS/MMA emulsion polymerization with azobisisobutyronitrile(AIBN) as initiator were investigated by GPC and particle size distribution results. With all these monomers, bimodal particle size distribution was observed at low conversions, which shows two peaks with molecular weights several millions and several thousands(possibly the result of two kinds of nucleation mechanisms), respectively. Bimodality is also observed in the GPC results(Fig.1). At about 40% conversion , however, this phenomenon disappears, and the GPC curve is quite similar with potassium persulfate(PPS) initiated polymerization.

The kinetic data show that, with the same initiator concentration in the polymerization recipe, the rate of polymerization with PPS as initiator is much faster than with AIBN as initiator.This is probably because the solubility in water of PPS is much higher than AIBN. In contrast to PMS and St, the difference is not that significant in case of MMA. This can be explained that more AIBN is incorporated into water phase with monomer since MMA is much more hydrophilic than St and PMS.

A series of experiments have also been conducted to study the dependence of kinetics on the solubility difference of monomers. AIBN was added into reaction system in two ways: dissolving AIBN in monomers before reaction, or adding AIBN powder into the systems directly. In case of PMS homopoly-merization, although the rate of polymerization are quite similar, a long induction period, about 60 min, was observed when adding AIBN directly without dissolving in monomer first. Similar result was found in PMS/MMA copolymerization exept that the induction time diminished to 30min. In case of MMA homopolymerization, however, the induction period was quite insignificant.

References:

1. W.T.Chang, Ph.D. Thesis, The University of Akron(1980).
2. M.Nomura, K.Fujita, Makromol. Chem., Rapid Commun. 10, 581-587(1989).
3. M.Nomura, A.Yamada, D.Jujita, A.Sugimoto, J.Ikoma, and K.Fujita, J. of Polym. Sci., Part A: Polym. Chem., 29, 987-994(1991).

A VIEW FROM THE U.S. NATIONAL SCIENCE FOUNDATION

Gary W. Poehlein

NOTE: This page does not contain any research results. Instead it focuses on potential areas for applying some polymer colloid knowledge and/or concepts in another area.

I am presently in the third month of a two-year assignment with the National Science Foundation in Arlington, Virginia, just outside of Washington, D.C. My position is within the Chemical and Transport Systems Division (CTS) of the Engineering Directorate. Particulate systems is one of the areas of interest in CTS. Since coming here I have discovered a really broad interest in particles and structures comprised of small scale components; not only at NSF but in other government agencies and industry. Actually I knew this before but now I have actually attended meetings where the prefix **NANO** is used with many other words -- particles, structures, clusters, tubes, layers, machining, building blocks, technology, etc.

Those who are involved with this new(?) nanotechnology, almost without exception, seem to ignore the massive amount of fundamental knowledge about polymer nanoparticles and how such particles can be economically produced with controlled processes and end product properties. Hence the purpose of this very brief note.

I suspect that there may be areas within this very interesting new field that could benefit from science and technology transfer from the polymer colloid arena. If any of you are searching for a potential new research thrust you might see what is happening with nanotechnolgy in fields such as electronics, optics, inorganic coatings, etc. Can you devise better ways of manufacturing and/or applying these materials? Maybe some of your old expertise with latexes can become new again.

Contribution to the International Polymer Colloids Group Newsletter

Gérard RIESS

Ecole Nationale Supérieure de Chimie de Mulhouse
Institut de Chimie des Surfaces et Interfaces
3 rue Alfred Werner, 68093 MULHOUSE CEDEX (France)
Fax (33) 03 89 43 79 99

In 1996, 3 PhD students of our research group working on colloidal systems have submitted their thesis.

Damien FERRAND has developped a series of new carboxy functionalized polymers based on acrylic dimers which were suitable for adsorption studies. Some typical results are given herewith.

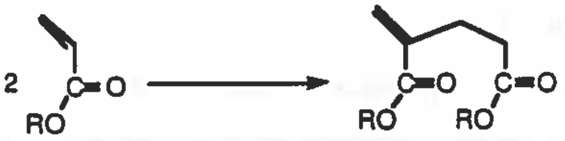
Jean-Philippe LERCH has synthesized homologous series of ABC triblock copolymers and has studied their micellization and adsorption behavior. He could demonstrate that such copolymers follow the theoretical predictions of HALPERIN and ZHULINA.

Philippe HOSOTTE was interested in the synthesis of "all acrylic" AB and ABC block copolymers and in their micellization behavior. For PMMA-b-PAA he examined also their efficiency as polymeric surfactants in emulsion polymerization.

Synthesis and copolymerization of acrylic dimers - Application to the dispersion and stabilisation of TiO_2 pigments in organic media.

Damien FERRAND*, Henri BALARD, and Gérard RIESS
Ecole Nationale Supérieure de Chimie de Mulhouse
Institut de Chimie des Surfaces et Interfaces
3 rue A. Werner 68200 Mulhouse (France)

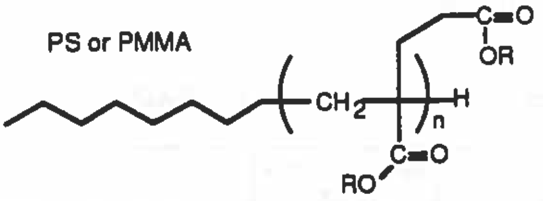
The synthesis of some acrylic dimers with the following structure



has been previously described by Rauhut[1] and Ito[2].

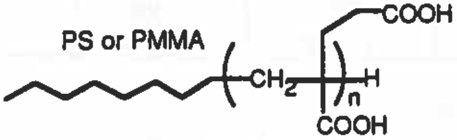
These derivatives of pentandioïc acid with an ester difunctionality are, in addition to maleates, fumarates, itaconates, an interesting class of monomers, as they can be obtained directly from the corresponding acrylates. Until now only the free radical homo- and copolymerization of these dimers have been studied to some extend.[3-5]

We were therefore interested to examine their behavior in anionic polymerization in order to prepare end-functionalized polymers and block copolymers having the following structure :



with poly(styrene) (PS) or poly(methyl methacrylate) (PMMA) as first block and poly(acrylic ester dimer) as second block with R= CH_3, C_2H_5, *n* C_4H_9, *ter* C_4H_9.

The selective hydrolysis of the poly(acrylic ester dimer) block (especially with R=*ter* C_4H_9), leads to hydrophilic end groups or to a hydrophilic block such as :



At first a series of different acrylic dimers has been synthesized by improving the reaction conditions previously described by Balard[6] and Hantz.[4]

---

* Ph.D. thesis submitted July 8th, 1996

As an original compound, the dimer of *ter*butyl acrylate could be obtained with a yield of 78%. The corresponding homopolymer was prepared by free radical polymerization and the reaction conditions for the selective hydrolysis of the *ter*butyl group were optimized. It turned out that using trifluoroacetic acid, as catalyst, is the suitable way to achieve rapid and complete hydrolysis.

As a second step, the anionic polymerization of the various acrylic ester dimers was examined systematically as a function of the reaction conditions (temperature, initiator type, etc.). We came, thus, to the conclusion that in order to limit or avoid side-reactions (cyclisation by back-biting, transfer reactions), its necessary to work at very low temperature (-90°C) with an initiator such as *ter*butyl potassium alcoholate (tBuOK).

Under these conditions oligomers with molar weight of 1600-1800 g/mol could be obtained.

The characteristics of PS or PMMA block copolymers with poly(*ter*butyl dimer) PtBAD are given in tables 1a and 1b.

Table1 a : Characteristics of copolymers PMMA-b-PtBAD

	first block MMA		second block tBAD	CopolymerPMMA-b-PtBAD		
	M_n a)	M_w/M_n a)	M_n b)	$M_{n\ tot}$ b)	M_w/M_n a)	% tBAD c)
DA 79	1.970	1,38	640	2.610	1,21	25
DA 80	4.500	1,27	720	5.220	1,23	14
DA 81	6.600	1,17	640	7.240	1,18	8,8
DA 82	11.600	1,25	1.000	12.600	1,27	7,9

a) As determined by GPC (PMMA standards)

b) calculated from the mol. weight of first sequence and copolymer composition (^{1}H NMR)

c) As determined by ^{1}H NMR (wt %).

Table 1 b : Characteristics of copolymers PS-b-PtBAD

	first block Styrene		second block tBAD	Copolymer PS-b-PtBAD		
	M_n a)	M_w/M_n a)	M_n b)	M_n b)	M_w/M_n a)	% tBAD c)
DA 91	5.670	1,24	1.675	7.350	1,30	20,0
DA 92	– 2.400	2,06	700	3.100	1,82	22,6
DA 95	20.000	1,29	1.800	21.800	1,39	8,7
DA 97	4.570	1,22	950	5.520	1,33	17,3
DA 98	4.100	1,26	805	4.905	1,30	16,4
DA 99	20.850	1,17	1.150	22.000	1,34	5,3

a) As determined by GPC (PS standards)

b) calculated from the mol. weight of first sequence and copolymer composition (^{1}H NMR)

c) As determined by ^{1}H NMR (wt %).

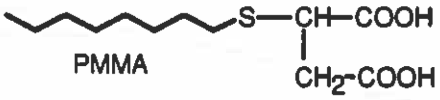
The short PtBAD block was then selectively hydrolyzed with trifluoroacetic acid in order to obtain acrylic acid dimer units acting as hydrophilic end groups.

Then, the adsorption isotherms of the series of PMMA based copolymers with 5-7 COOH end groups (PMMA-PAAD) was studied on TiO_2 dispersed in dioxane. The characteristics of the TiO_2 were the following :

anatase 99 %average particle size 200 nm
specific surface 10 m^2/g.

