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IPCG

INTERNATIONAL POLYMER COLLOIDS GROU

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NEWSLETTER

INDEX

FROM THE EDITOR'S DESK

We welcome as new contributors to the *Newsletter* Chee Ho of the University of Malaya and Masayoshi Okubo of Kobe University, Japan. IPCG members will be aware that polymer colloids have long been an area of very active research in Japan. This is reflected in the staging of the 7th Iketani conference on the Advanced Technology of Fine Particles, which is to be held in Yokohama in October, 1977. Details of the main themes of this Conference appear on page (iii). Haruma Kawaguchi is the Chair of the Organizing Committee and he has advised that first cicrular will be sent to all IPCG members shortly. Details of the Fourth meeting of the highly successful UK Polymer Colloids Forum, to be held at Keele University later this year, are presented on p(ii). Peter Lovell is the organizer as Chair of the Forum. Three outstanding plenary lectures appear on the program, as well as a rich variety of contributed lectures. A must for all devotees of polymer colloids in the UK.

e-mail Address: Jose Asua advised a correction to his email address published in the previous *Newsletter* which is: qppasgoj@sq.ehu.es

NEXT NEWSLETTER

Contributions should be sent to me by **AIR MAIL** by 1December, 1996

D H Napper
Editor
(e-mail: d.napper@chem.usyd.edu.au)

Fourth Meeting
of the
UK Polymer Colloids Forum

23-24 September 1996, Keele University, UK

with plenary lectures by

Professor Alain Guyot (CNRS, Lyon, France)
"Use of Reactive Surfactants in Emulsion and Dispersion Polymerisation"

Dr. Frank Heatley (University of Manchester, UK)
"Application of NMR Spectroscopy to the Characterisation of Emulsion Polymers"

Dr. Jenci Kurja (Eindhoven University of Technology, The Netherlands)
"Monomer Partitioning in Emulsion Copolymerisation"

About the Forum

The UK Polymer Colloids Forum was set up under MacroGroupUK in the Autumn of 1993 with expansion of UK academic activity in the field as one objective, particularly work on synthetic aspects, especially emulsion polymerisation. Another aim is to bring the UK polymer colloids community together for discussions of topics and issues that are of academic and industrial importance, the principal vehicle for this being the regular meetings of the Forum.

The provisional programme for the fourth meeting of the Forum is given in this circular and, as with previous meetings, provides a broad range of topics and issues for discussion.

Registration for the meeting

If you wish to receive a registration form, please contact Dr. Peter A. Lovell via fax (+44 161 200 3586) or e-mail (pal@umist.ac.uk) giving your name and address. Note that the deadline for receipt of registration forms/fees is 31 August 1996.

PROVISIONAL PROGRAMME

Monday 23 September

11.30 Registration
12.30 Lunch

13.30 Welcome and opening remarks: P.A. Lovell (UMIST, Chairman: UK Polymer Colloids Forum)

Session 1: Stabilisation of Polymer Colloids

13.40 Plenary Lecture: *Use of Reactive Surfactants in Emulsion and Dispersion Polymerisation*
A. Guyot (CNRS, Lyon, France)

14.40 *The Use of Block Copolymers as Stabilisers in the Dispersion Polymerisation of Styrene in Alcoholic Media*
F.L. Baines, S. Dionisio, L. Bartlett, S.P. Armes and N. Billingham (University of Sussex)
15.15 Tea & biscuits
15.40 *Scattering Studies of Bimodal Mixtures of Polymer Colloids*
R.H. Ottewill (University of Bristol)
16.15 *Effects of Hydrophobic Modification on the Physical Properties of Poly(ethylene glycol)*
T. Annable and R. Ettelaie (Zeneca Resins)
16.50 *Latex Flocculation using Chitosan*
J. Hearn and M. Ashmore (Nottingham Trent University)
17.25 Close of Session

18.15 – 19.30 Poster session

20.00 Dinner

Tuesday 24 September

Session 2: Preparation and Properties of Polymer Colloids

9.00 Plenary Lecture: *Monomer Partitioning in Emulsion Copolymerisation*
J. Kurja (Eindhoven University of Technology, The Netherlands)

10.00 *Preparation of Polymer Colloid Particles with a Complex Morphology*
R.H. Ottewill, A. Schofield and J. Waters (University of Bristol)
10.35 Coffee & biscuits
11.00 *Saturation Swelling and the Seeded Emulsion Polymerisation of Styrene at High Ionic Strength*
Z.F.M. Said (Yarmouk University, Jordan)
11.35 *Morphology and Transport in Polymer Latex Films*
J. Hearn, P.A. Steward and M.C. Wilkinson (Nottingham Trent University)
12.10 *Lucky Dip - Aspects of Latex Design for Synthetic Gloves*
D.V. Dodgson (Synthomer Ltd.)
12.45 Close of Session

13.00 Lunch

Session 3: Characterisation of Polymer Colloids

14.15 Plenary Lecture: *Application of NMR Spectroscopy to the Characterisation of Emulsion Polymers*
F. Heatley (University of Manchester)

15.15 *The Use of Field Flow Fractionation coupled with Multi-Angle Light Scattering for the Absolute Characterisation of Particle Distributions*
R.J. White (Optokem Instruments Ltd.)
15.50 *Characterisation and Application of Cationic Nanoparticles Produced by a Novel Submicroencapsulation Technique*
D. Fairhurst (sunSmart Inc, USA) and P. McFadyen (Brookhaven Instruments, UK)

16.25 Final remarks: P.A. Lovell (UMIST, Chairman: UK Polymer Colloids Forum)

Announcement of an International Conference

7th IKETANI CONFERENCE
International Symposium on Advanced Technology of Fine Particles

Conference Period: October 12-16, 1997 (Sun-Thu)
Location: Yokohama Symposia, Yokohama, Japan

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

Official Language: English

Coorganized by the Polymeric Microspheres Symposium Committee, Japan/
the International Polymer Colloids Group
Sponsored by Iketani Science and Technology Foundation

Organizations

Honorary chairman	S.Okamura (Professor Emeritus, Kyoto University, Japan)
Chairman	H.Kawaguchi (Keio University, Japan)
Vice-Chairman	M.S.El-Aasser (Lehigh University, USA)

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T.Okaya (Shiga Pref. University, Japan)
M.Okubo (Kobe University, Japan)
S.Omi (Tokyo Univ. of Agr. Tech., Japan)
J.H.Kim (Yonsei University, Korea)
P.Lovell (University of Manchester, UK)
D.H.Napper (University of Sydney, Australia)
Z.-R. Pan (Zhejiang University, China)
C.Pichot (CNRS, France)
T.G.M. van de Ven (McGill Univ., Canada)

Secretariat:
K.Fujimoto
Department of Applied Chemistry, Faculty of Science & Technology
Keio University
3-14-1 Hiyoshi, Yokohama 223, Japan
Phone: +81-45-563-1141 ext. 3457 Fax: +81-45-562-7625
E-mail: polymer2@applc.keio.ac.jp

First Circular of the Symposium will be sent to all of IPCG members very soon.

CONFERENCE SCHEDULE

CONFERENCE	LOCATION	DATE/CONTACT
	1996	
• 212th ACS National Meeting	Orlando, flo	25-30 August
• Water Soluble Polymers	Wrexham, Clwyd	11-13 September
• 4 UK Polymer Colloids Forum	Keele	23-24 September (Lovell)
	1997	
• 213 ACS National Meeting	San Francisco	13-17 April
• Gordon Conference on Polymer Colloids	Tilton School, NH	29 June - 2 July (Sundberg)
• 7th Colloid & Surface Science Symposium	Newark, DE	29 June - 2 July
• 214th ACS National Meeting	Las Vegas	7-11 September
• 2nd International Conference on Emulsions	Bordeaux	23-26 September
• 7th Iketani Conference	Yokohama	12-16 October (Kawaguchi)
	1998	
• 37th IUPAC Symposium	Gold Coast, Australia	13-17 July (Gilbert/Napper/ El-Aasser)

IPCG Membership FAX & Electronic Mail Numbers - June 1996

	Fax	Electronic mail
Asua JM	34-43-21-2236	qppasgoj@sq.ehu.es
Barton J	42-7-375-923	UPOLBART@SAVBA.SK (Internet)
Bassett DR	1-919-469-6797	
Candau F	33-88-41-4099	
Cohen Stuart M	31-317-48377	martien@fenk.wau.nl
DeSimone J	1-919-962-2388	desimone@email.unc.edu (e-mail)
Dodge JS	1-216-447-5544	
Downing S	44-1753-578-218	
El-Aasser MS	1-610-758-5880	mse0@lehigh.edu
Fitch RM	1-505-776-5930	bobfitch@laplaza.taos.nm.us
Gast AP	1-415-725-7294	gast@leland.stanford.edu (e-mail)
German AL	31-40-46-3966	tgtkag@chem.tue.nl
Gilbert RD	1-919-515-6532	
Gilbert RG	61-2-351-3329	gilbert@chem.usyd.edu.au (e-mail)
Goodwin JW	0225 722090	
Hansen FK	47-228-55542	f.r.hansen@kjemi.uio.no (Internet)
Ho, Chee-Chong	60-3-759-4193	
Ise N	81-6-465 0220	nise@mxa.meshnet.or.jp
Jayasuriya DS	1-414-629-2044	
Joosten JGH	31-46-761-200	
Kast H	49-621-609-2505	
Kawaguchi H	81-45-562-7625	polymer1@applc.keio.ac.jp
Kim Jung-Hyun (Jay)	82-2-312-6401	polylab@bubble.yonsei.ac.kr
Koper JG Ger	31-71-274-397	koper@rulfcl.leidenuniv.nl (e-mail)
Krieger IM	1-216-921-6145	
Lee Ik Do	1-517-638-7510	
Lovell PA	44-161-200-3586	pal@umist.ac.uk (Internet)
Lyklema J	31-317-483-777	fysko@fenk.wau.nl
Muroi S	81-462-21-7212	
Napper DH	61-2-351-3329	d.napper@chem.usyd.edu.au (e-mail)
Nomura M	81-776-27-8767	
Okubo T	81-58-230-1893	okubotsu@apchem.gifu-u.ac.jp
Okubo M	81-78-803-1169	okubo@icluna-u.ac.jp (e-mail)
Ottewill RH	44-117-925-1295	ottewill@siva.bris.ac.uk
Pelton R	1-416-521-1350	
Pichot C	33-72-72-85-33	christian.pichot@ens-bma.cnrs.fr
Piirma I	1-216-972-5290	
Poehlein GW	1-404-894-2866	gary.poehlein@che.gatech.edu (e-mail)
Riess G	33-89-59-9859	
Rowell RL	1-413-545-1232	rowell@chem.umass.edu (e-mail)
Russell WB	1-609-258-0211	
Sperry PR (Internet)	1-215-619-1626	Peter_R_Dr._Sperry@rhomhaas.com
Stannett VT	1-919-515-3465	

Stenius PJ	358-04514259	
Sundberg DC	1-603-862-1997	dcs@christa.unh.edu (Internet)
Tauer, K	3328 46255	ktau@mpikg.teltow.mpg.de
Takamura K	1-704-587-8294	
Ugelstad J	47-735-95047	
Uschold RE	1-302-695-2772	uschold@al.esvax.umc.dupont.com
Vrij A	31-30-533-870	a.vrij@pobox.ruu.nl
TGM van de Ven	1-514-398-6256	ax34@musica.mcgill.ca
Vanderhoff JW	1-215-758-5423	
Waters JA	44 1491 872436	
Winnick M	1-416-978-8775	
Zukoski CF	217-244-8068	zukoski@aries.scs.uiuc.edu

INTERFACIAL BEHAVIOR AS THE FACTOR CONTROLLING STRUCTURE AND PROPERTIES OF FLUORCONTAINING MICROCOMPOSITE LATEX POLYMER

T.R.Aslamazova, S.V.Bogdanova

Institute of Physical Chemistry-Russian Academy of
Science - Lenin prospect 31- 117915Moscow - Russia

INTRODUCTION

The role of phase interactions in the structure and physical properties of microcomposite polymer latex particles and the films derived from them, which have been produced by seeded emulsion polymerization of fluorcontaining (FA) and traditional acrylates (TA), has been studied. The investigation is carried out by using two reactive systems: 1) copolymerization of FA and TA significantly differed by monomer (polymer) polarity. As monomers, dihydroperfluorheptylacrylate (FHA) and methylacrylate (MA) are used; 2) copolymerization of FA and TA characterized by close polarity. As monomers, butylacrylate (BA) and fluorcontaining monomer (FOA) $CH_2C(CH_3)COOC_2H_4OCOCF_2(CF_2CF\ R)_5CF_3$ are used. It is shown that phase interactions at the boundary of polymer(monomer)/water (m/w) and polymer/air (p/a) are the controlling factor of localization of fluorcontaining polyacrylate at the surface of latex particles and films.

2. PHASE INTERACTIONS IN THE SYSTEM CHARACTERIZED BY DIFFERENT POLARITY OF COPOLYMERIZED MONOMERS.

It is known that under seeded emulsion polymerization of two monomers differed by polarity (water solubility), the more polar polymer tends to orient at the particles surface. This tendency depends on transmissional molecule mobility (glass temperature, T_g). It is also known that the formation of microcomposite polymer film in air may lead to phase inversion. The reason of the latter is the incompatibility of polymers and difference in viscoelastic properties. Physico-chemical properties of FHA and MA are given in Table 1.

Table 1. Properties of FHA and MA.

Monomer	Solubility in water,% (25°C)	Interface tension (m/w), mJ/m²	Polymer glass temperature, °C	Adsorption energy of emulsifier*, mJ/m²	Surface tension (m/a), mJ/m²
FHA	0.00	24.50	-40	10.50	10.90
MA	5.69	8.30	+10	7.00	25.37

*)At the boundary of m/w under saturation conditions. Emulsifier S-10.

FHA and MA are strongly differed in terms of their polarity and characterized by macromolecule mobility under polymerization temperature. By taking into account a significant decrease in the difference between the interface tensions of FHA and MA at aqueous boundary equal to 16.2 mJ/m², after saturation of particles surface with emulsifier it becomes 3.5 mJ/m². Even after saturation this difference is enough so that pMA is located in the particle"shell" and pFA in their "core". The latter is illustrated by transmission electron micrograph of microcomposite p(MA-FHA) latex prepared using "stained"pFHA (Fig.1).

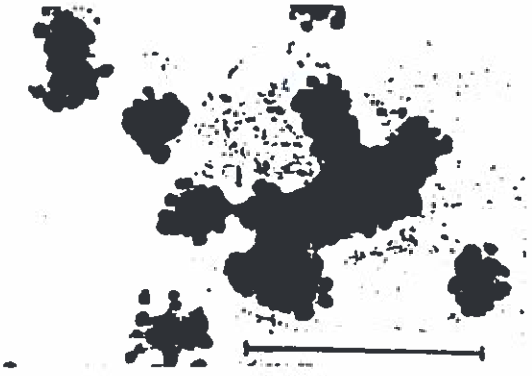

Fig.1. Micrograph of microcomposite p(MA-FHA) latex prepared in a 65:35 wt.% ratio using "stained"pFHA.

As followed from the values of surface tension at the p/a boundary (Table 1), their ratio is reversed relative to the situation for MA and FHA at an aqueous phase boundary. Hence when the latex is dried in air, the two-phase structure undergoes a morphological transformation. Due to the low T_g value of both polymers, phase inversion occurs and pFHA becomes the matrix. It is illustrated by mechanical behavior (Fig.2) and surface properties (Table 2) of microcomposite p(MA-FHA), pMA and pFHA films. As seen, the bulk and surface properties of the film is determined by pFHA properties.

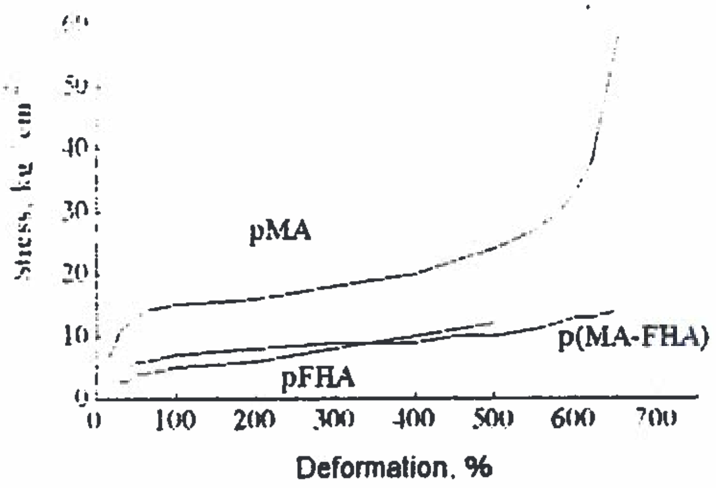

Fig.2. Stress-deformation curves for the films:
1) pMA; 2) pFA;
3) p(MA-FHA) prepared in an 80:20 wt.% ratio.

Table 2. Film contact angle (grad).

Latex	Water	Sulphuric acid	Petrolium oil	MA	FHA
p(MA-FHA) (65:35)	116	118	90	72	44
pMA	low	low	-	30	-
pFHA	100	122	95	-	50

3. PHASE INTERACTIONS IN THE SYSTEM CHARACTERIZED BY CLOSE POLARITY OF COPOLYMERIZED MONOMERS.

Physico-chemical properties of FOA and BA are given in Table 3.

Table 3. Properties of FOA and BA.

Monomer	Solubility in water, % (25°C)	Interface tension (m/w), mJ/m²	Polymer glass temperature, °C	Surface tension (m/a), mJ/m²
FOA	0.3	16.4	< room	23.3
BA	0.2	23.2	-40	24.5

The lower value of interface tension of FOA at the monomer/water boundary in comparison with BA and close value of surface tension of both polymers at the polymer/air boundary testify to the localization of pFOA in particles " shell" and film surface. The surface properties of microcomposite latex films are given in Table 4. They are close to the properties of fluorcontaining polymer.

Table 4. Film contact angle (grad).

Latex	Water	Petrolium oil
p(BA-FOA) (60:40 wt.%)	92	84
p(BA-FHA) (60:40 wt.%)	104	93
pBA	low	low

CONCLUSIONS

1. The localization of fluorcontaining monomer in particle "shell" during seeded emulsion polymerization is connected with the value of interface tension at the monomer/water boundary, whereas its localization at films surface with surface tension at the polymer/air boundary.

2. In case of the system characterized by monomers polarity strongly differed, phase inversion is observed when latex is dried in air.

3. The surface and mechanical properties of the films in the both systems studied indicate that their bulk and surface properties are largely determined by hydrophobic fluorcontaining monomer.

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

KINETIC AND THERMODYNAMIC PROCESSES CONTROLLING THE MORPHOLOGY OF LATEX PARTICLES.

Luis J. Gonzalez-Ortiz and José M. Asua

A mathematical model for the development of the particle morphology in emulsion polymerization has been developed. The model accounts for phase separation leading to cluster nucleation, polymerization, polymer diffusion and cluster migration. The model has been used to simulate batch emulsion polymerizations of methyl methacrylate on a polystyrene seed for which experimentally determined particle morphologies have been reported. A good agreement between experimental results and model predictions was achieved. On the other hand, sensitivity analysis showed that the final particle morphology was not significantly affected by neither the initial cluster volume nor the cluster nucleation rate constant.

APPLICATION OF THREE ANIONIC POLYMERIZABLE SURFACTANTS(SURFMERS) IN STYRENE-BUTYL ACRYLATE-ACRYLIC ACID EMULSION POLYMERIZATION

Harold A.S. Schoonbrood, Maria J. Unzué, Ole-Jacob Beck, José M. Asua, Amaia Montoya and David C. Sherrington

Three anionic (a methacrylic and a crotonic ester and a maleic diester) polymerizable surfactants (surfmers) were investigated with respect to their copolymerization behaviour in emulsion polymerizations of styrene, butyl acrylate and acrylic acid at high solids contents. The methacrylic surfmer appeared to be extremely reactive causing premature

coagulation. The crotonic surfmer reacted only to a low extent, and was not incorporated well enough. The maleic surfmer appeared to have intermediate conversions varying between 50% and 95%. It was clearly shown that the degree of conversion of the maleic 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 surfmer appeared to be buried if no special addition strategy for the surfmer was used. It was concluded that an ideal surfmer behaviour is low conversion throughout the semi-continuous reaction with a sharp rise at the end of the feeding period.

ON-LINE CONTROL OF EMULSION POLYMERIZATION REACTORS BASED ON CALORIMETRY

Isabel Sáenz de Buruaga, Antonio Echevarría, Philip D. Armitage, José C. de la Cal, José R. Leiza and José M. Asua

Reaction calorimetry was used to monitor and control unseeded semi-batch emulsion copolymerization of VAc and BuA. An external personal computer, using the information derived from a commercial reaction calorimeter, calculated on-line the thermal and material balances of the calorimetric reactor, and thus the monomer conversions. For a desired copolymer composition profile, previously calculated conversion-dependent monomer feed profiles were used to determine the rates of monomer addition every 20 seconds. Off-line gas chromatography andgravimetry confirmed that copolymers having the desired variable composition profiles were successfully obtained. The control strategy devised lends itself to polymer quality control and safe operation, since variable monomer inhibitor levels or sudden inhibition during the reaction do not lead to either the formation of off-composition polymer nor to monomer accumulation in the reactor. Furthermore, the rate of polymerization can be limited by fixing upper limits for monomer concentrations in the polymer particles, useful in cases where the minimum-time optimal feed profile, which corresponds to maximum swelling, might lead to thermal runaway. In addition, in a separate series of unseeded semi-continuous polymerizations of VAc andVeoVa 10, the heat of reaction was controlled according to a predefined limit by manipulating the monomer feed rate. This type of control strategy is applicable to industrial-type reactors with limited heat removal capacity, for producing polymers in the minimum time without risking thermal runaway.

RECENT DEVELOPMENTS IN MINIEMULSION POLYMERIZATION

Imanol Aizpurua, Javier Amalvy. María J. Barandiaran, José C. de la Cal
and José M. Asua

Some developments in miniemulsion polymerization aiming at taking advantage of its unique mechanisms minimizing the drawbacks of this technique are discussed. The discussion includes preparation of highly concentrated latexes, miniemulsion polymerization in continuous stirred tank reactors (CSTRs), and elimination of the low molecular weight hydrophobe.

SYNTHESIS AND CHARACTERIZATION OF LATEX PARTICLES WITH ACETAL FUNCTIONALITY

Rosa María Santos and Jacqueline Forcada

Core-Shell latex particles with surface-acetal functionality were synthetized for use in immuno-diagnostic testing. By acidification of the acetal groups to aldehydes, covalent bonding with the amino groups of biomolecules is possible. Acetal functionality was chosen due to the chemical instability of the aldehyde group. The synthesis of this kind of particles was carried out by a two-step emulsion polymerization in a batch reactor. Firstly, a monodisperse core of polystyrene was obtained. in a second step, a shell of styrene, methacrylic acid and methacrylamidoacetaldehyde di(n-methyl acetal was formed around the polystyrene cores. The shell has both acid and acetal functionalities. In order to analyze the effect of the pH of the reaction medium on the surface groups, reactions at acid and neutral pH were carried out. The latex characterization consisted of the determination of the particle size distributions and the amount of functionalized surface groups. The particles synthetized in neutral medium were covalently bonded with IgG a-CRP rabbit antibody. The complex latex-protein was immunologically active against the CRP antigen.

MODELING THE EFFECT OF MIXED EMULSIFIER SYSTEM IN EMULSION POLYMERIZATION

Elías Unzueta and Jacqueline Forcada

A mathematical model for the emulsion copolymerization of methyl methacrylate and butyl acrylate has been developed. This model, which applies the method of moments of a distribution to model the evolution of the particle size distribution, predicts the effects of the concentration and composition of anionic/non-ionic surfactant systems on the polymerization process and on the characteristics of the product obtained, including particle nucleation, growth and coagulation. Nucleation is a dynamic process in which the surfactant system affects the competition between homogeneous and heterogeneous nucleation, with simultaneous coagulative processes of precursor particles. The effect of surfactant system on nucleation is described mathematically using a variable radical critical chain length, jcr. The solution properties of surfactant mixtures, mainly cmc and micelle composition, were predicted using the thermodynamics of non-ideal mixtures. A good agreement between model predictions in batch and semicontinuous reactors and experimental results was found.

Contribution from the Department of Polymerization Reactions, Polymer Institute, Slovak Academy of Sciences, Dúbravská cesta 9, 842 36 Bratislava, Slovak Republic
Reported by Jaro Bartoň

Effect of Polymer Additive on Inverse Microemulsion Polymerization of Acrylamide.

(J.Bartoň. M.Stillhammerová)

The effect of polyacrylamide as an additive on preparation of inverse microemulsion toluene-AOT (AOT - sodium bis(2-etylhexyl)sulfosuccinate) -water-acrylamide-polyacrylamide and on the properties of polymer particles resulting from the free-radical polymerization of acrylamide was studied. It was found that the amount of polyacrylamide which can be added without hindering the formation of the inverse microemulsion depends on the toluene : AOT mole ratio (x_r). Macroviscosity of the inverse microemulsion depends on the value of volume fraction of aqueous phase (water-acrylamide-polyacrylamide), Φ_{aw}, in the inverse dispersion system. Besides influencing the formation and stability of inverse microemulsion, the presence of polyacrylamide in the inverse micelles enormously increases the final polyacrylamide particle size. On the other hand, addition of polyacrylamide only marginally affects the molecular mass of polyacrylamide formed in polymer particles.

(Chemical Papers, accepted)

Microemulsion Copolymerization of Butyl Acrylate.

(I.Capek, J.Chudej)

Abstract

The o/w microemulsion copolymerizations of butyl acrylate and acrylonitrile initiated by a water - soluble initiator in the presence and absence of additives were investigated. Copolymerizations show two distinct nonstationary rate regions. The addition of isopropanol was found to decrease the rate of polymerization and the decrease was more pronounced in the copolymerization runs. The rate of polymerization decreases with increasing the acrylonitrile concentration. The addition of acrylonitrile suppresses the dependencies of the of the rate of polymerization on the particle concentration.

Introduction

In the previous paper [1] we have reported on the effect of a partly water - soluble monomer AN on the kinetics of microemulsion polymerization for low and medium AN concentrations. A goal of this paper is to study the three or four components microemulsion copolymerizations of an oil - soluble monomer (butyl acrylate) with a partly water - soluble monomer (acrylonitrile) at a very high AN concentration. Acrylonitile partitions between water and micelles (or particles), whereas butyl acrylate is mostly located in the micelles (or the polymer particles). Thus, we intend to follow the effect of the monomer partitioning on the microemulsion copolymerization.

Experimental Part

Materials: Commercially available monomers butyl acrylate (BA) and acrylonitrile (AN), 2-propanol (IPA), initiator ammonium peroxodisulfate (APS) and emulsifier sodium dodecylsulfate (SDS) were purified by the traditional methods.

Polymerization procedure: The batch polymerizations were run at 60 °C. In all runs the recipe comprises 100 g of water, 20 g of SDS, 0.144 g of APS and 0.025 g of $NaHCO_3$. System A: 10 g of BA, system B: the weight ratio AN/BA = 75/25, 16 g of monomer, system C: the weight ratio AN/BA = 75/25, 20 g of monomer. Amounts of IPA varied as shown later. Conversion of monomer was determined by dilatometric measurements (checked by gravimetry).

Results and Discussion

Polymerization rate

In all BA polymerizations the final conversion close to 100% was reached after ca. 10 minutes. In the AN/BA copolymerizations the very slow polymerization (the limiting conversion) was observed above 70 or 80% conversion. This conversion (ca. 80%) was reached after 3 - 5 hours. The limiting conversion may be ascribed to the slow water-phase polymerization, the chain - transfer events (to isopropanol, IPA) in the aqueous phase, participation of IPA radicals in the termination events and the occludation events.

Variation of the rate of copolymerization with conversion is described by a curve with a maximum at 10 - 20% conversion. Thus, the polymerization rate - conversion curves show two distinct regions.

The (maximum) rates of (co)polymerization of BA and AN as a function of the IPA concentration ($[IPA] \leq 0.5\ mol.dm^{-3}$) obey the following equations (see Tab.1)

$$R_p \,\alpha\, [IPA]^{-0.2} \quad (BA) \text{ and } \quad R_p \,\alpha\, [IPA]^{-0.65} \quad (BA/AN)$$

These results show that IPA (soluble in both phases) decreases the rate of polymerization and the depress is a more pronounced in the copolymerization. In the BA/AN system the copolymerization proceeds in both phases and this may be a reason why IPA depresses more copolymerization. The maximum rate of polymerization is situated at 15% conversion with BA, at 30 -40% with IPA/BA and at 10% conversion with BA/AN/IPA. The decrease of the rate of polymerization beyond ca 20 - 30% is due to the depletion of free monomer (droplets) phase.

Variations of the rate of polymerization with the monomer feed composition and IPA concentration are expressed Table 1. Experimental results obey the relationship

$$R_p \,\alpha\, [BA]^{1.4} \qquad \text{(the BA system)}$$

$$R_p \,\alpha\, [AN]^{1.1}\, [BA]^{0.24} \qquad \text{(the system B)}$$

$$R_p \,\alpha\, [AN]^{-3.7}\, [BA]^{0.8} \qquad \text{(the system C)}$$

Table 1. Variations of the kinetic parameters of microemulsion (co)polymerization of BA and AN [a].

[BA] (	[AN] mol.dm^{-3}	[IPA])	$R_p.10^3$ (mol.dm^{-3}.s^{-1})	$R_{pp}.10^{21}$ (mol.particle^{-1}.s^{-1})	Q (particle^{-1})	D (nm)	$N.10^{18}$ (dm^{-3})
0.92	-	0.122	8.0	2.6	0.26	35	6.3
0.92	-	0.245	6.7	1.5	0.15	31	9.0
0.92	-	0.49	6.0	0.9	0.09	27	14.0
0.92	-	0.98	3.8	0.7	0.07	30	10.0
0.226	1.64	0.12	1.35	1.9	0.04	48	2.0
0.226	1.64	0.24	0.97	3.2	0.07	65	0.86
0.226	1.64	0.48	0.55	14.0	0.16	250	0.012

[a] In all runs 16 g of monomer per 100g water.

The rate of (co)polymerization was found to decrease with increasing [AN] and [IPA]. This may be connected with the dilution of the monomer phase, the desorption of radicals and the formation of more stable radicals. The same trend was found in the rate per particle in the BA system. The opposite trend observed in the BA/AN probably results from the coagulation nucleation mechanism and the growth of particles by the agglomeration. Desorption of radicals in the microemulsion polymerization of BA was experimentally proved by the increase of the particle number after the cessation of irradiation [2].