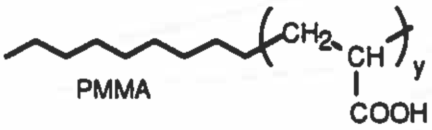
As a comparison, we have established also the adsorption isotherms with samples :

- of PMMA having 2 COOH groups with the following structure



Samples M_xT_1

- of PMMA-b-PAA block copolymers prepared by anionic polymerization.[7]



Samples M_xA_y

where "x" is the degree of polymerization of the PMMA sequence and "y" the degree of polymerization of the acid sequence.

In a similar way PMMA-b-PAAD will be noted $M_x D_y$. The characteristics of the different samples are given in the following table.

Table 2

Polymer	Mn a)	DP b) MMA block	DP c) acid sequence	number of COOH d)
PMMA $(COOH)_2$				
M48-T1	4800	48	1	2
M70-T1	7000	70	1	2
PMMA-b-PAAD				
M20-D3	2420	20	3.1	6.2
M45-D3	4900	45	2.6	5.3
M66-D3	7000	66	2.7	5.3
M116-D4	12100	116	3.8	7.5
PMMA-b-PAA				
M15-A11	2300	15	11	11
M77-A31	9900	77	31	31
M121-A81	17900	121	81	81
M384-A194	52400	384	194	194
Homo PMMA				
M134	13400	134	/	/

a) Molecular weight of copolymer. b) Degree of polymerization of the PMMA sequence (as determined by GPC). c) Degree of polymerization of the acid sequence. d) Average number of COOH groups, per chain, as determined by potentiometric titration

The figure 1 shows, as an example, the adsorption isotherm of the copolymer M116-D4 in comparison with that of a PMMA homopolymer of similar molecular weight (M134).

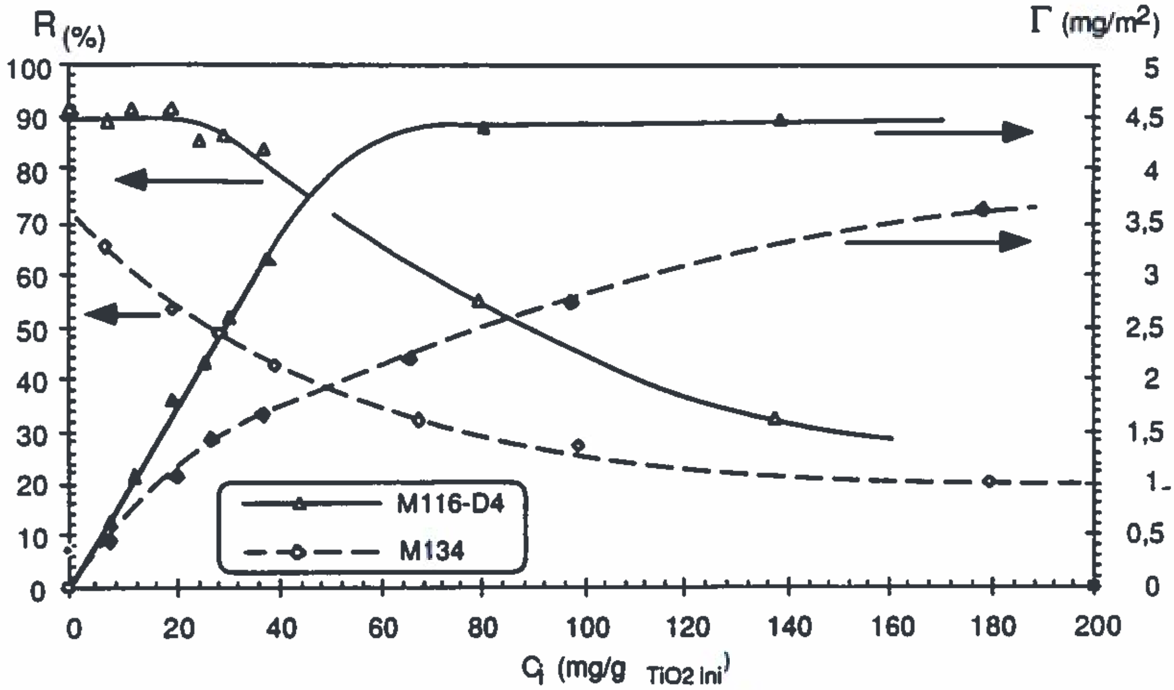


Figure 1: Influence of the presence of an acrylic acid block on the adsorption of PMMA chains on TiO_2 from a toluene solution. Comparison between the homopolymer M134 and the copolymer M116-D4.

On this figure is indicated, in addition to Γ (the amount of polymer adsorbed on TiO_2 expressed in mg/m^2), the efficiency of adsorption R vs. the concentration of polymer in solution.

R is given by : $$R = \frac{(C_i - C_e).100}{C_i} \quad (\%)$$

where C_i and C_e are respectively the initial and the final concentration of the polymer in solution.

As expected, there is a striking difference in the adsorption behavior between the PMMA homopolymer and the functionalized one.

In figure 2 we have plotted the value of Γ_{eq}, the amount of polymer adsorbed at equilibrium (in mg/m^2) as a function of the molecular weight of the PMMA block.

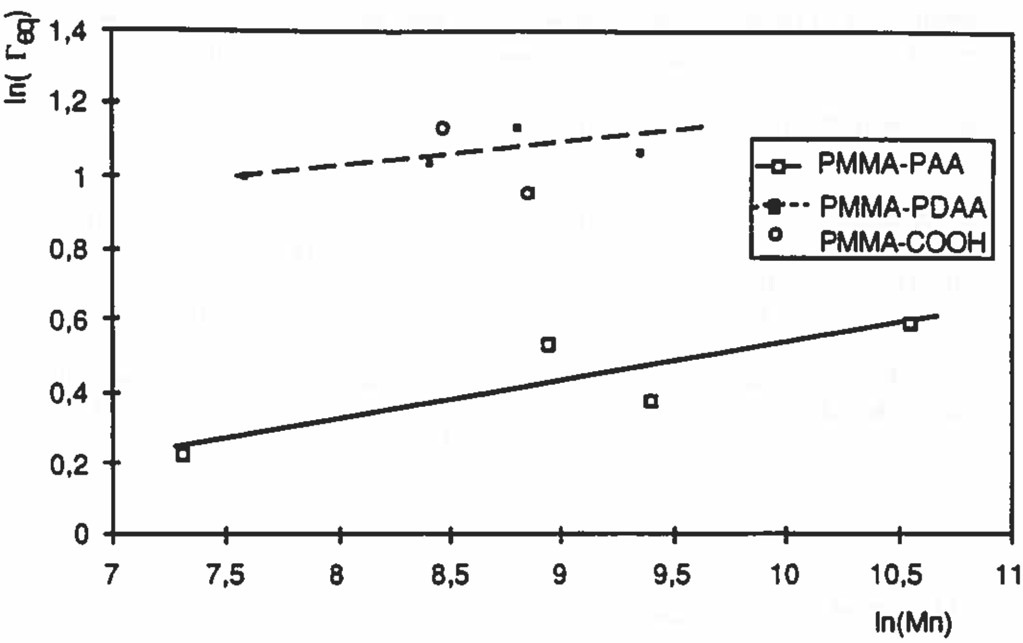


Figure 2: Amont of the copolymers adsorbed at equilibrium Γ_{eq} in dioxane, as a function of the corresponding molecular weight.

There is no major difference between the PMMA-PDAA and the PMMA-COOH samples, having respectively 5-7 and 2 carboxy end groups. However Γ_{eq} is systematically lower for the PMMA-PAA block copolymers, indicating that the "anchoring sequence" has a dramatic influence on the adsorption behavior.

For practical applications of these carboxy functionalized polymers it was also of interest to determine their dispersing and stabilizing efficiency for the TiO_2 pigment in organic medium.

The particle size distribution of untreated TiO_2 in toluene, determined by centrifugal particle size analyser (SHIMADZU SA-CP3) is given in figure 3a.

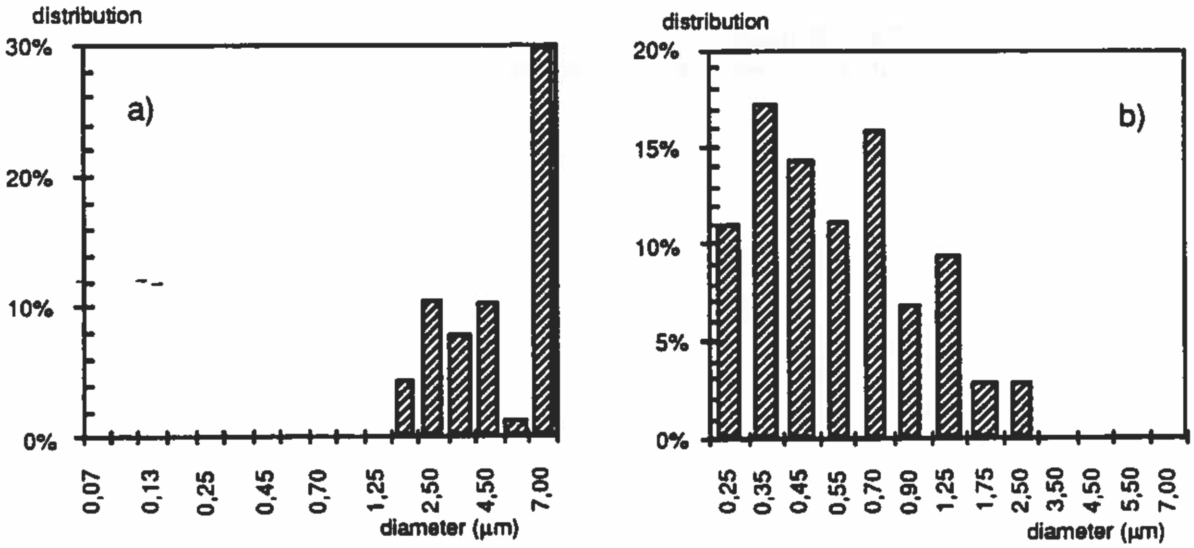


Figure 3: Granulometric analysis of TiO_2 particules in toluene medium, as a function of the amount of absorbed copolymer M20-D3 on its surface. Γ (mg /m²) a) 0; b) 3,49. The median diameters are as follows:ϕ (µm) a) 6,1; b) 0,49.