If the rates of polymerization are divided by the number of particles and the appropriate constants, the average particle radical number , Q, can be estimated according to the approach described earlier [3]. The values used were $k_{p(BA)}$ = 1360 dm^3.mol.$^{-1}$.s^{-1}, $k_{p(AN)}$ = 5000 dm^3.mol^{-1}.s^{-1}, [AN/BA] = 8.5 mol.dm^{-3} and r_{AN} = 1.08, r_{BA} = 0.816 [3,4]. The estimated values for Q are shown in Tab. 1. These results indicate that the Q in the AN/BA copolymer particles is smaller then that in the poly(butyl acrylate) particle [5]. The low radical concentration in the copolymer microparticles probably results from the higher desorption rate of monomeric radicals (mainly AN). The addition of IPA increases the radical concentration in copolymer particles.

The colloidical parameters

In the system A the diameter of monomer/polymer particle is nearly independent of conversion (30 - 32 nm). Here the size slightly increases above the critical conversion 80%. With increasing the AN concentration or the total monomer concentration the critical conversion is shifted to the lower conversion. Thus, the agglomeration of particles begins at the lower polymer fraction. The critical conversion in the system B and C is 60% (with D ca. 42 nm) and 30% (ca. 48 nm), respectively. The agglomeration of polymer particles is very effective at higher conversions.

The dependence of N versus conversion in the microemulsion AN/BA coploymerization is described by a curve with a maximum at 50% conversion in the system A (N = 5.5 .10^{18} dm^{-3}), at 40% in the system B (N = 3.0 .10^{18} dm^{-3}) and at

25% in the system C ($N = 2.0 . 10^{18}$ dm^{-3}). In the BA system the number of particles increases linearly with conversion [6]. In the comonomer systems the number of particles reaches the constant value at low or medium conversions. The decrease of the copolymer particle number with conversion, especially at high conversions, is caused by the increased agglomeration of polymer particles. This behaviour can be ascribed to the increased water-phase homopolymerization of AN, the change of copolymer composition on the particle surface and the decreased interaction polymer particle surface - emulsifier.

The surface area of the (initial) micelles is by several orders in magnitude larger then that of the polymer particles [1,5,6]. Thus, the small fraction of micelles is nucleated or used for the stabilisation of polymer particles. The polymer particles, thus, can only slightly compete with the monomer containing micelles in capturing radicals. The each entry of radical to monomer-swollen micelle leads to the nucleation event (formation of a primary particle). The very large number of micelles ($N_{micelles} >> N_{particles}$) indicates that radicals are predominantly captured with the monomer-swollen micelles.

The number of particles was found to vary with increasing [AN], [BA] and [IPA]. The exponents a, b, and c from the relationships $N \alpha [AN]^a$, $[BA]^b$ and $[IPA]^c$ is estimated to be

the BA system (see Tab. 1): b = 1.4, c = 0.56
the system B (see Tab. 1): a = - 0.41, b = 9.3, c = - 3.7
the system C: a = - 3.7, b = 0.8

Conclusion

Copolymerizations of transparent o/w microemulsions of BA and AN initiated by APS do not produce stable microlatexes. These latexes contain spherical AN/BA copolymer particles with diameter ranging from 40 to 60 nm.

The dependencies of the rate of polymerization and the number of the particles versus conversion are described by a curve with a maximum at certain conversion. These results were discussed in terms of the variation of the monomer concentration, the nucleation of particles and the agglomeration of particles.

The addition of IPA decreases the rate of (co)polymerization and favours the formation of larger number of polymer particles.

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Superposition of Oscillations on Steady Shear Flow as a Technique for Investigation the Structure of Associative Polymer Solutions

V. Tirtaatmadja [a], K. C. Tam [a], R. D. Jenkins [b], M. L. Farmer [c], and D. R. Bassett [b]
[a] School of Mechanical and Production Engineering, Nanyang Technical University, Singapore
[b] Union Carbide.Corporation, UCAR Emulsion Systems, Cary, North Carolina, USA
[c] Union Carbide Corporation, Technical Center, Singapore

Introduction

A contemporary problem in associative polymer science is measuring how an associative network in solution breaks down under applied shear stress. Since the breakdown and reformation of associative network junctions in solution is the primary mode of relaxation, measuring how the relaxation time function depends on shear rate or shear stress measures the dissociation of the network under applied shear. By superimposing small amplitude oscillations on shear flow at constant stresses, the linear viscoelastic properties (including the relaxation time function) of the associative network under various applied stress conditions can be obtained. The network structure is not perturbed from its conformation in the steady shear flow field as long as the strain amplitude of the oscillation is sufficiently small.

The equations for the shear stress τ_{12} and γ_{12} strain for when oscillatory flow is superimposed on simple shear flow are as follows:

$$\tau_{12} = \tau_s + \tau_0 \sin(\omega t) \quad ; \gamma_{12} = \dot{\gamma}_s t + \gamma_0 \sin(\omega t + \delta)$$

where τ_s and $\dot{\gamma}_S$ are the steady shear stress and shear rate, respectively, τ_0 and γ_0 are the amplitudes of the oscillatory stress and strain at frequency ω, respectively, and δ is the phase shift between the oscillatory stress and strain. This was accomplished experimentally by applying a prescribed steady shear stress τ_s or rate $\dot{\gamma}_S$ to the sample until steady state was reached, and subsequently superimposing an oscillatory flow at a frequency ω and a specified stress amplitude τ_0 or strain amplitude γ_0 on the shear flow.

By resolving the response stress or strain curve into its steady and oscillatory components, the steady shear viscosity and dynamic properties can be determined in the usual manner. The superposition experiments were carried out over a range of frequencies to determine the dynamic viscoelastic properties of the fluid at the applied shear rate or shear stress. Analogous to determing the Maxwell - type relaxation time of the fluid at rest, the relaxation time function at each applied stress was calculated using the relationship:

$$\lambda(\tau_s, \omega) = \frac{G'(\tau_s\,, \omega)}{\omega^2\, \eta'(\tau_s, \omega)}$$

Experimental

The associative polymer studied in this report was the product of the emulsion copolymerization of ethyl acrylate, methacrylic acid, and a macromonomer containing an 35 mole ethoxylate chain with a terminal C20 hydrophobe. The synthesis of the polymer is described elsewhere [2,3]. At high pH, the polymer solubilizes to form a network of both intra- and inter- molecularly associating hydrophobic junctions.

The rheological properties of a 1 wt. % solution the associative polymer solution at a pH adjusted to 9.5 were measured on a controlled stress rheometer, Carri-Med model CSL500, using a cone-and-plate fixture with a 40 mm diameter, 2° angle cone. The measurements were carried out at 25±0.1°C. In addition to the customary steady shear and oscillatory shear measurements, measurements using superposition of oscillations on steady shear flows at constant shear stresses ranging from 1 to 60 Pa were carried out. As described in our previous contribution to the IPCG Newsletter [1], oscillatory strain sweeps were performed at various imposed shear stresses and frequencies to determine the linear viscoelastic region. The dynamic properties reported here were in the linear viscoelastic region, where the amplitude of the oscillatory strain employed was a sufficiently small value so that the responses were independent of the applied strain.

Results And Discussion

Figure 1 plots the relaxation time function against frequency for various applied shear stresses. The maximum value with respect to frequency at a given applied shear stress may be taken as an estimate of the longest relaxation time of the fluid under the prevailing stress conditions. Figure 2 plots these longest relaxation times as they depend on applied stress. The terminal relaxation time function of the polymer network diminished by almost four orders of magnitude as the applied stress increased from 1 to

60 Pa, indicating that intermolecular associations between the hydrophobic units in the network were disrupted by the increase in applied stress

Since the network junctions formed by the intermolecular hydrophobic associations are temporary junctions that are continually being destroyed and reformed, this shows that the hydrophobically associating intermolecular junctions are being destroyed at a faster rate than their rate of formation, resulting in a decrease in the junction density and a drop in steady shear viscosity.

Work is underway to study the effect of association bond strength by varying the number of carbons in the hydrophobe as well as the number of ethylene oxide units between the hydrophobe and polymer backbone [3].

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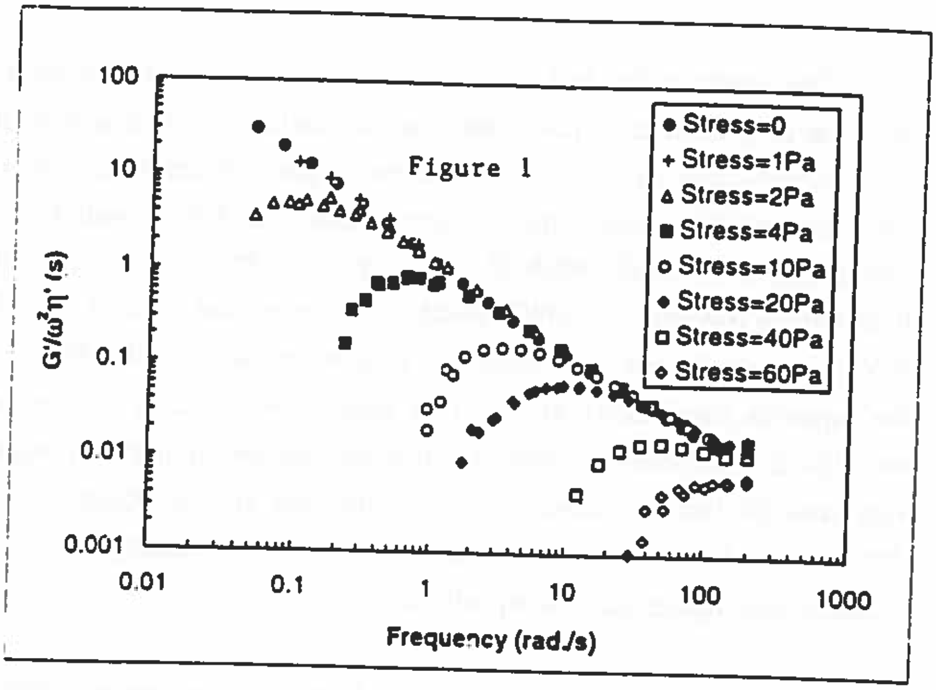

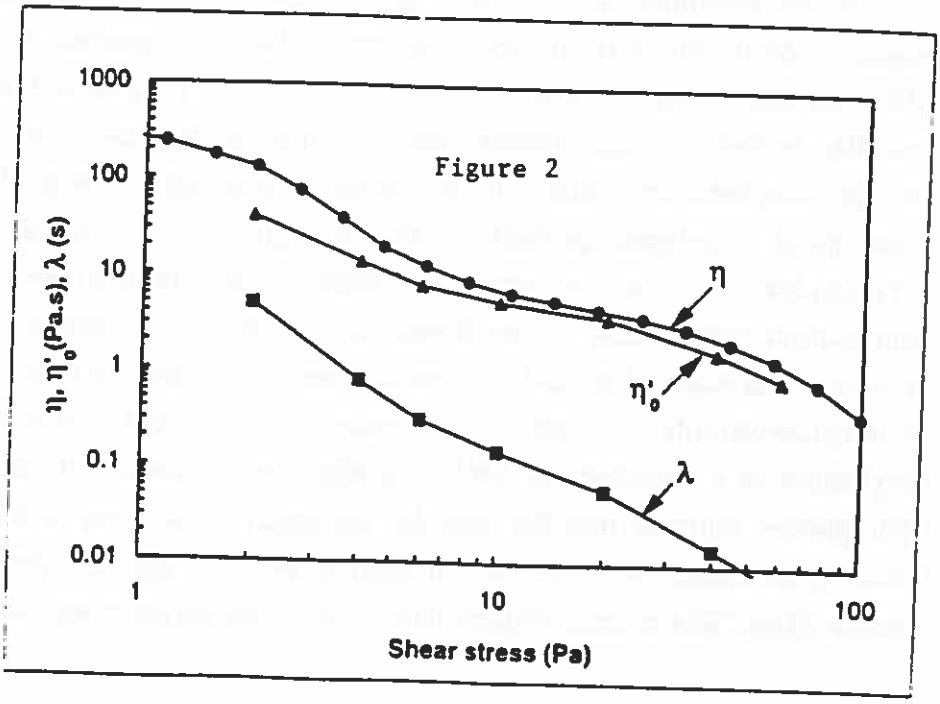

POLYMER COLLOID GROUP NEWSLETTER

Contribution from the Institut Charles Sadron (CRM-EAHP)
6, Rue Boussingault, 67083 Strasbourg Cédex, France.

· Reported by Françoise CANDAU

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

Influence of the Hydrophobe Structure on Microstructure and Rheology in Associating Polyacrylamides Prepared by Micellar Polymerization (E. Volpert, J. Selb, F. Candau)

Our recent studies in hydrophobically modified polyacrylamides prepared by micellar polymerization have aimed at elucidating the mechanism prevailing in these systems and the compositional heterogeneity effects occurring in some cases. Our first studies dealt with polyacrylamides modified with low amounts of ethylphenylacrylamide (eϕAM) (see previous reports). In this process, the hydrophobe (eϕAM, 1-3 mol% based on the monomer feed) is solubilized within SDS micelles whereas the hydrophilic monomers (acrylamide, AM) is dissolved in the aqueous continuous phase. This method was found to generally lead to multiblock copolymers in which the number and length of the hydrophobic blocks vary with the initial number of hydrophobes per micelle. Kinetic studies showed that the eϕAM was consumed at a faster rate than AM, leading at full conversion to a sample heterogeneous in composition.

As the monomers have the same polymerizable group and therefore similar reactivity ratios, this drift in copolymer composition was ascribed to a micellar effect. In order to check whether the observed drift was a universal feature of the micellar polymerization process, we undertook a systematic study on the incorporation behavior of different types of hydrophobes and on their effects on the rheological copolymer properties. Interestingly, the use of disubstituted acrylamides leads to homogeneous samples with an average copolymer composition independent of the degree of conversion, in contrast to what is observed with monosubstituted acrylamides (see the example of Figure 1 relative to hexylacrylamide (HexAM) as a monosubstituted AM and methylhexylacrylamide as a disubstituted AM). Solubility measurements of both types of hydrophobes indicate that the micellar dynamics is not responsible for this behavior but rather the difference in polarity between the bulk phase and the micellar phase. This microenvironment effect modifies the reactivity ratios of those hydrophobes capable of forming hydrogen bonds or an amide-enol equilibrium whereas the reactivity of other hydrophobes remains unaffected. More details on this work are given in Ref. 1.

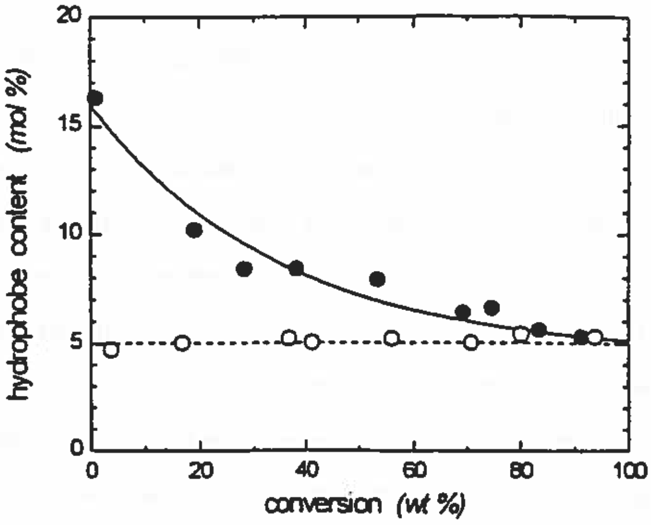

Fig.1. : Variation of the average copolymer composition with conversion for AM-HexAM (●) and AM-MeHexAM (O) copolymers.

These results illustrate in a clear manner the role played by interfacial and microenvironment effects on the copolymerization mechanism in micellar media. A practical conclusion of this work is that an adequate choice of the hydrophobic monomer can correct for the drift in composition often observed in this type of process and eventually lead to samples homogeneous in composition. This difference in microstructure of the copolymers formed affects in turn their rheological properties. These have been studied as a function of the copolymer microstructure and type of hydrophobe used (bulkiness, degree of branching and alkyl chain length). For example, at similar hydrophobe levels, double-chain hydrophobes considerably enhance the thickening efficiency with respect to single-chain hydrophobes.

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"Influence of the Hydrophobe Structure on Composition, Microstructure and Rheology in Associating Polyacrylamides Prepared by Micellar Copolymerization"

Mechanisms of latex film formation

F. Dobler and Y. Holl
Trends in polymer Science 4 (1996) 145

We reviewed the literature dealing with the mechanisms of film formation from a latex. Three main steps can be distinguished in the process: concentration of the latex; deformation of the particles; and healing of the interfaces between particles by interdiffusion of the macromolecules from one particle to its neighbours. The main emphasis is on the second step, as it is the most controversial, with several key questions remaining open. The article is divided into two parts. The first recalls the classical theories proposed in the past to account for the deformation of latex particles in the film-formation process, namely, the dry sintering theory by Dillon et al., Brown's capillary theory, the wet sintering theory by Vanderhoff et al., and the surface layer theory by Sheetz. The second part deals with subsequent works, which were all attempts to experimentally verify and/or improve the main theories.

Key words : Latex film formation mechanisms; Deformation step; Dry sintering; Wet sintering; Capillary theory; Surface layer theory.

SPREADING OF POLYMER MOLECULES ON SOLID SURFACES

Martien Cohen Stuart*, Marcel C.P. van Eijk, Jaap C. Dijt, Nynke G. Hoogeveen

Department of Physical and Colloid Chemistry
Wageningen Agricultural University
Dreijenplein 6
6703 HB Wageningen

ABSTRACT

When a homopolymer adsorbs from dilute solution onto a solid surface it first attaches and then maximizes its number of contacts with the substrate by means of a kind of spreading process. Evidence for this spreading process can be obtained from experiments on the adsorption kinetics. We report on a case where the saturation adsorbed amount depends on the rate at which the polymer was supplied to the surface (dextran adsorbing on zirconia). Also, we discuss competitive adsorption experiments in which one kind of chain molecule attempts to displace another one from the surface. In these cases, the desorption rate of the displaced species reflects the spreading rate of the displacer. When this rate is slower than the supply of displacer molecules, oversaturated layers result that spontaneously eject polymer. We have measured the rate of these displacement-driven desorption processes in various cases and conclude that it depends strongly on the energy of the segment-surface bond. A model involving the diffusion of defects over the surface may account for this finding.

INTRODUCTION

Even though it is obvious that attachment of long homopolymers from solution to a flat solid surface must involve a change in conformation form a coil-like shape to a relatively flat structure (a kind of *spreading*), it is not at all clear how rapidly this takes place. Static properties of adsorbed chains have received a good deal of attention and much understanding has been obtained from a combination of theory and experiment. However, dynamic properties have been much less investigated, even though these are essential in many applications where adsorbed polymers play a role (Ref. 1). Of course, much less investigated, even though these are essential in many applications where adsorbed polymers play a role (Ref. 1). Of course, these properties are much harder to determine. To the best of our knowledge, the molecular spreading process has never been followed directly. Indirect evidence can be obtained from experiments which follow the build-up and/or decay of adsorbed layers. It is the purpose of this paper to discuss these experiments as well as the conclusions that can be drawn from them.

EXPERIMENTAL TECHNIQUES

Polymer adsorption processes can be quatitatively followed by means of various reflectivity techniques. Ellipsometry is the classical example, but in the context of kinetic studies, two other methods have proven particularly useful: ATR-IR spectroscopy and optical reflectometry. The ATR technique, using the CIRCLE flow cell has been exploited succesfully by Granick *et al.* (Ref. 2) and offers the advantage of giving specific information on the type of polymer being adsorbed. Optical reflectometry in combination with an impinging-jet flow cell has been used by us in a number of studies (Refs. 3-5). It has the particular advantage of giving access to fast processes with very accurate control over transport conditions near the surface. However, it is not polymer-specific, as it is based upon the difference in refractive index between the polymer and the solvent.

Effects of spreading in adsorption

The first example that we discuss is the adsorption of a water-soluble polymer, dextrane, from water on zirconia (ZrO_2) in the form of a thin film sputtered onto silicon wafer. Dextran (Pharmacia) is a bacterial polyglucose polymer with about 5% of its weight in side chains (50-100 units), as shown schematically in fig. 1 (Ref. 6). Its adsorption was followed by the reflectometric

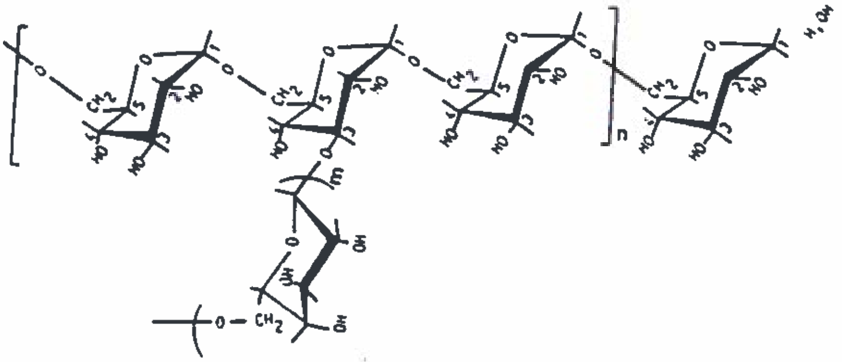

Fig. 1. Primary structure of dextran .

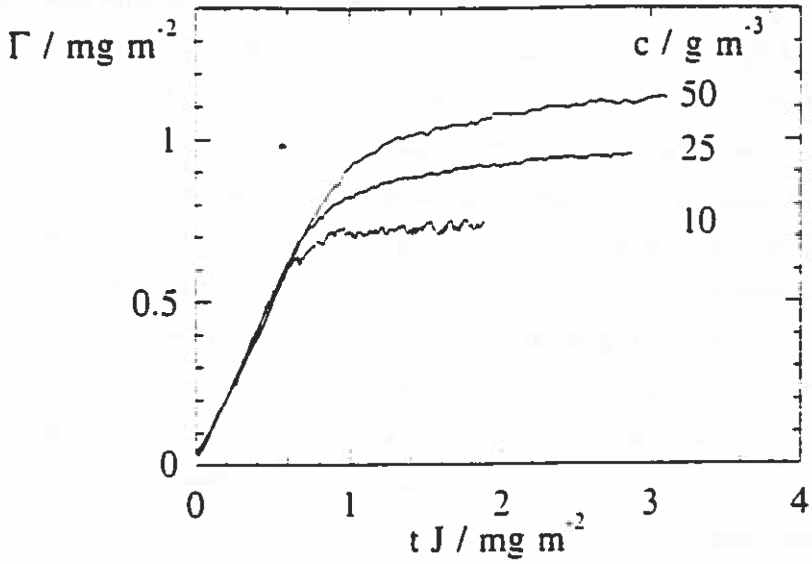

Fig. 2. Adsorbed amount of dextran on zirconia as a function of time for three different polymer concentrations at a constant flow rate of 0.6 ml/min. The time is given in reduced units tJ (where J is the initial polymer flux towards the surface) in order to superimpose the initial part of the curves.

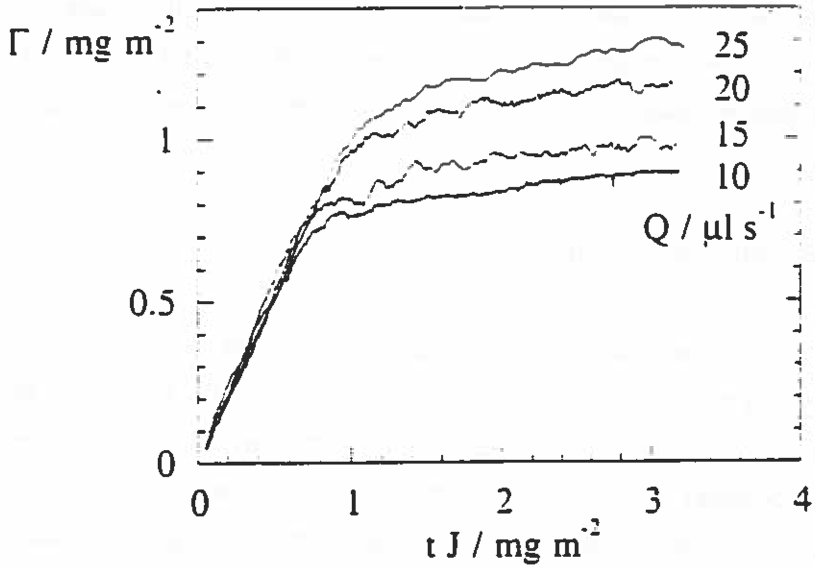

Fig. 3. Adsorbed amount of dextran on zirconia as a function of time for four different flow rates, at a constant polymer concentration. The time is given in reduced units tJ (where J is the initial polymer flux towards the surface) in order to superimpose the initial part of the curves.

technique as a function of the rate of supply of polymer towards the surface, which can be done either by varying the concentration of polymer in the solution, or the flow rate. Figs. 2 and 3 give examples of the results for either case, respectively. The data are plotted as adsorbed amount Γ (mass/unit area) versus the total amount of polymer supply Jt, where J is the polymer flux towards the surface (mg/m^2 s) and t the time. As can be seen, Γ initially rises linearly with time, meaning that a steady-state condition, with constant flux, is almost immediately reached in these measurements. The remarkable feature of these data is that the *saturation level* reached at the end of the experiment becomes larger as the supply of polymer occurs more rapidly, i.e., at high concentration or at high flow rate. Such a pronounced effect of sample history has, so far, not been found by us. Pefferkorn *et al.* (Ref. 7), studying the adsorption of a polyvinylpiridinium sample, reported saturation adsorptions that were also different for fast and for slow supply. In particular, at rapid supply the adsorbed mass had a temporary overshoot that tended to relax back to a lower value, supposedly corresponding to equilibrium. Such a relaxation clearly involves the displacement of part of the adsorbed chains by other chains that increase their occupied surface area. Overshoots were also reported in several cases where polymers were used with fluorescent labels attached to them (Refs. 8, 9). However, these overshoots appear to occur with all kinds of polymers, e.g., also with proteins, and could in some cases not be reproduced with other techniques (Refs. 10, 11). It is therefore more likely that they reflect a change in the quantum yield of the fluorescent probe (due to contact with the surface) rather than an overshoot in the polymer's adsorbed mass.

The qualitative explanation of our dextran results is that at low rate of supply individual chains have more time to spread (unfold) on the surface, so that the average extent of spreading that the molecules reach is higher (and Γ correspondingly lower) than at rapid supply. Such an explanation implies, however, that spreading at the empty, or partly covered surface is quite possible, but that on the staturated surface spreading is essentially blocked. Hence, in a competitive situation on a crowded surface spreading occurs very much slower than when there is ample area available to the macromolecules. The data provided by Pefferkorn (Ref. 7) suggest, however, that also on a saturated surface spreading may well occur. Below we present evidence that corroborated this conclusion.

Spreading in competitive adsorption

Our second example refers to experiments where long chains compete with chemically identical, but shorter polymer chains. We discuss two cases: poly(ethylene oxide) (PEO) adsorbing from water, and polystyrene (PS) adsorbing from decaline, respectively. In both cases the substrate was silica in the form of an oxidised silicon wafer. In these experiments, a binary mixture of short and long chains was supplied, and the total adsorption Γ(t) was followed by reflectometry. Fig. 4 gives the data for PEO and fig. 5 those for PS. As is seen, the adsorption process has three different stages. In the first stage, there is a rapid linear increase. In this stage, there is sufficient surface area available to accomodate all the chains that arrive, and Γ increases linearly with time (steady state). In the second, intermediate stage, the rate of adsorption is clearly reduced. This is the stage in which exchange occurs: the longer chains are displacing the shorter chains from the surface. The final stage is the approach towards saturation which, in the case of PEO involves a second maximum in the adsorption rate. Careful checks (Ref. 12) have led us to conclude that

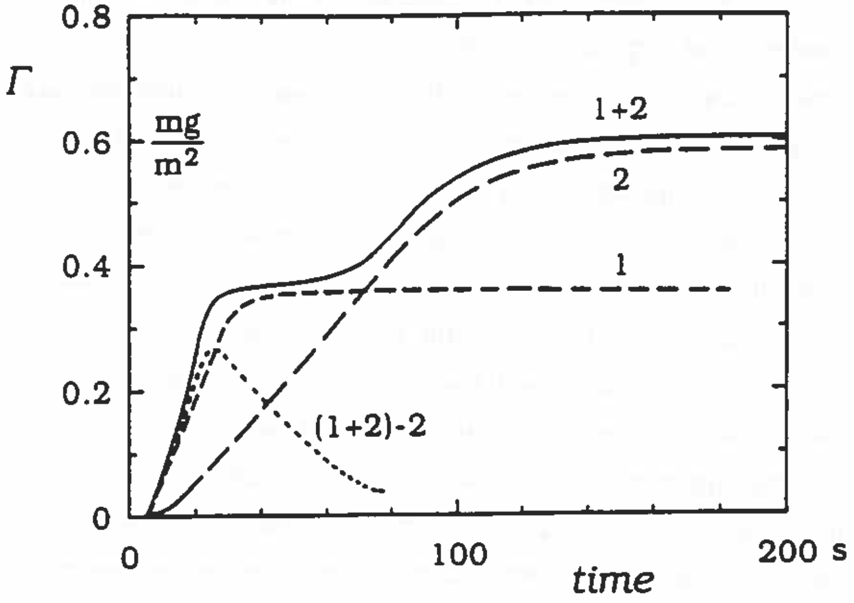

Fig. 4. Competitive adsorption kinetics in a mixture of two poly(ethylene oxide (PEO) polymers of different molar mass M, from water onto silica. The molar masses were 7000 and 400,000, respectively. The full curve gives the overall adsorbed amount, the dashed curve labeled "2" gives the adsorption, from the mixture, of the high M component, and the curve labeled "(1+2)-2 gives that of the low M component. The curve labeled "1" gives the adsorption of the low M component in the absence of competing high M polymer. Concentrations: c_l = 5 ppm, c_h = 10 ppm.