From this Figure it is evident that the individual TiO_2 particles of 200 nm of diameter have a tendency to aggregate in organic medium.

By addition of carboxy functionalized PMMA or PMMA-PAA block copolymer, the distribution is shifted to a much lower size as shown in figure 3b.

In conclusion, it appears that acrylic dimers, in spite of their lower reactivity with respect to the starting unimer, open interesting possibilities for the synthesis of "superfunctionalized" polymer, e.g. polymers having a high density of end standing functional groups such as carboxy groups.

In addition to their use for the surface modification of dispersed pigments, such carboxy functionalized polymers could find interesting application possibilities as polymeric surfactants in emulsion polymerization.

References

1) RAUHUT M., H. CURRIER; (American Cyanamid Co.).
U. S. Pat. 3,074,999 (Jan. 22, 1963);

2) ITO H., K. KIMURA; (Toa Gosei Ind. Co. Ltd)
Fr. Pat.69.01735 (Jan. 29, 1969)

3) TRUMBO D. L. , R.A. ZANDER
J. Polym. Sci. Part A: Polym Chem, 34, 95-108 (1996)

4) HANTZ A.
Thesis, Université de Haute Alsace, Mulhouse, France, (1992)

5) KOBATAKE S, BUNICHIRO YAMADA
J. Polym. Sci. Part A: Polym Chem, 34, 95-108 (1996)

6) BALARD H. , J. MEYBECK;
Europ. Polym. J.; 13, 611 (1977).

7) HOSOTTE - FILBERT C.
Thèse de l'Université de Haute Alsace (1994)

W.B. Russel
Princeton University
Department of Chemical Engineering
and Princeton Materials Institute
Princeton, NJ 08544

High frequency shear modulus of polymerically stabilized dispersions

S. L. Elliott and W. B. Russel

Department of Chemical Engineering, Princeton University,
Princeton, New Jersey 08544

Experiments indicate that colloidal dispersions stabilized by a grafted polymer layer can exhibit rheological behavior different from that of dispersions consisting only of bare particles. Although such differences are attributed to the ability of the polymer layer to deform, the exact nature of the interactions between such particles is not understood quantitatively. Recently, Lionberger and Russel (1994) successfully interpreted high frequency dynamic measurements through a nonequilibrium statistical mechanical theory, relating hydrodynamic interactions at small separations of concentrated hard sphere colloids to experimental observations of either a plateau or a divergence in the shear modulus at high frequencies. We now extend this concept to polymerically stabilized colloids in general in an effort to clarify the role of interparticle interactions in the rheological behavior of such systems. Both the steric repulsion and hydrodynamic interactions between particles are considered. A functional form for the pair mobility is extracted from the solution to Brinkman's equation in the lubrication limit, while an expression for the repulsion comes from mean field theory. We study how the strength of the repulsion, characterized by the graft density, and the structure of the polymer layer, characterized by the permeability coefficient, affect the high frequency limits of the dynamic viscosity and the shear modulus at various particle radius to layer thickness ratios. Results should enable the interpretation of rheological measurements in terms of interparticle potentials for polymerically stabilized colloids and facilitate accurate predictions of steady shear properties.

Lionberger, R.A. and Russel, W.B. (1994). *J. Rheology* 38, 1885-1908.

The Role of Adsorbed Layers in the Rheology of Dispersions Containing Associative Polymers

Q. T. Pham, W. B. Russel, and W. Lau[+]

Department of Chemical Engineering, Princeton University,
Princeton, New Jersey 08544
[+]Research Laboratories, Rohm and Haas Company,
Spring House, Pennsylvania 19477

Hydrophobically-modified water-soluble polymers of a triblock or telechelic structure form associative networks of enhanced solution viscosity and viscoelasticity. Consequently, addition of the polymers to aqueous latex dispersions produces rheological properties greatly different from those of the dispersions alone. Our objective is a quantitative model, based on both theory and experiment, of the rheology, incorporating interactions between latices and associative polymers that govern the mechanisms. This study involves measurements of the adsorption of associative polymers onto PMMA latices and the rheology of dispersions containing the polymers. Our associative polymers are linear poly(ethylene oxides) endcapped with alkanol hydrophobes. Adsorption isotherms and layer thicknesses are readily measured for dilute concentrations of polymers and latices via centrifugation and dynamic light scattering. Measurements of steady shear viscosity and viscoelasticity moduli as functions of shear rate and frequency, respectively, characterize the rheology over full ranges of dispersion and polymer concentrations. The low shear viscosity then is represented in terms of the polymer solution viscosity η_s, the intrinsic viscosity $[\eta]$, Huggins coefficient k_h, and hydrodynamic particle volume ϕ_{eff}, with η_s and ϕ_{eff} depending on the adsorption density and layer thickness. The Huggins coefficient, intrinsic viscosity, and relaxation times obtained from viscoelastic measurements reflect the nature of the interactions of the particles with the polymer network and among themselves. This information will be interpreted via extant theories for the configuration of adsorbed layers and the forces transmitted between the coated particles.

Phase Transitions, Equation of State, and Limiting Shear Viscosities of Hard Sphere Dispersions

See-Eng Phan, William B. Russel
Department of Chemical Engineering, Princeton University, NJ

Zhengdong Cheng, Jixiang Zhu, Paul M. Chaikin
Department of Physics, Princeton University, NJ

John H. Dunsmuir
Exxon Research & Engineering Company, Annandale, NJ

Ronald H. Ottewill
School of Chemistry, University of Bristol, Bristol, England

Despite an interparticle potential consisting of only an infinite repulsion at contact, the thermodynamics and dynamics of concentrated dispersions of hard spheres are not yet fully understood. Colloidal poly-(methyl methacrylate) spheres with a grafted layer of poly-(12-hydroxy stearic acid) (PMMA/PHSA) comprise a common model for investigating structural, dynamic, and rheological properties. These highly monodisperse spheres can be index-matched in nonaqueous solvents, reducing van der Waals forces and allowing characterization via light scattering. In this work, we test the behavior of these dispersions against expectations for hard spheres through observations of the phase behavior, x-ray densitometry of equilibrium sediments, and Zimm viscometry. We set the effective hard sphere volume fraction by the disorder-order transition, thereby accounting for the polymer layer, any swelling due to the solvent, and polydispersity. The melting transition then occurs close to the expected value and the equation of state for the fluid phase, extracted from the equilibrium sediment with x-ray densitometry, conforms to the Carnahan-Starling equation. However, the osmotic pressure of the crystalline phase lies slightly above that calculated for a single FCC crystal even after accounting for polydispersity. Likewise the high shear viscosity of the fluid compares well with other hard sphere dispersions, but the low shear viscosity for PMMA/PHSA hard spheres exceeds those for polystyrene and silica hard spheres, e.g. a relative viscosity of 45±3 at ϕ=0.50 rather than 24. Our low shear viscosities are consistent with other PMMA/PHSA data after rescaling for both the polymer layer thickness and polydispersity and may represent the true hard sphere curve. We anticipate that the equation of state for the crystal deviates due to polycrystallinity or a direct effect of polydispersity, while the low shear viscosities reflect slight permeability of the polymer layer.

University of New Hamsphire

Polymer Research Group

Contribution to IPCG Newsletter Fall 1996

Donald C. Sundberg

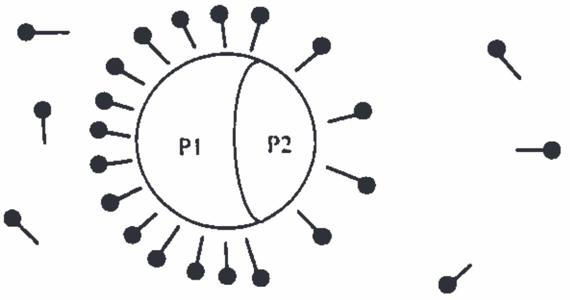
G106 Parsons Hall Durham, NH 03824, USA

Fax: (603) 862 3617 Email: dcs@christa.unh.edu

SURFACTANT ADSORPTION STUDIES ON LATEX BLENDS

Doris Garvey and Yvon Durant

The present objective is to develop a set of data and a model for competitive adsorption of surfactant on two polymer surfaces. During a seeded polymerization various morphologies can develop, and many of them have both polymers in contact with the water phase as in the following figure.



Each polymer surface has a different adsorption area A_0, and also a different adsorption isotherm.

If one considers an amount X_t of surfactant added to the emulsion, it is fractionated in 3 parts. One fraction X_w is dispersed in the water phase, a fraction X_1 is adsorbed on polymer 1 and a fraction X_2 is adsorb on polymer 2. The amount adsorbed on each surface modifies its interfacial tension, γ polymer / aqueous phase. If during polymerization the morphology changes significantly, the amount of surfactant is redistributed and the interfacial tension varies accordingly. It is consequently important for us to be able to understand and predict this competitive phenomenon. In order to study this basic phenomenon we used a simple mixture of two latices that we call blends. A blend presents the analogous surface characteristic to a structured particle such as shown above in regards to the surfactant adsorption. We used at first blends of PS and PMMA, both for their higher stability when no surfactant is present and due to the great difference in polarity (i.e. affinity for the surfactant).

We also developed our own data for other homopolymers, PbuMA, PMA and PBuA.

Experiments

Various latices were made by emulsion polymerization at 70°C with conditions creating reasonably monodispersed particles of low charge density by using a significant amount of SDS while remaining under the CMC. The latices were dionized by ion exchange with a mix of cationic and anionic resins. The resulting latices were titrated with NaOH by recording the conductivity of the latex as a function of the volume of NaOH added to calculate the sulfate end group charge density and further neutralize the latices. Each latex was titrated 3 times. The charge densities were in the range of 0.2 - 0.5 μC/cm^2.

We observed experimentally that in order to obtain adsorption area and isotherms of good quality we needed to titrate our latices around room temperature. We used an experimental setup providing reliable data by using an automated syringe to add the surfactant solution to the latex and direct computer acquisition from the conductivity meter to record latex conductivity as a function of added surfactant. Then the data were directly available in a spreadsheet software (Excel) for numerical treatment. By plotting the conductivity as a function of the square root of the surfactant concentration one obtains a curve with a break point characteristic of the CMC. This break point is well defined at temperatures below 30°C but very difficult to locate at higher temperature. Consequently we kept our measuring cell thermostated at 20°C.

We also determined that the most reliable technique to evaluate the adsorption area is to measure the apparent CMC (water + particles) at various solids content and to plot the amount of surfactant (moles) at the CMC as a function of the weight of polymer titrated (g). These various points are aligned and the slope of the line they create is directly related to the adsorption area, for the surfactant.

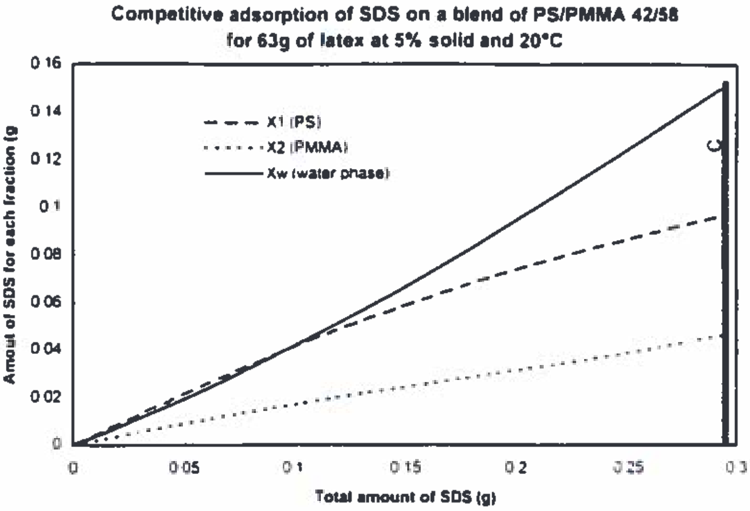
Following this procedure we found the following equilibrium adsorption areas (Å^2/molecule) for SDS: PnBuMA =31, PS =43, PnBuA=44, PMMA = 134.

The isotherms are created by reploting the conductivity curves as a function of surfactant concentration using $\frac{\lambda - \lambda_{c=0}}{\lambda_{c=cmc} - \lambda_{c=0}}$ as a normalized conductivity (0 to 1 scale) and the relative surfactant concentration (concentration divided by CMC). Then by using the isotherm obtained for pure DI water, one obtains the relation between the amount of surfactant added to the latex and the amount of surfactant freely dissolved in the water. It is then possible to plot the difference as the amount of surfactant absorbed on the polymer, as a function of the amount of surfactant in the water.

Application

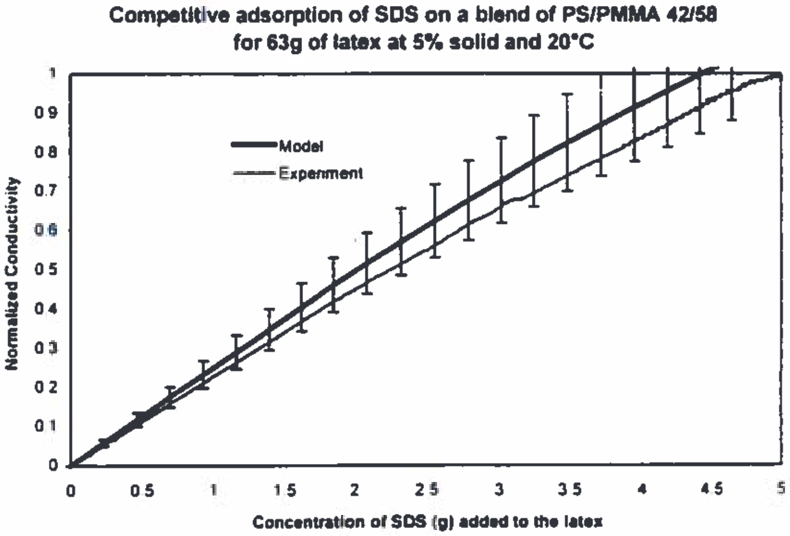
Using the above ideas, we have measured some competitive adsorption behavior in PS/PMMA blends. There is a great difference between the equilibrium adsorption areas for SDS on these polymer surfaces (43 Å^2/molecule for PS and 134 Å^2/molecule for PMMA) and as such we expect that in a latex blend the PS surface will compete more strongly for SDS than will PMMA. For a particular experiment the results are shown in the following figure.

Here we note, as expected, that the surfactant partitions very much unevenly between the two polymers and the water. We are nowworking with a preliminary model of the competitive adsorption process (we know of no published treatments of the phenomenon - please contact us if you know of some published or unpublished information), and have tried to test it with the above data.



Because we can measure only the resulting latex conductivity, we can experimentally obtain only the cumulative adsorption on both polymers. The following figure is a plot of our prediction from the model (with 15% error bars) compared with our experimental results.

All our data are based on particles sized determined with a Coulter nanosizer, for which we attribute a 5% inaccuracy. We expect to improve significantly our accuracy with particles size determined by electron microscopy.



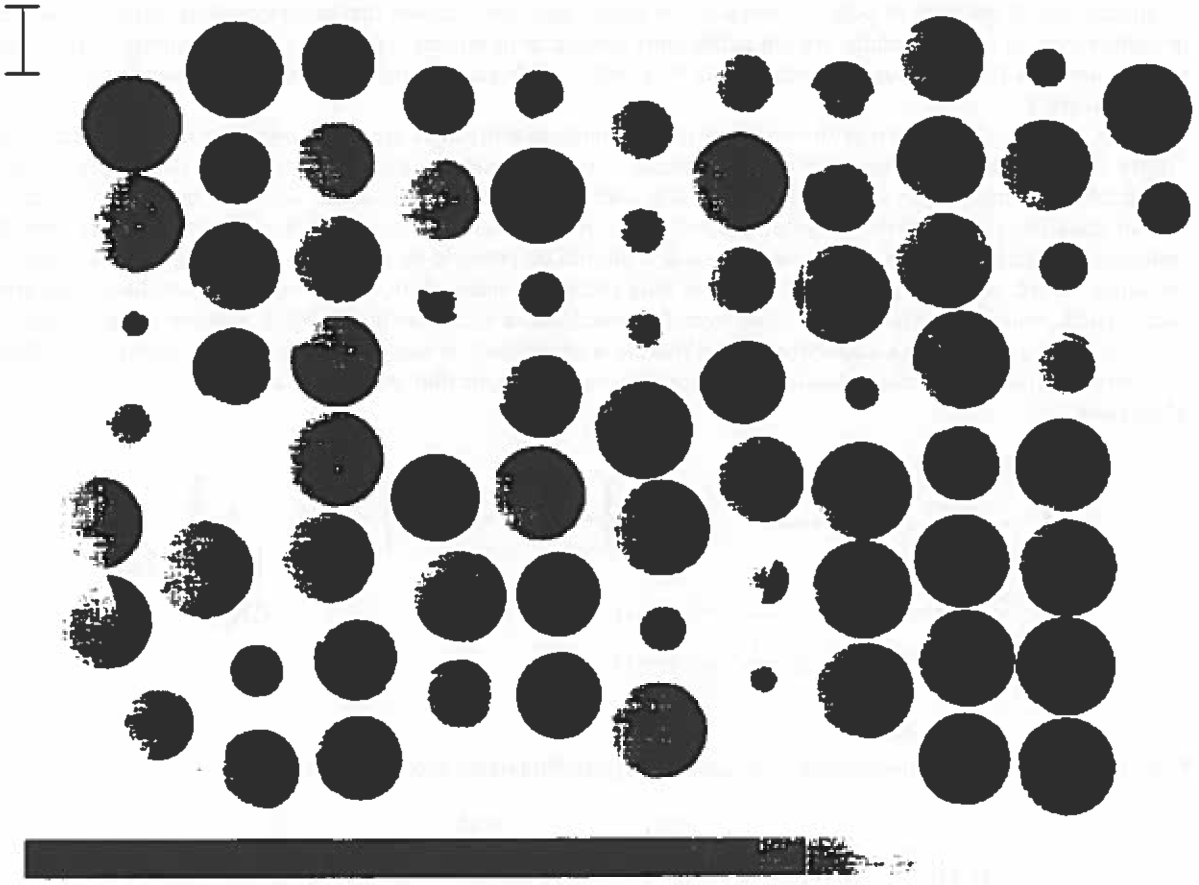
Conclusion

We have developed an initial model, that is reasonably promising, but we are facing several experimental observations that we have not read about before. We are currently working on expending the domain of observation and getting a better understanding of fundamental phenomena of competitive surfactant adsorption on different polymer surfaces.

PREDICTIONS OF LATEX MORPHOLOGY

Robert Carrier and Yvon Durant

We now have a software package capable of producing predicted morphology results in the form of electron micrographs. This is an option within the software program and allows the user to display the predicted morphology as an SEM or TEM micrograph. For the TEM one is able to choose to look at the whole particle or microtomed sections of the particle. In the latter case, one has the option of changing the microtomed section thickness and level of staining. The output graphics are intended to appear as standard electron micrographs so as to be comparable to those obtained from actual microscopes. We provide an example of microtomed TEM output. Here the section through the center of the predicted morphology appears in the upper right hand corner. Ramdom microtomed slices of 90 nm thickness are displayed in the figure and show preferential staining to obtain phase contrast. The reference bar on the upper left hand side is a 250nm.