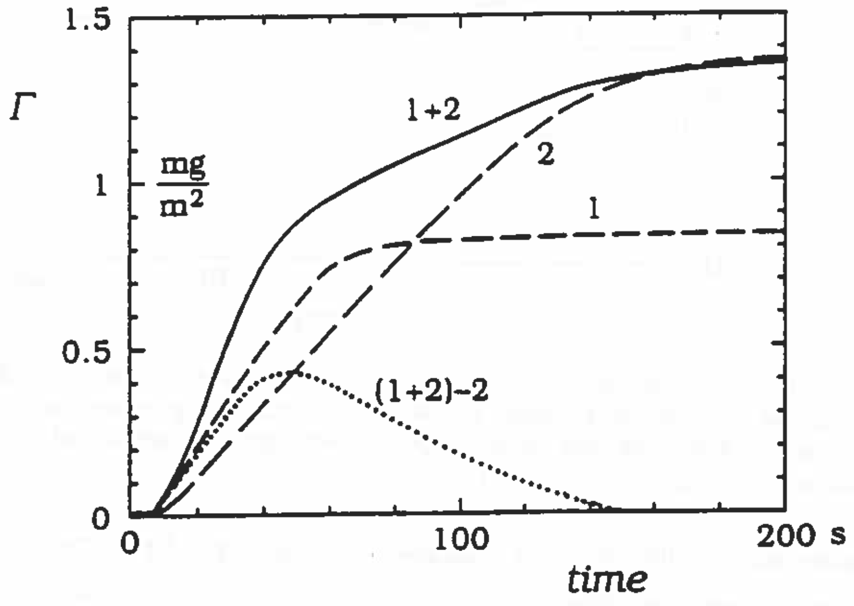

Fig. 5. Competitive adsorption kinetics in a mixture of two polystyrene polymers of different molar mass M, from decaline onto silica. The molar masses were 9000 and 3,400,000, respectively. The full curve gives the overall adsorbed amount ("1+2"), the dashed curve labeled "2" gives the adsorption, from the mixture, of the high M component, and the curve labeled "(1+2)-2 gives that of the low M component. The curve labeled "1" gives the adsorption of the low M component in the absence of competing high M polymer. Concentrations: c_l = 5 ppm, c_h = 10 ppm.

the $\Gamma(t)$ curves can be decomposed, as indicated in the figure, into the separate contributions from short (dashed) and long (dotted) chains.

The important aspect to note is that in the PEO case the exchange takes place *at constant adsorbed mass*. Theoretical calculations have convinced us that this implies that the composite layer is *in equilibrium* . Apparently, the exchange takes place fast enough, so that the supply of long polymers is the rate determining step in the process. Hence, throughout the exchange process, the adsorbed layer is in a relaxed state. This is *not* so for PS. Here, the desorption of the short chains does not take place at the rate at which long chains adsorb. Γ is therefore higher than it should be in equilibrium: we have an overshoot. Further proof of the non-equilibrated nature of the PS layer comes form experiments shown in fig. 6 where the supply of long molecules was interrupted before saturation. Clearly, Γ decreases spontaneously in this case with a characteristic relaxation time of about 1 minute. The exchange experiment can also be carried out more slowly, and this does indeed produce curves more like the one found for PEO.

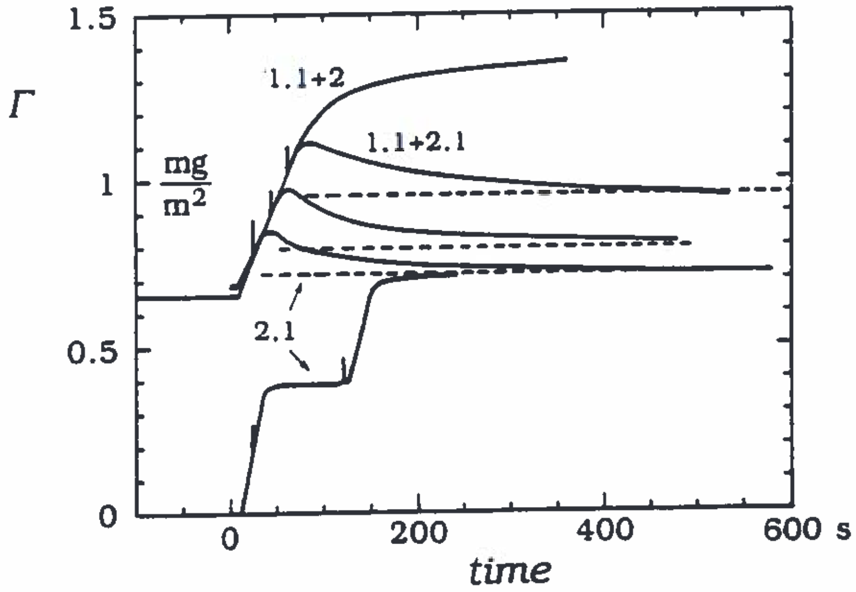

Fig. 6. Desorption of polystyrene by relaxation of the adsorbed layer. In these experiments the supply of high M polymer is stopped at the point indicated by a vertical marker. The dashed horizontal lines represent the final value expected after total desorption of all the low M polymer. Concentrations: c_l = 5 ppm, c_h = 50 ppm.

Our interpretation of the data just discussed is visualized in fig. 7. The exchange process by which long chains take the place of short ones on the surface would seen to occur in two steps. First, each incoming long chain attaches to the surface, thereby rapidly displacing some short chains. Further displacement of short chains requires the gradual increase in the number of polymer-surface attachment points, i.e., spreading of the long chain. In the case of PEO, this spreading occurs rapidly, and the mixed adsorbate layer remains in an overall state of equilibrium (path A). Eventually, the longer chains build up a layer with more loops and tails and Γ increases to the saturation value for long PEO chains. In the PS case, however, spreading occurs more

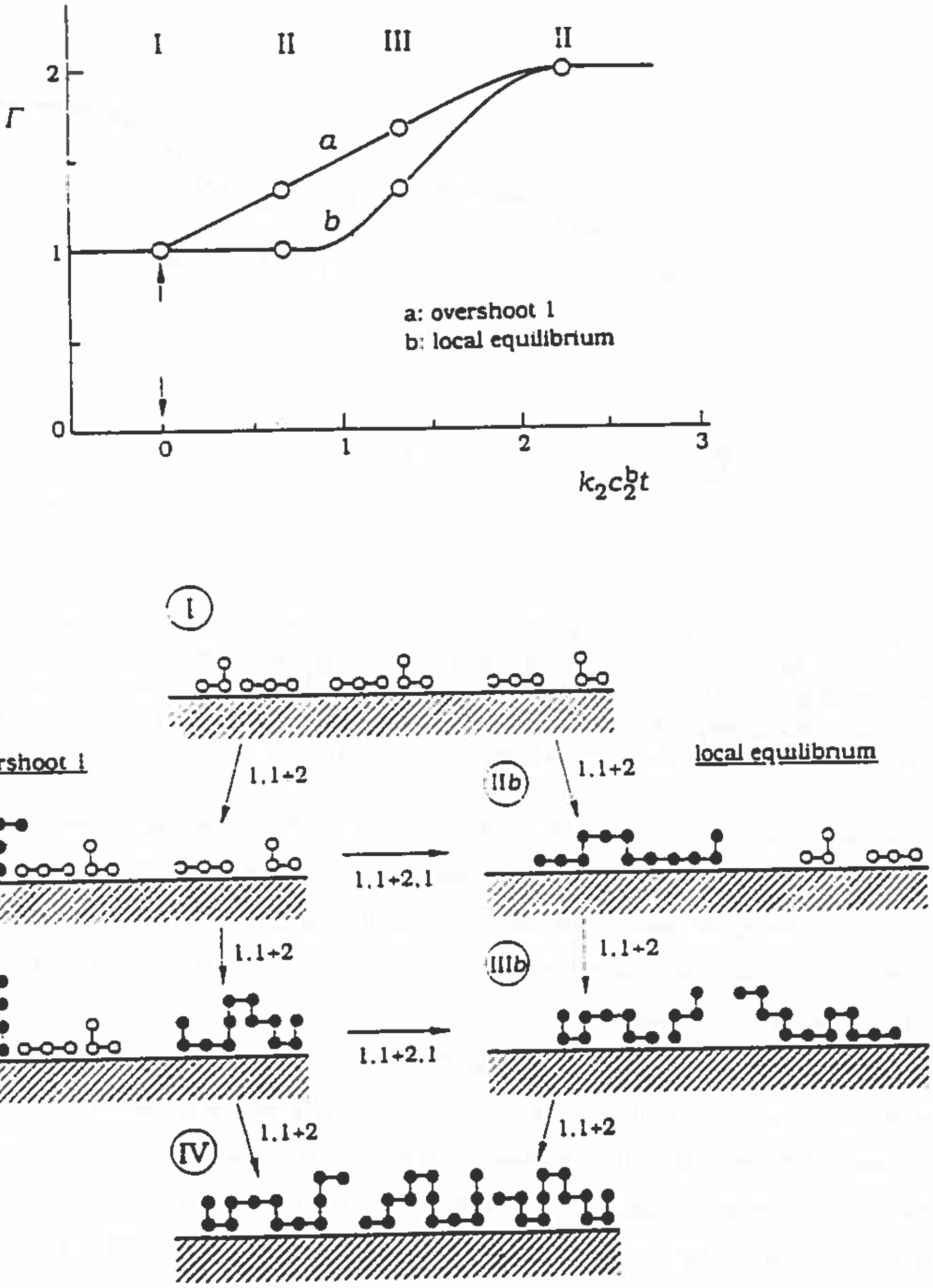

Fig. 7. Pictorial representation of the adsorbed layer during exchange. The open circles in the upper graph (labelled I, IIa, II*b* etc.) refer to the cartoons below. Route *a* (top curve, left-hand side cartoons) represents the non-equilibrated (slow spreading) situation, route *b* (bottom curve, right-hand side cartoons) the situation according to an equilibrated layer (fast spreading).

slowly, and there is no equilibrium during exchange. The long chains spread less and retain their loops and tails that eventually characterize the saturated layer.

What determines the differences in spreading rate between PEO and PS? Two possibilities would come to mind. The first possibility is that PEO relaxes faster because it is more flexible than

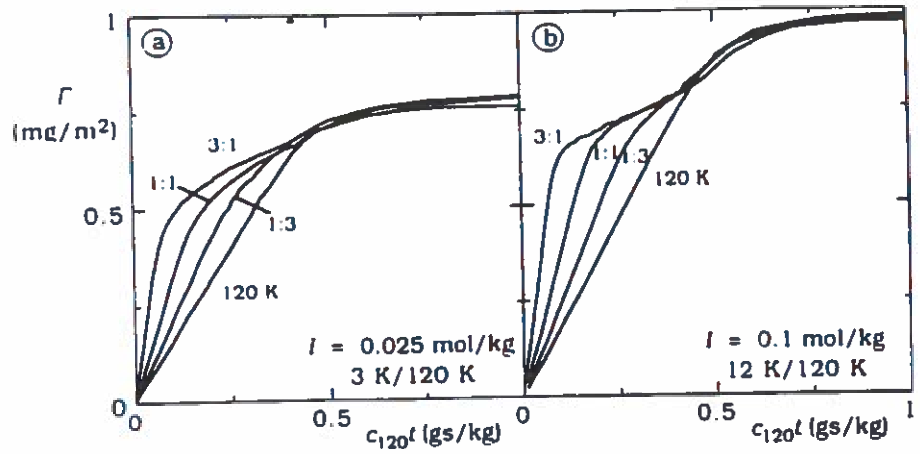

Fig. 8. Competitive adsorption kinetics in a mixture of two polyvinylpyridinium polymers of different molar mass M, from aqueous salt solution onto TiO_2. Two data sets are given: one for a low ionic strength (a) and one for a high ionic strength (b). The molar masses used for diagram a were 3000 and 120,000, respectively. Those used for diagram b were 12,000 and 120,000, respectively. Different curves correspond to different mixing ratios of low to high M.

PS. In particular, rotation around the ether bonds in PEO does hardly encounter energy barriers, whereas the bulky phenyl groups in PS make rotation relatively slow. The second possibility is that the strength of binding between monomer units and the surface is stronger in the case of PS. Segmental adsorption energies have been determined for PS from a number of solvents (Ref. 13) but for PEO in water, no data are available.

That at least the second effect plays a role is demonstrated by our next example. It is again a long chain/short chain competition experiment, but this time with a polyelectrolyte (polyvinyl pyridinium chloride, PVP^+) adsorbing from aqueous salt solution onto titania (TiO_2). Fig 8 gives the data for two different salt concentrations, 0.025 M (left diagram) and 0.1 M (right diagram). If these two diagrams (inparticular the curves labeled "3:1") are compared with the ones for PEO and PS, respectively, one immediately sees that the diagram for the higher salt concentration has an inflection point, much in the same way as PEO does, but that the other one does not and is more like the PS case. Clearly, the rate of spreading is enhanced by an increase in salt concentration. Because the polymer is the same in both cases, the flexibility cannot cause this difference. Since one expects the effective strength of the monomer-surface ionic bond to be weakened by the addition of salt, we can conclude that at least one factor that determines the rate of the spreading process is the rate at which monomer-surface bonds break, and this rate would of course go up when the bonds become weaker.

Competition between chemically different polymers

Our last example concerns the displacement of one polymer by a chemically different one. We have investigated several of these cases (Ref. 5), from which we select one, namely the displacement of PS by poly(butyl methacrylate) (PBMA). The solvent is decaline, and the substrate again an oxidised silicon wafer. Since the refractive index increment of PBMA in decaline is very close to zero, the adsorption of this polymer is hardly detected by the reflectometric technique. Therefore, the effect of PBMA on the adsorbed amount of PS is rather directly detected as a decrease in the signal $\Delta S/S_0$, corresponding to a decrease in the amount of adsorbed PS. In fig. 9 we thus show the desorption of PS induced by the introduction of PBMA into the system, as indicated by the arrow labeled "PBMA". Several curves are shown, each one corresponding to a different concentration of ethyl acetate added to the solvent. As can be seen, PBMA displaces PS in all cases. This is to be expected because the ester group that the PBMA posesses gives it a stronger hydrogen-bonding interaction with silica, i.e., a higher adsorption energy, than PS.

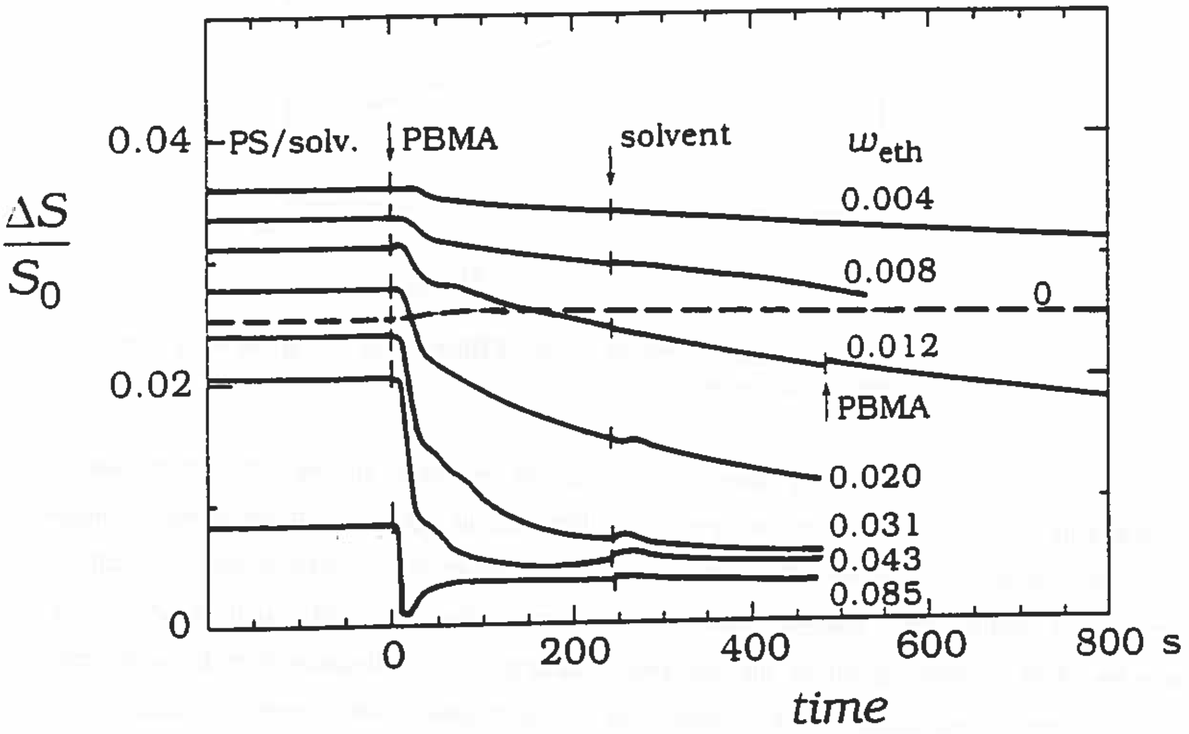

Fig. 9. Displacement kinetics of adsorbed polystyrene (PS) by poly (butylmethacrylate) (PBMA) from silica in decaline solution. The first arrow indicates the point where PBMA was introduced. The second arrow ("solvent") indicates the point where the supply of PBMA was terminated. Each curve corresponds to a different weight fraction of ethyl acetate added to the solvent.

Two other point are worth mentioning. Firstly, the supply of PBMA has been stopped at the point in the figure indicated by the arrows. This implies, clearly, that in this stage the displacement process is an autonomous surface process, which does not require any supply of molecules from the solution. Apparently, the PBMA molecules have already adsorbed, but not yet driven off the

PS molecules. Secondly, the rate of displacement is strongly affected by the presence of ethyl acetate. In pure decaline, the rate is extremely slow. With increasing concentration of ethyl acetate,however, the rate increases enormously. Estimates of the desorption time constant have been plotted in fig. 10 as a function of the ethyl acetate concentration, and it can be seen that the time constant falls by almost three orders of magnitude. In earlier studies, it was shown that ethyl acetate affects the segmental binding energy of PS on silica very strongly (Ref. 13). Combining this information with the kinetic results in fig. 10 we must conclude that the segmental binding strength plays a very important role in the displacement process.

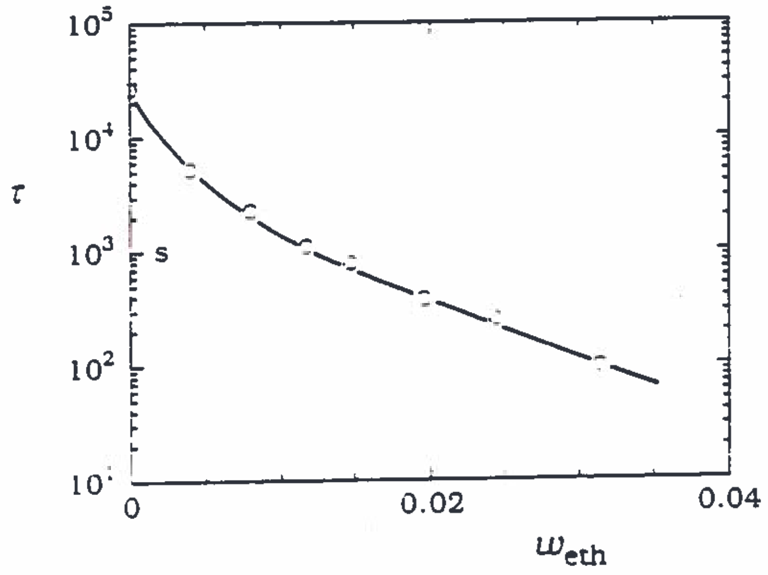

Fig. 10. The rate constant for displacement of PS by PBMA (data of fig. 9) as a function of the concentration of added ethyl acetate w_{eth}.

On closer inspection of the displacement curves we note another important feature. The displacement process occurs in *two steps*. The first step is rapid, and in fact almost simultaneous with the adsorption of PBMA. The amount of PS displaced in this step is also a function of the amount of added ethyl acetate, being small in pure decaline, and much larger in 3% ethyl acetate. This is reminiscent of the two-step character of the displacement between chains of unequal length discussed above. These data are qualitatively very similar to data obtained by Granick and coworkers for a variety of systems. In most cases, they observed a rapid initial desorption, followed by a much slower process. In their experiments, a tangential flow of solution was employed, which leads to Lévêque kinetics, i.e., the supply rate decreases in the downstream direction, and averaging over the exposed surface may blur out some details that we tend to see. Granick fitted the desorption curves to a 'strechtched exponential' which would probably also work to some extent for our data. Variation of solvent composition was not reported by Granick.

Tentative explanation: displacement and spreading

· What information can we draw from the data presented above, on the actual mechanism of spreading, in particular in the competitive case?

Granick has proposed the view that the incoming polymers would form an overlayer over the preadsorbed chains, thereby pinning them to the surface. This would confine the pinned chains to a kind of tube from which they would have to wiggle their way out during the exchange process. In other words, the desorption would be a kind of reptation process. Strong evidence in favour of this viewpoint was that whereas linear PS would readily desorb, star-branched PS would not, indicating that a topological constraint was operative (Ref. 14).

This scenario raises various questions. Firstly, it is somewhat difficult to see what driving force makes a pinned chain desorb at all. This should come from changes in conformation of the overlaying chains which are already supposed to lay relatively flat. Secondly, there is evidence suggesting that chains first land on the surface in a coil-like conformation which implies that they occupy initially a small area (Ref. 15). We can therefore envisage a different scenario, namely that the *spreading* of the displacing chains is the rate-determining process.

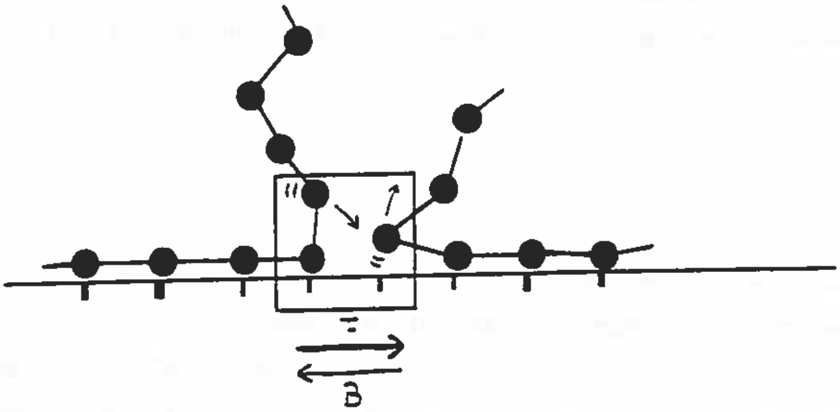

Fig. 11. A 'defect' in the adsorbed layer (an unoccupied site and two segments from different chains competing for it) must travel to the end of one chain before it can desorb. For two chemically identical chains, this process takes place at constant free energy; it is purely diffusive: forward (F) and backward (B) rate are the same.

Let us first consider a simple 2-D situation in which polymers A and B adsorb on a line, thereby competing for adsorption sites offered by the line, see fig. 11. Clearly, displacement of A by B requires the repeated detachment of an A segment from a site, followed by the attachment of a B segment. Hence, the elementary step in the forward process is the detachment of a segment. This should occur with a characteristic time τ determined by the energy of the A-surface bond. Of course, the backward process is also possible, and its rate depends on the energy of the B-surface bond. For A and B chemically identical, the forward and backward rates are equal, and all that remains is a pure diffusive displacement of the 'defect' (the point where A and B meet) along the line. This leads to the desorption of the shortest chain (say, A) after a time $T \sim N_A^2 \tau$.

In reptation, the basic process is also defect diffusion. In this sense, there is a similarity between displacement and reptation. It is known that branching points effectively eliminate the diffusing defect, which causes them to strongly suppress reptation. It is possible that branching points have a similar effect on the displacement process: they suppress it because they eliminate the diffusing defects. This could perhaps account for the results reported by Granick, without invoking a pinning phenomenon. Indeed did we find that the branched dextrane shows also a remarkable reluctance to be displaced. For real (3-D) chains adsorbed on a 2-D surface the displacement process cannot be described as simply as above. Yet, it seems likely that also for this case the displacement process involves a kind of defect diffusion. This may explain both the pronounced dependence on χ_s and the topological effects signalled by Granick. It should be useful to substantiate these ideas with help of a detailed molecular simulation, trying to identify the influence of χ_s and chain length.

ACKNOWLEDGEMENT

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The Effect of Surfactants on Water Based Pressure Sensitive Adhesives

J. Delgado, D.J. Kinning, Y.Y. Lu and T.V. Tran
3M Adhesive Technologies Center
3M Center, Bldg. 236-GB-16
St. Paul, MN 55144, USA

I. Introduction

The Pressure Sensitive Adhesive (PSA) market has been traditionally dominated by materials synthesized and delivered from solvents. Their performance was unchallenged for many years by solventless technologies. With a change in the environmental and economic climate, water based PSAs are finding more opportunities to replace solvent based materials, overcoming very significant barriers in the process. The heterogeneous nature of the emulsion polymerization process and the stability needed to be imparted to the colloidal particles during synthesis and handling has been the root of the technological barriers mentioned before. Surfactants, stabilizers, wetting agents and defoamers used with emulsion PSAs affect the adhesive properties of the materials.

It has been recognized for a long time that surfactants used during the synthesis and processing of emulsion polymers affect the properties of the film. Clasical works by Voyutskii [1] and Vanderhoff et al. [2] pointed out to the different behaviors that surfactant have upon film formation and their effect upon subeequent use. More recently Zhao et al.[3,4] investigated the surface composition of acrylic latex films by XPS and SIMS and observed a significant enrichment in surfactant at the film surface. Depending on the surfactant type (sodium dodecyl diphenyl ether sulfonate or sodium lauryl sulfate), they reported increases or decreases in peel strength. This work presents results on the behavior of different surfactants on acrylic

PSAs, their effect on the adhesive properties of tapes prepared with the PSA materials and responses upon aging.

II. Experimental Techniques

All the PSA emulsions were coated on 40 µm thick primed polyester film backing using a knife coater to provide a final PSA thickness of 25 µm after drying. The PSA coated tapes were dried in an oven at 65°C for 10 to 15 minutes. Unless otherwise indicated the coated and dried samples were conditioned overnight in a constant temperature and humidity room at 72° F and 50% relative humidity.

Peel adhesions to glass were measured at a 180° peel angle and at a peel rate of 90"/min. according to ASTM P3330-78 or PSTC-1(11/75). Shear holding power was determined by applying a piece of tape with dimensions of 0.5"x0.5" to a stainless steel panel and hanging a 1 Kg weight from the ape at a 2° angle from the panel according to ASTM D3654-78 or PSTC-7. The time to failure was recorded.

X-ray photoelectron spectroscopy (XPS) and static secondary ion mass spectrometry (SIMS) were done using a Perkin-Elmer Physical Electronics 5100XPS/6000SIMS instrument. For XPS, Mg Kα_{12} incident x-rays and a hemispherical analyzer were used. The angle θ between the sample surface and the analyzer (takeoff angle) was varied between 15 and 90 degrees. The depth in the sample, normal to the surface, from which 95% of the observed signal intensity is derived is given roughly as $3\lambda \sin\theta$ where λ is the inelastic mean free path of the photoelectrons [5]. For organic materials, and the experimental conditions used here, λ will be roughly 30 A [6]. Therefore sampling depths for takeoff angles of 15, 30, 55 and 90 degrees are about 25, 45, 75 and 90 A respectively. Atomic concentrations were determined by normalizing the areas under the high resolution spectra of each element by the atomic sensitivity factors determined for the instrument (using a series of homopolymers of knwon composition).

III. Results and Discussion

1. Effect of amount of surfactant level and aging on peel adhesion

Using known methods, a master acrylic PSA batch was synthesized using a sulfur free radical initiator, a difunctional crosslinker and ammonium lauryl sulfate as surfactant in an amount of 0.62% by weight based on the total monomer amount. After the polymerization, increasing amounts of ammonium lauryl sulfate surfactant were added to the master PSA batch to vary the bulk concentration of the surfactant between 0.62% and 2.17% by weight based on polymer. The PSA samples prepared by this procedure thus have the same particle size and copolymer composition being the surfactant concentration in the PSA the only variable between samples. Because the PSA was synthesized using a sulfur free radical initiator, the surfactant is the only source of sulfur in the PSA and the only source of nitrogen.

Figure 1 shows a plot of the peel adhesion of the PSAs to glass after 1 minute dwelling time as a function of the total percentage of surfactant in the PSA. It can be seen that the addition of the surfactant to the bulk of the emulsion decreases the initial peel adhesion of the PSA tapes. The effect is very significant as a four fold increase in bulk surfactant concentration results in a decrease in initial peel adhesion by a factor of seventeen (12.2 oz/0.5" to 0.7 oz/0.5"). It has to be pointed out that amounts of surfactant in the vicinity of 2% based on polymer are not uncommon for emulsion PSAs prepared at high solids. The effect of the surfactant on the peel adhesion of the tape is dynamic. Open face aging of the coated samples for a week in the constant temperature and humidity room resulted in an overall increase in peel adhesion as shown in Figure 2.

Figure 1

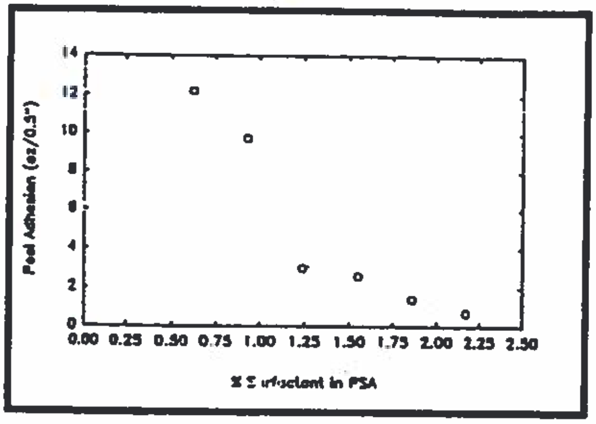
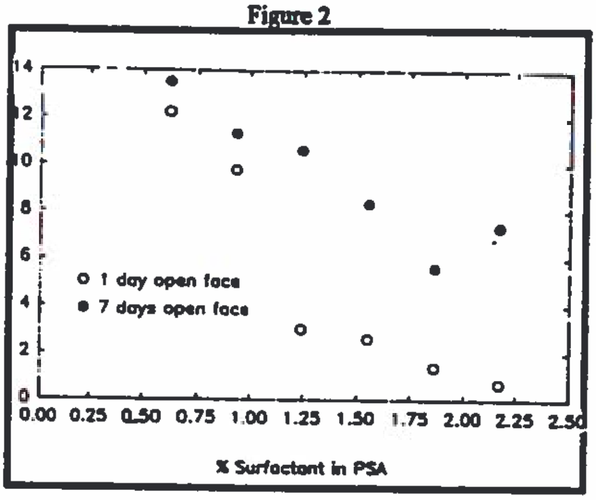


Figure 2

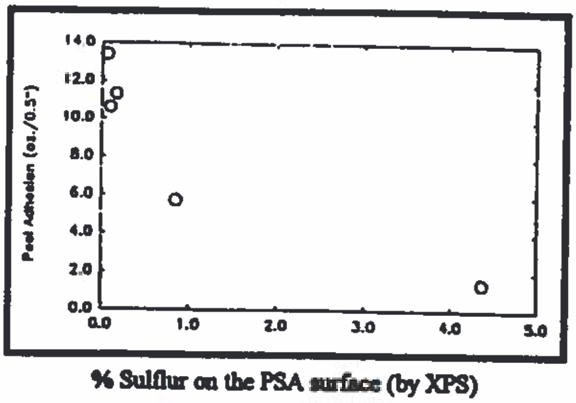


The sample containing 1.86% surfactant in the bulk was coated, dried and analyzed inmediatly by XPS. XPS analysis at a 35° angle determined 4.37% atomic sulfur at the tape surface versus 0.86% atomic sulfur determined at the same angle after the sample was aged for 1 week in the constant temperature and humidity room. The reduction in the amount of surfactant at the PSA surface corresponded with an increase in the peel adhesion of the tape. Peel test showed a peel adhesion of 1.4 oz/0.5" for the unaged sample versus 5.7 oz/0.5" for the aged sample. These results are indicative of the dynamic nature of the equilibrium between the surfactant at the surface of the PSA and the surfactant in the bulk.