Contribution to the Internatinal Polymer Colloids Group News Letter
Reporter: Klaus Tauer
MPI Kolloid- und Grenzflächenforschung
Kantstraße 55
D-14532 Teltow, Germany

Polyelectrolyte Block Copolymers as Effective Stabilizers in Emulsion Polymerization

Since the beginning of the 80s experimental and theoretical investigations have been carried out concerning the association behavior of amphiphilic block copolymers in aqueous solutions in dependence on block lengths and ionic strength. SELB and GALLOT investigated poly(styrene)-b-poly(4-vinyl-N-ethylpyridinium bromide) [1-4]. VALINT and BOCK reported on poly(tert-butylstyrene)-b-poly(styrene sulfonate) [5]. EISENBERG reported in a series of papers on the micellization behavior of poly(styrene)-b-poly(sodium acrylate) [6-8]. As the combination of one uncharged hydrophobic block with a charged block in one molecule exhibits some unusual association behavior. These structures are also a matter of intensive theoretical considerations [9-12]. Looking at all these activities over the last nearly 20 years it is the more surprising that application of such block copolymers as stabilizers in emulsion polymerization has not taken place.

Examinations of micelles of polyelectrolyte block copolymers have shown that polyelectrolyte block copolymers in comparison to low molecular weight surfactants require at interfaces with high interface energy rather large surface areas [13]. This might be translated in a rather high stabilization effiency, for instance in emulsion polymerization.

The aim of this contribution is to report on the behavior of poly(ethyl ethylene)-b-poly(styrene sulfonate) (cf. Figure 1) as stabilizer for emulsion polymerization. The motivation for these investigations is fourfold. First, it is possible to prepare exclusively electrosterically stabilized polymer dispersions. Second, the rate of migration of that stabilizers in the final polymer product (film or bulk material) is expected to be much lower than for common low molecular weight emulsifiers, and it should be possible to overcome technological drawbacks of the latter. Third, one can expect in films or in bulk materials made of these dispersions microphase separation occur which would keep the polar entities even dispersed inside a continuous, unpolar volume phase. Fourth, if the architecture of the block copolymers is tailored in a proper way, it was argued that the polyelectrolyte blocks are more effective in interface stabilization than common low molecular weight surfactants.

Materials

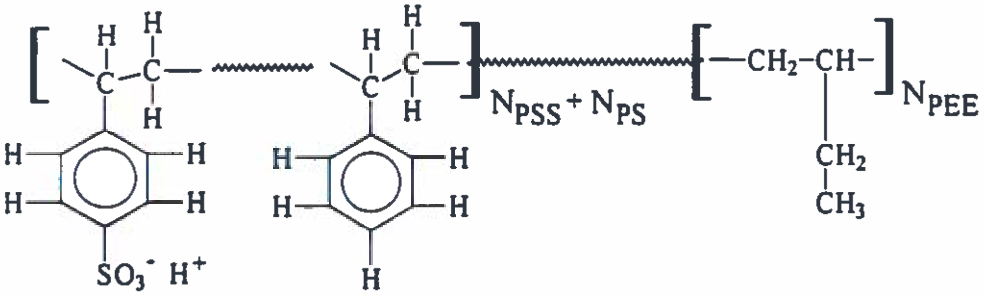
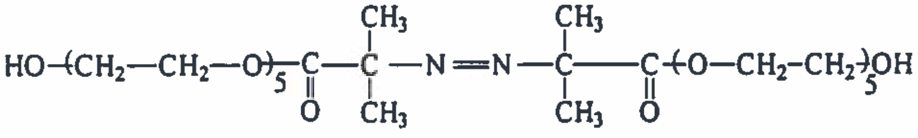


Figure 1: Structure of poly(styrene sulfonate)-b-poly(ethylethylene) block copolymer.



$$HO\left(CH_2-CH_2-O\right)_5 C(=O)-C(CH_3)_2-N=N-C(CH_3)_2-C(=O)\left(O-CH_2-CH_2\right)_5 OH$$

Figure 2: Structure of the initiator PEGA200.

Results

In order to investigate the stabilizing capability of the block copolymers a symmetrical, nonionic poly(ethylene glycol)-azo-initiator PEGA200 with five ethylene glycol units on each side of the azo group (cf. Figure 2) was employed [15, 16]. The block copolymer 1-H52 exhibits a degree of sulfonation of 52%, whereas in case of 1-H100 the degree of sulfonation of the styrene block is 100 % (N_{PS}=0).

Surfactant free emulsion polymerizations in water with PEGA200 alone do not lead to latices but to complete coagulum formation proving that this initiator does not contribute to latex stability as for instance potassiumpersulfate (KPS). The reason to use PEGA200 instead of well-known 2,2'-azo-bis-isobutyronitrile

(AIBN) is the fact that much less coagulum is formed with PEGA, as known from standard emulsion polymerizations with surfactant.

All emulsion polymerizations were carried out batchwise in either a glass reactor or a reaction calorimeter RM2-S (Chemisens, Sweden) with a stainless steel reaction vessel.

The application of 1-H52 as stabilizer in emulsion polymerization leads to some surprising results. Figure 3 shows the mean hydrodynamic diameter D_i from dynamic light scattering as a function of the amount of blockcopolymer 1-H52 relative to styrene, T.

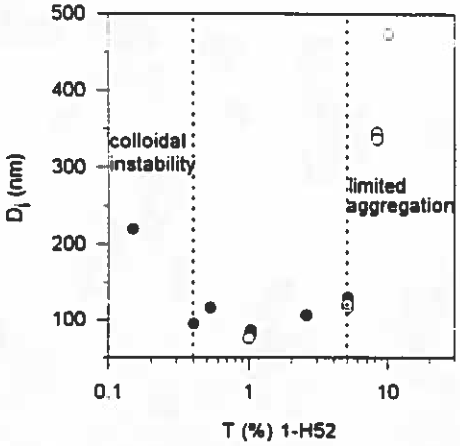


Figure 3: Apparent average latex particle size $\mathbf{D_i}$ (DLS) as a function of block copolymer concentration (1-H52) as a fraction of monomer weight T, ● calorimeter (steel reactor), O glas reactor experiments.

In a range of about 0.4 wt% - 5 wt%, the particle size is about constant or slightly increases with the amount of block copolymer; in this range, the polydispersity constantly increases with amount of amphiphile. At T > 5 wt%, the particle size and polydispersity increases rapidly. This is apparently the opposite behavior to the one of common low molecular weight surfactants in a classical emulsion polymerization [17] as well as nonionic block copolymers either with potassium persulfat as initiator [18] or with PEGA200 [19].

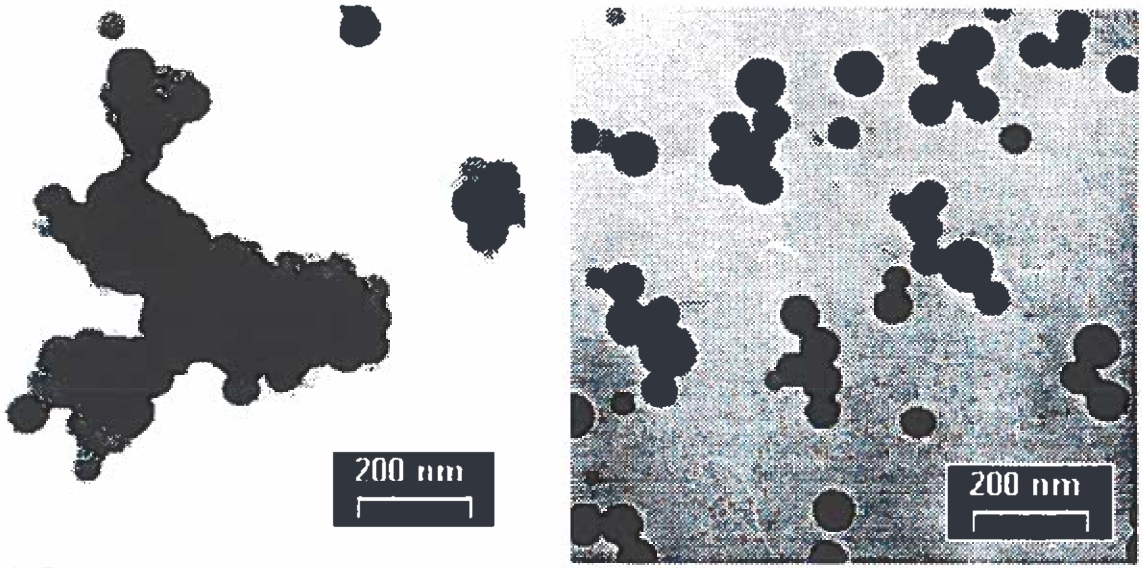
On the other hand, coagulum formation during polymerization shows the expected behavior, i.e. the lower the stabilizer concentration the higher the amount of coagulum Table 1. The lowest 1-H52 concentration (T = 0.147 wt%) clearly evades from the colloidal stable region where 98 wt% of the polymer material coagulates.

Table1: Results of latex synthesis: **BS** block copolymer stabilizer 1-H52, **T** block copolymer weight as a fraction of monomer weight, **SC** solid content of the final latex, **CG** coagulum wt% of polymer, $\mathbf{D_i}$ hydrodynamic diameter from DLS without special treatment, C refers to polymerization in the calorimeter (15 g styrene) and G to the glass reactor (10 g styrene), **PD** polydispersity.

Latex	BS (g)	T (%)	SC (%)	CG (%)	D_i (nm)	PD	remark
R01C	0.022	0.147	1.56	98.0	219	0.25	instability
R02C[1]	0.060	0.400	17.9	13.6	94.2	0.18	colloidal
R03C	0.079	0.527	17.0	19.3	116	0.36	stability
R04G	0.100	0.996	19.5	7.4	75.4	0.37	
R05C[1]	0.153	1.02	18.5	11.0	78.5	0.29	
R06C	0.154	1.03	18.4	12.9	85.4	0.42	
R07C	0.379	2.53	17.4	18.9	105	0.36	
R08G	0.506	5.06	21.6	0.0	115	0.47	
R09G[1]	0.507	5.07	21.3	0.0	121	0.47	
R10C[1]	0.750	5.00	20.3	5.0	129	0.53	
R11G	0.830	8.30	21.8	1.5	344	0.63	limited
R12G	0.837	8.40	21.7	2.0	336	0.62	aggregation
R13G	1.013	10.1	22.3	0.5	474	0.57	

[1] without crosslinker

The increase of the average particle size with increasing stabilizer concentration is not a result of colloidal instability as the amount of coagulum is decreasing or even vanishing. That this phenomenon is caused by the use of this special kind of stabilizer is revealed by TEM micrographs. Figure 4a shows that a high amount of stabilizer (R13G, T = 10.1 wt%) leads to the formation of flocks with a size in the µm-range which consist of separate small particles. A stabilizer concentration of around 5 wt% (R08G) leads to a much smaller number of flocks of much smaller size and at 1 wt% there are almost no flocks present. In this case the particles are clearly separated, Figure 4b. The primary particles of all three latices have a similar size.



(a) R13G (b) R04G

Figure 4: TEM micrographs showing the separate particles of the flocks in case of latex R13G (a) and latex R04G (b).

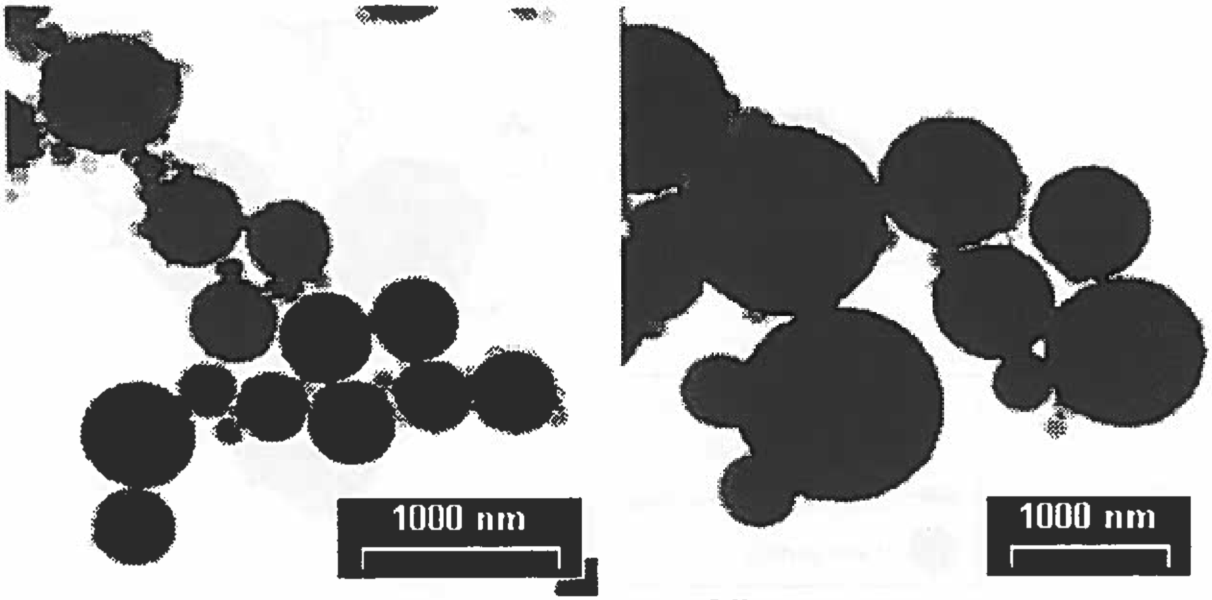
Looking closer at the flocks it seems that these particles are only stuck together but did not grow together. Although they do not seperate after dilution with deionized water, the redispersion is successful by ultrasonification of the diluted latex or by dilution with a nonionic surfactant solution (e.g. with the CHDF eluate) even without ultrasonification.

All results described so far have been obtained in practically salt-free conditions. (Salt-free means that there was no addition of salt and there were no ionic groups in the system except the sulfonate groups with their counter-ions.) We expect that the situation completely changes if the polymerization is carried out in an aqueous phase of higher ionic strength. Two possibilities to achieve higher ionic strengths are applied: the addition of an inert salt to the monomer emulsion or the use of potassium persulfate (KPS) as the initiator instead of PEGA200. In the latter case, we have to expect an additional electrostatic stabilization by sulfate groups from the initiator.

Table 2: Influence of ionic strength on latex properties: **T** block copolymer / monomer, K refers to KPS as initiator, S refers to polymerization in presence of sodium chloride, **CG** coagulum, **D_i**, **D_i^{US}** hydrodynamic diameter from dynamic light scattering before and after ultrasonification.

Latex	T (%) 1-H52	CG (%)	D_i (nm)	D_i^{US}(nm)	Electrolyte
R04G	1.0	7.4	75.4	73.0	No additional electrolyte
R04G-K	1.0	10.6	1100	940	Initiator: 19.1 mM KPS
R04G-S	1.0	69.0	440	440	100 mM sodium chloride
R13G	10.1	0.5	470	152	No additional electrolyte
R13G-K	10.1	69.5	350	240	Initiator: 19.4 mM KPS
R13G-S	10.1	9.7	720	218	100 mM sodium chloride

The results of polymerizations with a low stabilizer concentration summarized in Table 2 show that in both cases (R04G-K, R04G-S) a large amount of coagulum and big particles are formed. The resulting particles are depicted in Figures 5a & b; in both samples particles with a diameter of around 1µm together with some small particles are present.



(a) R04G-S (b) R04G-K

Figure 5: TEM micrographs showing the infuence of electrolyte: (a) R04G-S, 100 mM sodium chloride, (b) R04G-K 19.4 mM potassium persulfate.

This result has to be expected, since the increase in ionic strength leads to a screening of the electrostatic fields between the protruding polyelectrolyte chains; the density of charged domains is increased and the stabilization efficiency is lowered. The increase of the amount of coagulum and the mean particle size clearly reflect the sensitivity of the electrosteric stabilization at low grafting densities against salt. It is interesting to note that all latices coagulate if a 1 M sodium chloride solution is added after polymerization.

At higher block copolymer concentrations the dependence of the particle size after ultrasonification D_i^{US} on ionic strength of the solution is less pronounced. Within the framework of electrostatics this reflects the fact that higher amounts of polyelectrolyte block copolymer at constant primary particle size increase the local charge density in the formed polyelectrolyte shell to such high values that additional salt has only minor influence.

The limited aggregation of the latex particles caused by the block copolymer 1-H52 applied in amounts higher than 5 wt% can be speculatively explained following this route. At low ionic strength of the aqueous phase and at low polyelectrolyte load, the repulsion between the (partially) charged blocks as well as between the primary particles is high. Since the ionic groups of the poly(styrene sulfonate) block (degree of sulfonation is 52%) are distributed statistically it is very likely that there are some hydrophobic domains present. In this case, we expect the block copolymer to be adsorbed not only with the poly(ethyl ethylene) block but also with these hydrophobic moieties leading to multiple adsorption points per molecule on a particle and charged loops into the water phase. Increasing the polyelectrolyte block copolymer concentration in the interface results in a screening of the Coulomb interaction until the elctrostatic interaction is less extended than the distance between the different hydrophobic domains of the blockcopolymers. Exceeding this critical value, each chain can adsorb onto different primary particles leading to limited aggregation through interparticular bridging which depends on blockcopolymer as well as on latex concentration. The formation of flocks at higher block copolymer concentration is also enhanced by hydrophobic interaction of those non-sulfonated domains which are not adsorbed or of the hydrophobic backbone of the polyelectrolyte block. Figure 6 schematically illustrates this stabilization and controlled aggregation mechanism.

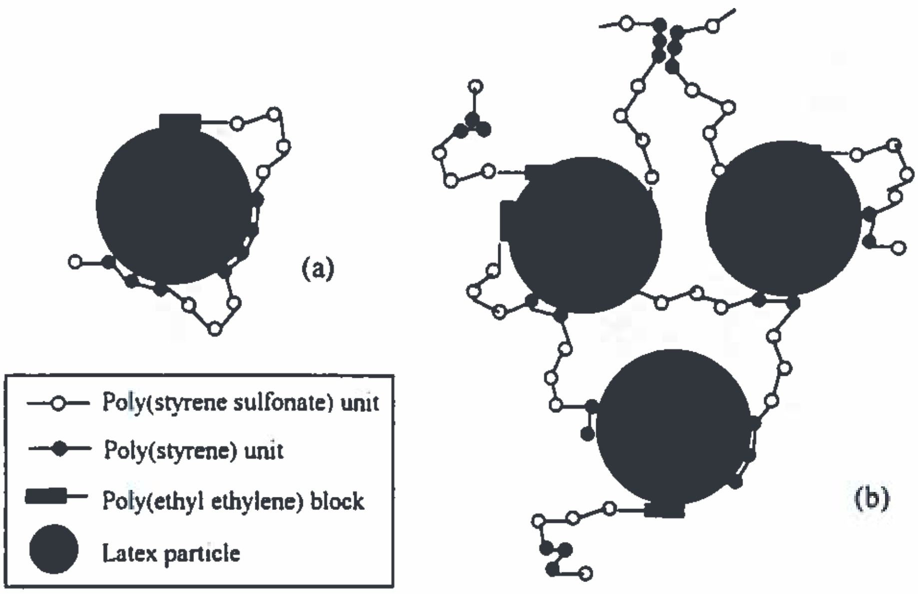


Figure 6: Illustration of the adsorption behavior of the block copolymer 1-H52, (a) block copolymer concentration up to 5 wt%, (b) block copolymer concentration above 5 wt% (limited coagulation).