2. Surfactant Configuration at the PSA Surface and Its Effect of Peel Adhesion

A clear correlation is observed between the amount of surfactant on the surface of the PSA tape and the peel adhesion of the tape when XPS analysis results determining the amount of surfactant on the surface of the PSA are compared with the peel adhesion of the tape as shown in Figure 3.

Figure 3



The higher the amount of surfactant on the surface of the PSA (identified as atomic % sulfur in Figure 3), the lower the peel adhesion of the tape. The effect is very significant as the main drop in peel adhesion occurs over a very small increase in surfactant amount at the surface. The possible reason for the reduction in the peel adhesion of the tapes by the surfactant can be found in Figure 4.

Figure 4

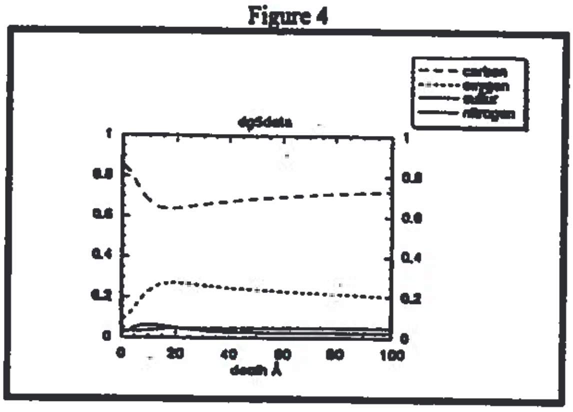


Figure 4 shows the atomic composition profile obtained by inverting the angle resolved XPS data, following the method of Tyler et al. [7], for the surface of the PSA containing 1.8 wt% ammonium lauryl sulfate. It needs to be indicated that the mathematical solution to determine the depth dependent concentration based on integral experimental depth data is not a unique solution. The sample was analyzed right after coating and drying. The profile shows a maximum in the amount of carbon just at the surface of the PSA tape and a minimum at a depth of about 15 A. On the other hand, oxygen, sulfur and nitrogen show minimum concentrations at the surface of the other hand. However, sulfur shows a maximum concentration at a depth of about 10A. From this analysis a picture of the probable surface of the PSA tape can be drawn. The surfactant is adsorbed on the PSA surface with its hydrophobic hydrocarbon tail oriented towards the air interface and its hydrophilic head towards the bulk of the tape. This is in contrast with the usual way that surfactants adsorb on the surface of the polymer particles while in the latex form, where the hydrophobic hydrocarbon tail is in contact with the polymer particles. The type of orientation of the surfactant at the surface of the PSA tape provides a large concentration of low energy CH_3 groups for contact with the substrate. This would result in an initial lower adhesion. On the other hand, the presence of the surfactant at the surface can also provide a weak boundary layer for failure during peeling. This will also result also in a reduction in peel adhesion. For either phenomenon, the higher the amount of surfactant at the surface of the PSA tape the lower the peel adhesion.

In order to corroborate the results observed with ammonium lauryl sulfate, the same PSA composition used in the previous experiments was synthesized using lithium perfluorodecyl sulfonate as a surfactant. The fluorinated surfactant was used at an amount of 0.5% by weight based on monomer. A sulfur free initiator was also used. The peel adhesion of a tape coated with this was measured as a function of the open face aging time of the tape in the constant temperature and humidity room. Figure 5 shows that increases and decreases in peel adhesion correspond to decreases and increases in fluorine in the tape surface repectively. Being the surfactant the only source of fluorine in the tape the increase and decrease in peel adhesion correspond thus to decreases and increases, repectively, of surfactant at the PSA surface.

Figure 5

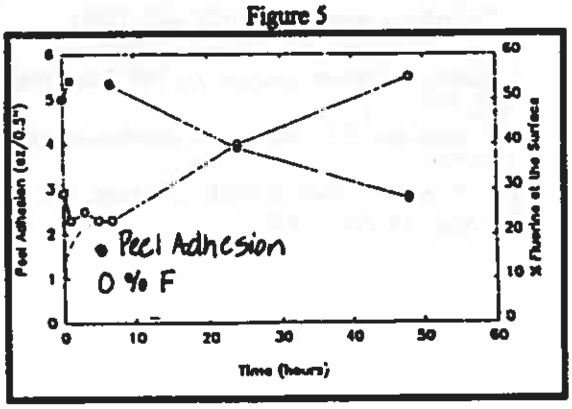
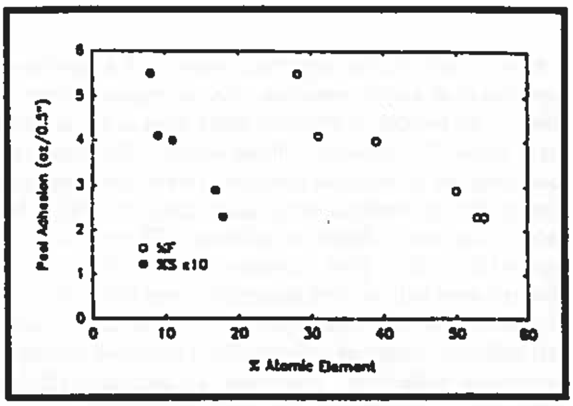


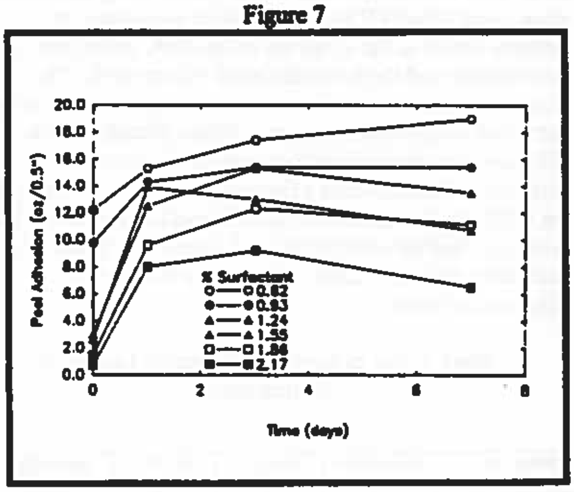
Figure 6 shows the strong correlation for this system between the peel adhesion and surfactant amount at the surface of the PSA tape (measured as %fluorine and % sulfur at the surface in Figure 6)

Figure 6



For the system using ammonium lauryl sulfate as surfactant the peel adhesion of the tape was monitored as a function of the dwell time of the tape against the glass surface it was adhered to. Figure 7 shows these results.

Figure 7



For all surfactant concentrations there is an steady increase in peel adehsion as a function of dwell time. The values for the peel adhesion seem to level off after a dwelling time of three days against the adhered glass surface, regardless of the amount of surfactant. Optical microscopy of the wetted area indicated that there was no macroscopic increase in the wetted area that could explain the increase in peel adhesion. A likely explanation for the increase in peel adhesion of the tapes having these crosslinked polymer particles is based on surfactant rearrangement at the PSA surface. It is hypothesized that when in contact with a high energy surface the highly mobile surfactant reorients itself within the PSA and at the PSA/substrate interface resulting in an increased adhesion between the polymeric material and the substrate.

3. Effect of the nature of the surfactant on PSA properties.

A series of ethoxylated surfactants were used during the synthesis of an acrylic emulsion PSA to understand the effect of the number of ethylene oxide units in the surfactant chain on the PSA properties of the latexes. These latexes containing the ethoxylated surfactants were compared with a latex of similar chemical composition prepared with sodium dodecyl benzene sulfonate as surfactant. The results are reported in Table I. Peel adhesions are from glass. The PSA prepared with sodium dodecylbenzene sulfonate (Siponate DS-10) has the highest shear value and the lowest peel adhesion compared with the PSAs prepared with the ethoxylated surfactants. The higher the number of ethylene oxide units in the surfactant chain the higher the peel adhesion and the lower the cohesive strength of the PSA. It seems as if the ethoxylated surfactants act as a plasticizer or a chain transfer agent increasing the peel adhesion but reducing the cohesive strength. This hypothesis is further reinforced by the results presented in Table II where the same latex PSA compostion was prepared using increasing amounts of Alipal EP 110. The higher the amount of surfactant used in the synthesis of the PSA, the higher the peel adhsion and the lower the shear values of the PSA. This is in contrast with the results presented for ammonium lauryl sulfate previously where a drastic decrease in peel adhesion was observed with increasing amounts of surfactant. This different behavior is a good illustration of the different dynamics of surfactants and their effect on PSA properties and the complexity, and sometimes frustration, associated with the choice of surfactant systems for polymeric colloids.

Table I: Effect of Surfactant Types on Latex PSA Performance

Surfactant Type % active based on Monomer	Siponate DS-10 2.0	Alipal CO 436 2.25	Alipal EP 110 2.25	Siponate DS10/ Igepal CO 630 1.0/1.0
Adhesion (oz/0.5")	9.4	23.6	26	9.6
Shear(min)	6300	40	37	345

Table II:Effect of Surfactant Concentrations on Latex PSA Performance

Surfactant % active based on Monomer	Alipal EP 110 1.5	Alipal EP 110 2.25	Alipal EP 110 3.0
Adhesion (oz/0.5")	23	27	28
Shear(min)	110	35	25

Siponate DS10 :	Sodium dodecyl benzene sulfonate (0 EO)
Alipal CO 436 :	Ammonium salt of sulfated nonylphenoxy poly(ethyleneoxy) ethanol, (6 EO)
Alipal EP110 :	Ammonium salt of sulfated nonylphenoxy poly(ethyleneoxy) ethanol, (10 EO)
Igepal CO 630 :	Nonylphenoxypoly(ethyleneoxy)ethanol (9 EO)

IV. Conclusions

Two different behaviors have been observed with two different classes of surfactants. Increasing amounts of alkyl sulfates and perfluoroalkyl sulfates in PSAs result in decreases in the peel adhesion of the tapes prepared from the PSAs. The reduction in peel adhesion corresponds to an increase in the amount of surfactant at the tape-air interface. For any of the surfactant concentrations studied, open face aging of the tapes coupled with PSA performance testing and XPS analysis of the tape air interface have shown that the amount of surfactant at the surface of the PSA changes over time resulting in very significant changes in peel adhesion. Depth profiling of the tape surface indicated that very likely the alkyl sulfate surfactant (ammonium laury sulfate) is oriented with its hydrophobic tail towards the air and its hydrophilic head towards the bulk of the tape. This orientation can explain the observed decrease in adhesion.

For ethoxylated surfactants an increse in peel adhesion is observed as the amount of ethylene oxide repeating units in the surfacant is increased. At the same time a decrease in shear holding power is observed. The higher the amount of ethoxylated surfactant used in the synthesis of the PSA the higher the peel adhesion and the lower the shear holding power. For these PSA it is hypothesized that the ethoxylated surfactant acts as a plasticizer of the PSA or a chain transfer agent during the polymerization process.

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Contribution from
Professor Joseph M. DeSimone

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

Our group is currently composed of 18 graduate students and 9 postdoctoral fellows. We are concerned with the study and application of amphiphilic macromolecules in a carbon dioxide continuous phase. The following abstracts outline some of the research topics currently being pursued by members of the DeSimone group.

The Tailoring of the Amphiphilic Nature of Surfactants for CO_2 - The Concept of a Critical Micelle Density. Douglas E. Betts and Joseph M. DeSimone

Currently we are considering the design and synthesis of several amphiphilic block copolymers composed of a CO_2-philic fluorocarbon block and a CO_2-phobic block in which the CO_2-phobicity is tailored such that at higher CO_2 densities the originally CO_2-phobic block becomes soluble in CO_2. The aggregation of such a material in CO_2 would be dependent on the density of the CO_2, 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). These block copolymers are being synthesized using the "iniferter" controlled free radical technique for use as surfactants in numerous applications including the stabilization of dispersion polymerizations in CO_2.

Siloxane-Based Stabilizers for the Dispersion Polymerization of Styrene in Supercritical Carbon Dioxide. Dorian A. Canelas and Joseph M. DeSimone

Recent advances have demonstrated that carbon dioxide presents an environmentally benign alternative to the aqueous and organic solvent systems which have been traditionally used by the polymer industry. The design and synthesis of stabilizing molecules which are active in a carbon dioxide continuous phase has proven to be the key to achieving successful dispersion and emulsion polymerizations. Current work focuses on investigating the scope and limitations of siloxane-based diblock copolymers as stabilizers for the dispersion polymerization of styrene in supercritical carbon dioxide. Using this methodology, high yields of high molecular weight polystyrene can be produced, and the resulting sub-micron sized polystyrene particles are recovered in the form of a dry, white, free-flowing powder. Reaction parameters such as stabilizer composition, reaction time, and carbon dioxide pressure were systematically varied and the effects on the resulting polystyrene colloids are discussed.

Free Radical Dispersion Polymerizations in Liquid Carbon Dioxide Using a Redox Initiator. E. Dessipri, Y.-L. Hsiao, A.C. Juventin-Mathes, K.A. Shaffer, and J.M. DeSimone

The successful use of the combination of BPO and DMA as a low temperature redox initiating system for the radical dispersion polymerization of MMA in liquid carbon dioxide has been demonstrated. Polymerizations were run at room temperature and a pressure of 76 bar using a variety of polymeric stabilizers. The effective stabilization by PDMS homopolymer is of particular importance in view of its low cost, commercial availability, and solubility in common organic solvents. The rate of radical production by the BPO/DMA redox initiating system in liquid CO_2 is being determined by UV/Vis spectroscopy in the presence of diphenylpicrylhydrazine (DPPH) radical scavenger.

Characterization of Polymers and Amphiphiles in Supercritical CO_2 Using Small Angle Neutron Scattering and Viscometry. J.B. McClain, J.D. Londono, D.E. Betts, D.A. Canelas, E.T. Samulski, G.D. Wignall, and J.M. DeSimone

The solution characteristics of 1.5×10^6 g/mol poly(1,1-dihydroperfluorooctyl acrylate) (PFOA) and 16.5×10^3 g/mol poly(hexafluoropropylene oxide) (Krytox) were examined in supercritical CO_2 over a range of temperature, pressures, and polymer concentrations by small angle neutron scattering (SANS). CO_2 was found to be a thermodynamically good solvent for PFOA as evidenced by a positive second virial coefficient ($A_2 \sim 2.2 \times 10^{-5}$ cm^{3}mol/g^2) at both 65 °C and 40 °C at 340 bar. Krytox solutions in CO_2 (65 °C, 340 bar) were found to be at the Theta condition as evidenced by $A_2 = 0.0$ cm^{3}mol/g^2. SANS experiments were also performed for a 3.0 w/v % solution of PFOA over pressures ranging from 350 bar to the visual cloud point (P = 240 bar) at 65 °C. Microscopic phase separation was in evidence 55 bar above the visual cloud point, suggesting that PFOA remains entrained in CO_2 at densities below the point where CO_2 ceases to be a good solvent. Viscosity studies of PFOA in CO_2 (6.7 w/v%, 50 °C and 340 bar) result in a relative viscosity of approximately 6.0.

The following publications have appeared since the previous Newsletter:

Hsiao, Y.-L.; Maury, E. E.; DeSimone, J.M.; Mawson, S.; Johnston, K.P. "Dispersion Polymerization of Methyl Methacrylate Stabilized with Poly(1,1-dihydrooctyl acrylate) in Supercritical Carbon Dioxide." *Macromolecules* **1995**, *28*, 8159-8166.