The paper has been submitted to ***Macromolecules*** *for publication.*

References

[1] Selb, Y. Gallot, *Makromol. Chem. 181*, 809 (1980).
[2] Selb, Y. Gallot, *Makromol. Chem. 181*, 2605 (1980).
[3] Selb, Y. Gallot, *Makromol. Chem. 182*, 1491 (1981).
[4] Selb, Y. Gallot, *Makromol. Chem. 182*, 1513 (1981).
[5] L. Valint, J. Bock, *Macromolecules 21*, 175 (1988).
[6] Astafieva, X. F. Zhong, A. Eisenberg, *Macromolecules 26*, 7339 (1993).
[7] Khougaz, Z. Gao, A. Eisenberg, *Macromolecules 27*, 6341 (1993).
[8] Moffitt, K. Khougaz, A. Eisenberg, *Acc.Chem.Res. 29*, 95 (1996).
[9] Rabin, J. F. Marko, *Macromolecules 24*, 2134 (1991).
[10]F. Marko, Y. Rabin, *Macromolecules 25*, 1503 (1992).
[11]Dan, M. Tirrell, *Macromolecules 26*, 4310 (1993).
[12]P. Shusharina, I. A. Nyrkova, A. R. Khokhlov, *Macromolecules 29*, 3167 (1996).
[13]Förster, M. Zisenis, E. Wenz, M. Antonietti, *J. Chem. Phys. 104*, 9956 (1996).
[14]Förster, W. Leube, to be published.
[15]Walz, B. Bohmer, W. Heitz, *Makromol. Chem. 178*, 27 (1977).
[16]Tauer, K.-H. Goebel, S. Kosmella, K. Stähler, J. Neelsen, *Makromol. Chem. Symp. 31*, 107 (1990).
[17]V. Smith, R. H. Ewart, *J. Chem. Phys. 16*, 592 (1948).
[18]Berger, W. Richtering, R. Mülhaupt, *Polym.Bull. 33*, 521 (1994).
[19]Müller, K. Tauer, unpublished results.

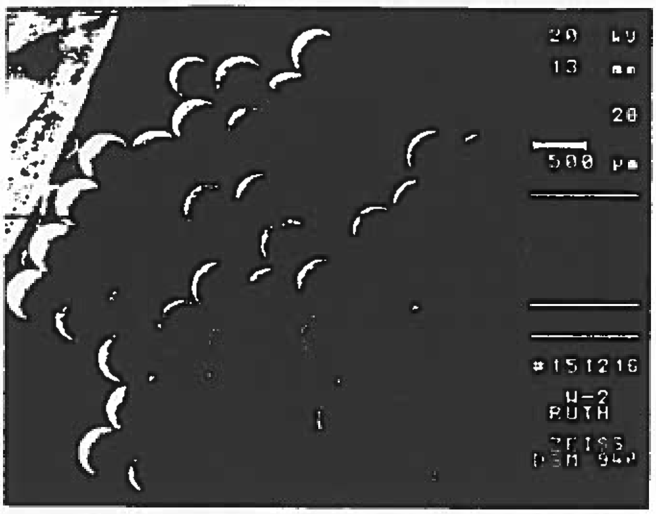
Polymer Colloid Group. (Newsletter).

John Ugelstad, Arvid Berge

Department of Industrial Chemistry, NTNU, Trondheim Norway.

1. PREPARATION OF LARGE MONOSIZED PARTICLES BY STEP POLYMERIZATION.

We have developed a new process, (Arvid Berge, John Ugelstad, et al. Patent Application) which allows monodisperse particles of predetermined size up to > 1000 µm to be produced by various step polymerization processes. The particles can be prepared from different monomers. The particles presented in the figure below is made up of resorcinol-formaldehyde, and have a size of 420 µm. Work is going on with different monomers and with preparation of particles with various morphology (e.g. porosity). These particles has met with great interest, e.g. for use in immunology.



SEM of Resorcinol-formaldehyde particles, 420 µm.

2. FURTHER WORK ON MAGNETIC PARTICLES.

2.1. Nonspecific binding of proteins and cells to the surface of the particles.

<u>a) Proteins.</u> When coupling antibodies and the like to the surface of our magnetic particles we often apply particles with relatively hydrophobic surfaces. This is the case even when we aim at binding the antibody covalently. By use of a hydrophobic surface we get a preadsorbtion of the antibody at the surface which ensures a rapid and effectiv binding of the antibody. Moreover we get a favourable orientation of the antibody, with the Fc part pointing to the surface, and the Fab parts (fraction antigen binding) in an optimal orientation, pointing out from the particles. For some of the applications, both particles with an antibody coupled to the surface, as well as for particles with protein A, for extracting monoclonal IgG antibodies from ascites, (where now in this case IgG antibodies are the antigens to be isolated), the hydrophobicity represents a disadvantage as we get

an unwanted non-specific binding of various substances.
We have investigated a number of more hydrophilic particles,and have just recently brought on the market a new particle with epoxy groups which has a much more hydrophilic surface. In that case one most often experiences that the covalent binding of antibodies is slow and unefficient. This may be overcome by use of salts. Our studies have involved measurements of various particles, various hydrophilic layers,and various salts to optimize the type and amount of salt applied, in order to optimize the covalent attachment of the ligand and the consecutive antigen binding capacity of the antibody, respectively protein A on the particles.
As said the use of hydrophobic particles have many advantages. Ideally we would prefer to have particles which were hydrophobic during attachment of the antibody to the particles, and then as soon as we have established the covalent coupling of the antibody, the particle surface is shifted to become hydrophilic. In fact we then search for a compound which is capable to break hydrophobic bindings leaving the surface hydrophilic and then with the antibody in a favourable orientation.
Among the substances we have investigated is casein. We have showed that a pretreatment with casein is 100–1000 times more effective in hindering IgG antibodies to add to our magnetic particles than is albumin, which is normally used. This general effect on hydrophobic surfaces was shown by Vogt. We have also investigated the capacity of casein to replace IgG physically bound to the particle surface. Again casein is far more effective than albumin,and will with short incubation times for IgG practically completely displace IgG from the surface. The displacement efficacy is gradually reduced by increasing incubation time with IgG. And which is very important, casein does not influence the antigen binding capacity when we first covalently bind antibody and then treat the particles with casein.

<u>b) Cells.</u> In many cases where we intend to get a pure subset of cells, e.g. from blood or bone marrow, by positive selection, we are burdened with nonspecific binding of cells to the particles.
As an example we may look upon the isolation of progenitor stem cells from mobilized blood or bone marrow. When carrying out autologuous bone marrow transplantation,in connection with cancer that has methastisized to bone marrow, an alternative procedure to that of removing the cancer cells from the marrow before reinfusing the purified marrow, is to carry out a positive selection of progenitor stem cells, where we after magnetic isolation of the stem cells detach the beads from the stem cells and reinfuse the liberated free stem cells.
A difficulty one is met with in this case is the non-specific binding of tumor cells to the particles. It turns out that the cancer cells generally seem to have a tendency to stick to the particles which is much higher than that of the normal blood cells. For instance we find that breast cancer cells when present in marrow or blood has a tendency to stick to the particles non-specificially, which is 20 times higher than the other normal cells present. We are for the moment doing a thorough investigation on non-specific binding of *various type of cancer cells* to various particle types. The non-specific binding is as expected considerably lower in the case of more hydrophilic particles,but even there it is clearly noticable. With cells we do again see a remarkable effect of casein which dramatically lowers non-specific binding of any cells on hydrophobic surfaces, and does so to a much larger degree than do albumin. Even casein causes a substantial reduction of non-specific-binding of cancer cells on *hydrophilic* surfaces.

2.2 GRADIENT CENTRIFUGATION.

When isolating specificially various cell types by immunomagnetic separation we sometimes use a large excess of beads compared to the target cells. This is the case when the target cells are present in very small concentration as for instance when we want to detect and determine very small quantities of breast cancer cells which have methastazised to the blood. Preferably we should be able to detect one tumor cell in ten million normal cells.
We have developed a gradient centrifugation method,which allows removal of 98 % of free beads to be removed as bottom fraction while substancially all cancer cells with attached beads remain in the top fraction.

Most of the recent work on magnetic particles referred to above is referred to in some of our review papers which will appear soon.
A more complete description of the procedures and the results appear in the thesis of our coworker Wenche S. Prestvik; to be finnished in 1997.

New papers from our group:

P. C. Mørk, B. Sæthre, and J. Ugelstad, *Vinyl Chloride,* (Minisuspension polymerization) in *Polymer Materials Encyclopedia,* (ed. J.C Salamone Vol 11, 8559–65 (1996)

J. Ugelstad, *et al. Monodisperse polymer particles* (Nonmagnetic and Magnetic) in *Polymer Materials Encyclopedia,* (ed. J.C Salamone) Vol. 11, 4501–19, 1996)

J. Ugelstad, W.S. Prestvik, P. Stenstad, L. Kilaas, and G. Kvalheim, *Monodisperse Magnetic Particles in Cell Separation.* in *Magnetism in Medicin,* (eds W. Andra and H. N Nowak. Akademia verlag) 1997 (in preparation)

W.S. Prestvik, J.Ugelstad, P. Stenstad, *New Developements in Preparation and Applications of Dynabeads,* in *Scientific and Clinical Applications of Magnetic Carriers,* (eds W.Shutt, J. Teller, U. Hafeli and M. Zborowsky) 1997 (in preparation)

B. Christensen, M.H. Myhr, O. Aune, S. Hagen, A. Berge, and J. Ugelstad, *Macroporous, monodisperse particles and their application in aqueous size exclusion chromatography of high molecular weight polysaccharides. Carbohydr. Polym.,*(in press)

A. VRIJ
Contribution of the Van the Hoff Laboratory for the Polymer Colloid Group Newsletter.

4372 *Langmuir* 1996, *12,* 4372–4377

Paramagnetic Silica Particles: Synthesis and Grafting of a Silane Coupling Agent Containing Nickel Ions onto Colloidal Silica Particles

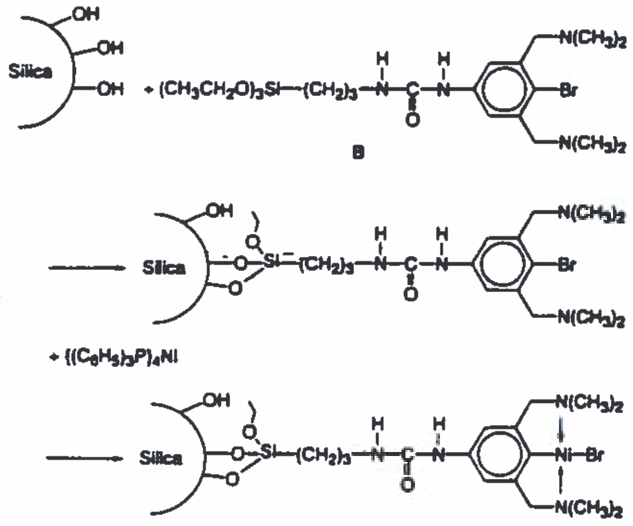
Chellappah Pathmamanoharan,[†] Peter Wijkens,[‡] David M. Grove,[‡] and
Albert P. Philipse*[,†]

Van't Hoff Laboratory for Physical and Colloid Chemistry, Debye Institute, Utrecht University, Padualaan 8, 3584 CH Utrecht, The Netherlands, and Department of Metal-Mediated Synthesis, Debye Institute, Utrecht University, Padualaan 8, 3584 CH Utrecht, The Netherlands

Received April 12, 1996. In Final Form: June 21, 1996[⊗]

A method is presented for the preparation of stable model dispersions of paramagnetic silica particles. A specially designed silane coupling agent containing Ni^{2+} ions is grafted onto silica particles which are either commercially obtained or prepared by the Stöber synthesis. A wet process is described which avoids aggregation of ungrafted and grafted silica particles. The resulting magnetic silica particles have been characterized by dynamic light scattering, transmission electron microscopy, elemental analysis, and infrared spectroscopy. Preliminary magnetization measurements and magnetic relaxation (NMRD) experiments illustrate some of the possibilities for studying model silica colloids with a covalently bonded paramagnetic surface layer.

Scheme 2



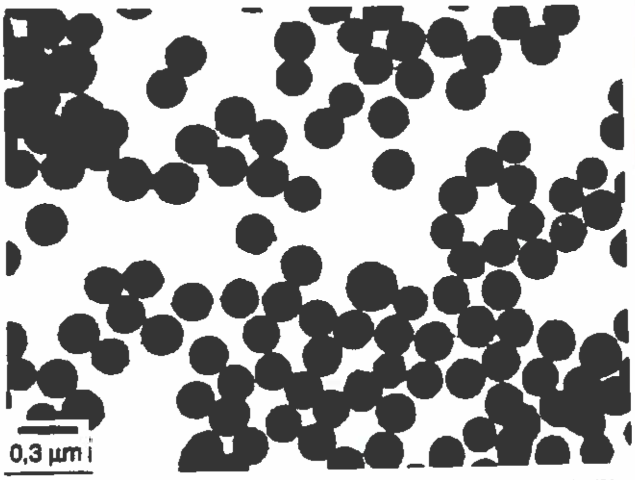


Figure 2. Transmission electron micrograph of SH1Ni silica particles.

A. VRIJ
Contribution of the Van 't Hoff Laboratory for the Polymer Colloid Group Newsletter.

Langmuir 1996, *12*, 3844–3854

Preparation and Properties of Organic Dispersions of Monodisperse Silica Receptor Colloids Grafted with Calixarene Derivatives or Alkyl Chains

A. M. Nechifor,[†,∥] A. P. Philipse,[*,‡] F. de Jong,[†] J. P. M. van Duynhoven,[§]
R. J. M. Egberink,[†] and D. N. Reinhoudt[†]

Enschede, The
Netherlands, Van't Hoff Laboratory for Physical and Colloid Chemistry, University of Utrecht,
Padualaan 8, 3584 CH Utrecht, The Netherlands, and Department of Chemical Analysis,
University of Twente, P.O. Box 217, 7500AE Enschede, The Netherlands

Received January 22, 1996. In Final Form: May 24, 1996[⊗]

We introduce cation-selective receptor colloids consisting of a monodisperse inorganic silica core grafted with an organic layer containing calixarene receptor molecules. The surface layer is designed to provide chemical selectivity (toward Cs^+) as well as colloidal stability in organic solvents of interest in which silica spheres otherwise may flocculate. Grafting procedures for commercial- and laboratory-made silica dispersions are investigated for 25,27-bis[1-(11-hydroxyundecyl)oxy]calix[4]arene-crown-6 (designed and synthesized for this purpose), octadecyl alcohol, and mixtures ("cografting") of both compounds. Special attention is given to the nature of the solvent, which markedly influences grafting densities and colloidal stability during and after grafting procedures. NMR, elemental analysis, and light scattering are used to characterize a variety of carefully purified, grafted silica dispersions and to demonstrate, among other things, the presence of calixarene groups on the silica spheres. Preliminary complexation experiments with cesium chloride are reported. NMR and electrophoresis indicate that calixarene–silica colloids indeed are receptors for cesium cations.

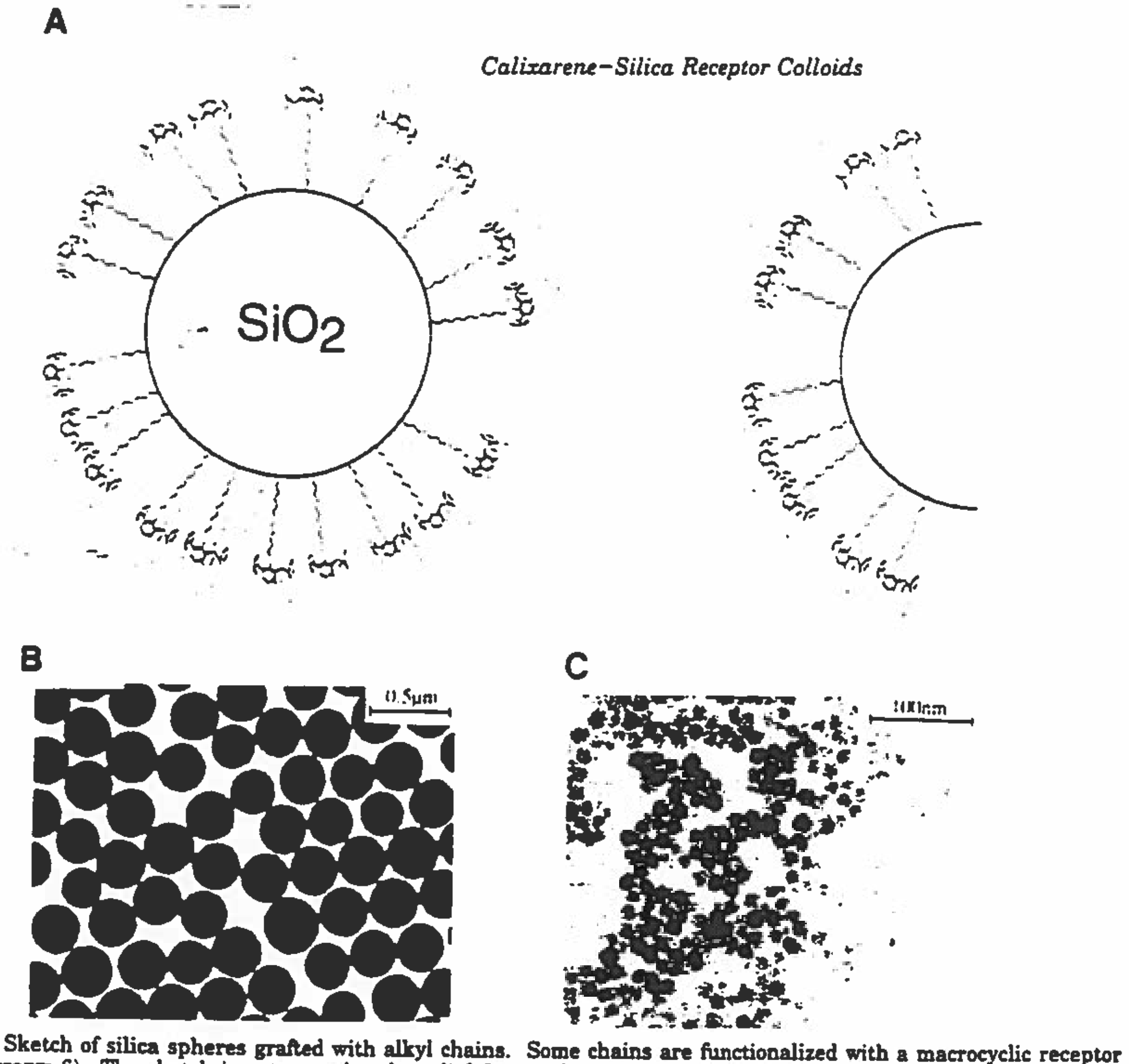


Figure 1. (A) Sketch of silica spheres grafted with alkyl chains. Some chains are functionalized with a macrocyclic receptor (calix[4]arene-crown-6). The sketch is not on scale: the calix[4]arene derivate occupies an area of about 1 nm^2, and the radius of Stöber silica spheres on transmission electron micrographs such as in part B is about 85 nm. Part C depicts Ludox particles.