Kappellen, K.K.; Mistele, C.D.; DeSimone, J.M. "Synthesis of Poly(2,6-dimethyl phenylene oxide) in Carbon Dioxide" *Macromolecules* **1996**, *29*, 495.

McClain, J.B.; Londono, D.; Combes, J.R.; Romack, T.J.; Canelas, D.A.; Betts, D.E.; Wignall, G.D.; Samulski, E.T.; DeSimone, J.M. "Solution Properties of a CO_2-Soluble Fluoropolymer via Small Angle Neutron Scattering" *J. Am. Chem. Soc.* **1996**, *118*, 917.

Shaffer, K.A., Jones, T.A., Canelas, D.A., DeSimone, J.M., Wilkinson, S.P. "Dispersion Polymerizations in Carbon Dioxide Using Siloxane-Based Stabilizers" *Macromolecules* **1996**, *29*, 2704.

Canelas, D.A.; Betts, D.E.; DeSimone, J.M. "Dispersion Polymerization of Styrene in Supercritical Carbon Dioxide: Importance of Effective Surfactants" *Macromolecules*, **1996**, *29*, 2818.

nucleation process. The particle size distributions were unimodal in this case. Characterizations of the oil and aqueous phases of the initial emulsions showed that Triton X-405 partitions between the two phases and this behavior differs for styrene and n-butyl acrylate. This difference in partitioning affects the kinetics of these homopolymerizations to a great extent. In styrene homopolymerizations, the nucleation periods are attributed to homogeneous and micellar mechanisms, respectively, which are controlled by the changing partitioning of the surfactant between the phases during the reaction. The homopolymerization of n-butyl acrylate, however, is not greatly affected by the partitioning of the surfactant between the oil and water; instead, it is the relative instability of the particles which form and aggregate in the early stages of the reaction.

2. Enhanced Droplet Nucleation in Miniemulsion Polymerization: A Kinetic and Mechanistic Study

P. John Blythe

Miniemulsions are comprised of relatively stable oil droplets, ranging in size from 50 to 500 nm, suspended in an aqueous phase. The stability of these systems arises from the use of an ionic surfactant and a low molecular weight, highly water-insoluble cosurfactant in the emulsification process. In miniemulsion systems, the main locus of nucleation is the monomer droplets due to their small size. However, nucleation of the droplets is typically an inefficient process by which only a fraction of the initial number of droplets become particles.

Some debate still exists over the mechanism by which single radicals appear inside the droplets/particles in emulsion polymerizations when oil-soluble initiators are used. One theory is that the single radicals are formed by the desorption of one of the radicals formed by initiator decomposition within the droplets/particles. The second theory asserts that the small amount of initiator dissolved in the water phase dissociates forming radicals which subsequently enter the oil droplets. Thus, this theory predicts essentially the same behavior as observed using water-soluble initiators.

This presentation will focus on two main areas: (1) the relative importance of initiator decomposition in the oil and aqueous phases in emulsion polymerizations when oil-soluble initiators are utilized; and (2) methods of increasing the radical capture efficiency of miniemulsion droplets. Results of adding polymer and various aqueous phase inhibitors to emulsion systems initiated with an oil-soluble initiator will be presented. Of primary interest are findings showing a significant increase in the polymerization rate from a small addition of an aqueous phase inhibitor, dipotassium salt, prior to polymerization.

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. 45, January, 1996, which can be found at the end of this report. Abstracts of several presentations made at the recent Annual Review Meeting of the Emulsion Polymers Institute's Industrial Liaison Program are given below.

1. Role of the Nonionic Surfactant Triton X-405 in Emulsion Polymerizations of Styrene and n-Butyl Acrylate in the RC1

Eser Özdeğer

Gravimetry, dilatometry, and gas chromatography are some of the techniques used to follow emulsion polymerization kinetics. Using these techniques, one can obtain conversion-time curves from which rates of polymerization can be derived. In contrast to these techniques, one can obtain the rate of polymerization curve directly from the heat of reaction data in an almost continuous manner (every 2 seconds) using the Mettler RC1 reaction calorimeter. In this way, the details of a reaction can be easily followed. Other advantages of using the Mettler RC1 include its comparability with industrial large scale reactors and its capability of conducting chemical reactions under realistic conditions such as variable agitation speed and continuous addition of reagents.

Over the last two decades, nonionic surfactants containing ethylene oxide groups have become popular as the sole surfactants in commercial latex products. This is due to the lower sensitivity of these latexes to acidity or ionic strength of the medium. The hydrophile-lipophile balance (HLB) can be adjusted through the length of the poly(ethylene oxide) units on the surfactant chains to achieve an optimum latex stability. Little work related to the mechanistic aspects of emulsion polymerizations using nonionic surfactants can be found in the literature.

In this work, batch emulsion copolymerizations of styrene and n-butyl acrylate were carried out in the RC1 to monitor the reaction kinetics of the process. It was seen that the heat of reaction curve, which is proportional to the rate of polymerization curve, did not follow the rate behavior observed in classical emulsion polymerizations. Homopolymerizations of these monomers, carried out to help explain the copolymerization results, showed similar behaviors. Styrene homopolymerizations were relatively slow (taking hours) and two nucleation periods were observed leading to bimodal particle size distributions. On the other hand, butyl acrylate homopolymerizations were fast (taking minutes) with limited aggregation occurring during th

3. The Role of the Polymerizable Surfactant Sodium Dodecyl Allyl Sulfosuccinate in the Emulsion Polymerization of Styrene

Johanna Chu

Polymerizable surfactants differ from conventional surfactants in that they can copolymerize with the monomer(s) used in emulsion polymerizations. Hence, they can exhibit behavior unlike that found in conventional polymerizations. Previous work on the role of sodium dodecyl allyl sulfosuccinate (TREM LF-40, Henkel) in the emulsion polymerization of vinyl acetate showed a decrease in the rate of polymerization when the concentration of surfactant was increased. Results from parallel experiments using TREM LF-40 and its non-polymerizable derivative suggested the influence of copolymerization in the aqueous phase and at the particle surface between vinyl acetate monomer and TREM LF-40, as well as the presence of chain transfer to TREM LF-40 at the particle surface. This latter reaction was concluded to be the main reason for the unusual kinetic behavior.

In contrast to vinyl acetate, homopolymerization of styrene is favored over its copolymerization with TREM LF-40 as indicated by the reactivity ratios. Results from bulk polymerizations of styrene with TREM LF-40 at 60 °C showed that there was no measurable chain transfer to the surfactant. Moreover, the rate of polymerization increased with increasing concentration of the reactive surfactant, as in conventional emulsion polymerization. However, a non-proportionality between the rate of polymerization and the final number of particles was found which might be attributed to some copolymerization of the TREM LF-40 with styrene or the formation of water-soluble polymers of TREM LF-40 which may influence the reaction. Emulsion polymerizations of styrene were run with a homopolymer of TREM LF-40 as stabilizer, and these were compared to reactions carried out with TREM LF-40. The former reactions gave stable latexes, but were quite different from the latter ones, i.e., a longer nucleation stage, lower heat of reaction (closer to that listed in the literature for styrene), and broader particle size distributions were found.

4. Electrokinetic Lift Effect Associated with the Transport of Latex Particles in Capillary Hydrodynamic Fractionation (CHDF)

Andrew D. Hollingsworth

Colloidal forces play an important role in the transport of latex particles through microcapillary tubes in CHDF, a recently developed analytical method for particle size characterization. We have discovered that at very low ionic strength, the average residence time and axial dispersion of monodisperse polystyrene latexes being pumped under laminar flow conditions are strongly affected by eluant flow rate. This behavior is inconsistent with an inertial lift mechanism, becoming more pronounced with decreasing fluid conductivity and increasing particle size. The present CHDF model which was developed from first principles without the use of any adjustable parameters, predicts that particles in this size range will not be influenced by hydrodynamic forces when the dimensionless product group RepPe (product of the particle Reynolds number and Peclet number) is less than 3 which was the case for most of our work. The incorporation of the Bike-Prieve lift force theory [Bike, S.G. and Prieve, D.C., *J. Colloid Interface Sci.*, **175**, 422 (1995)] into the model allows the qualitative prediction of average particle velocities, indicating the existence of a strong repulsive force of electrokinetic origin. Electrokinetic lift originates when a charged particle and the diffuse part of the electrical double layer surrounding it are made to move relative to each other near another surface. In the CHDF process, this lift force may be due to an induced streaming potential in the particle-wall gap or the asymmetry of the electric field caused by the presence of the capillary wall. Coupled with these anomalous results is the effect of particle-particle interactions which appears to become significant as the fluid conductivity is reduced. Particle separation experiments have demonstrated that the use of very low ionic strength eluants in CHDF will provide better resolution of colloidal particles than that presently obtained using higher electrolyte concentrations.

5. Crosslinking of Isocyanate-Functional Acrylic Latex with Telechelic Polybutadiene

Jiangtian Xu

Isocyanate-functional acrylic latexes are candidates for ambient-curable, low VOC thermosetting acrylic coatings. Their crosslinking behavior with a telechelic polybutadiene (PBD) curing agent is presented here.

Telechelic polymers have low molecular weights and are terminated with functional groups capable of further reactions such as chain extension and crosslinking. Initial investigations in our lab showed that telechelic PBD can crosslink with a functionalized polymer latex during film formation.

Amino-terminated PBD was obtained by polymerizing butadiene with 2,2'-azobis(2-amidino propane) dihydrochloride (V50) as initiator in an ethanol/water medium, and modifying the end groups with lithium aluminum hydride. The number average molecular weight of the PBD was 2000~3000. The amino functionality was 2.0. This telechelic PBD was miniemulsified to form an artificial latex with ~20% solids content. This was then mixed with the isocyanate-functional acrylic copolymer latex which was obtained by emulsion terpolymerization of styrene/*n*-butyl acrylate/dimethyl *m*-isopropenyl benzyl isocyanate (TMI) with a weight ratio of ca. 49/49/2.

A room temperature curable latex film was obtained from a blend of the copolymer latex with the PBD artificial latex. When the content of the PBD was increased, the swelling ratio of the film in toluene decreased, indicating that the crosslinking density of the film increased with the concentration of the telechelic PBD, which acted as a crosslinking agent in the film. The crosslinking reaction was studied by FTIR observation of the NCO group. The crosslinking mechanism was studied using a core/shell model latex with a St/n-BA/TMI core and a St/n-BA shell. The effects of shell thickness, telechelic chain length and functionality on the crosslinking were studied. The use of the telechelic crosslinking agent provided the advantage of low isocyanate content in the latex formula and good storage stability.

EMULSION POLYMERS INSTITUTE
Lehigh University

Graduate Research Progress Reports
No. 45 January 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)

Preparation of High Solids Content Latexes Through Semicontinuous Miniemulsion Polymerization (J.R. Leiza)

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)

Influence of Chain Transfer Agents (CTA) on the Grafting Reactions Occurring in the Emulsion Polymerization of Vinyl Acetate Using Poly(Vinyl Alcohol) as Emulsifier (B.M. Budhlall)

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

Preparation of Uniform Micron Size Particles of Polystyrene by Anionic Dispersion Polymerization (M.A. Awan)

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

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

Elastomeric Films from Structured Latexes (Y. He)

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)

Rheology of Associative Thickener Solutions (L. Zhuo)

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

Contribution to the International Polymer Colloids Group Newsletter

Alice P. Gast

Department of Chemical Engineering, Stanford University, Stanford, CA 94305-5 025

The Gast research group is made up of six Ph.D. students and one postdoctoral student. Ben Frank, Joanne Promislow, Ja Phalakornkul, and Albert Lee are advised by Alice P. Gast, Ssu Wang and Mike Yatcilla are jointly advised by Alice P. Gast and Channing R. Robertson, and Patrick Doyle is jointly advised by Alice P. Gast and Eric S. G. Shaqfeh. We are interested in the study of colloids and macromolecules, and the following pages contain abstracts from three research projects from members of the group.

Evanescent Wave Dynamic Light Scattering (EWDLS) to Study Polymer Dynamics Near a Wall

Albert S. Lee, Alice P. Gast

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

Abstract:

An aqueous suspension of polystyrene beads near a glass wall was studied by setting up an evanescent wave correlation spectroscopy (EWDLS) experiment very similar to that of Lan, *et al.*[1] Using EWDLS, particle diffusivities were measured in order to observe the hydrodynamic interaction between the particles and the wall. In the EWDLS experiment, light is totally internally reflected at the interface between the glass and particle suspension, giving rise to an evanescent wave. The evanescent wave penetrates into the suspension, scattering off of the particles. The scattered light is collected and analysed to calculate the diffusivity. Because the evanescent wave decays with distance into the suspension, diffusivities are measured only for particles which are near the wall. The effective penetration depth of the evanescent wave into the suspension varies with the angle of incident light, such that diffusivities of particles at different distances from the wall can be measured. The experiments were conducted for 220 nm diameter particles at a volume fractions of 5×10^{-4}. Diffusivities were measured for particles at penetration depths ranging between 400 nm and ∞. At large distances from the wall, the diffusivity is close to the bulk value, but at closer distances from the wall, the measured diffusivity is lower. Hydrodynamic theory predicts that the mobility of a particle should decrease as the particle moves closer to the wall, beasye the wall exers a hydrodynamic force on the particle. From EWDLS, this predicted slowing down of the particles near the wall is experimentally observed.

Currently, the dynamics of adsorbed chain polymers is being studied, using EWDLS. Polyethylene Oxide (PEO) at molecular weights on the order of 100k are adsorbed onto glass, and the dynamics of these chains at the glass-water interface are observed. Thus far, the bare polymer chains do not scatter enough light from the evanescent wave in order to produce an appreciable signal. Charged polystyrene particles are adsorbed as probes onto the PEO chains in order to scatter enough light. From the dynamics of the particles, the dynamics of the polymer chains can be inferred. One possible way to infer the chain dynamics is to model the tethered chains as springs with an average spring constant[2].

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[1] N. H. Lan, N. Ostrowsky, and D. Sornette, *Phys.Rev.Lett.* **57**, 17 (1986).

[2] M. Kamiti and T. G. M. van de Ven, *Macromolecules* **29**, 1191 (1996).

Influence of pH on Two-dimensional Streptavidin Crystals

Michael T. Yatcilla, Alice P. Gast, Channing R. Robertson

Department of Chemical Engineering, Stanford University, Stanford, CA 94305-5 025

Abstract:

Two-dimensionally streptavidin crysrals grown on a lipid monolayer at an air-water interface exhibit crystallographic and morphological changes as a function of solution pH. Experiments are performed on a Langmuir microtrough beneath a preformed biotinylated lipid film. Macroscopic features of crystal graowth are observed using an epifluorescence microscope, and the crystal structure is determined using transmission electron microscope. Large 2D crystalline arrays (up to 1 mm in extent) form within minutes across a pH range from 1.5 to 11. Crystals have two pH-dependent strucutres, Type I (pH tange 1.5 - 4.5) with P1 symmetry [Darst, *J.Mol.Bio.*, **246**, 308 (1995)] and Type II (pH range 5 to 11) with C222 symmetry [Darst, *Biophys.J.*, **59**, 387 (1991)]. Type I crystals have a high nucleation rate and form thin needle-shaped crystals consistent with a strong growth anisotropy between the two crystallographic directions. Macroscopic features of Type II crystals include H- and X-shapes, both at early and later stages of growth, indicating lesser growth anisotropy. Type II crystals also exhibit pH-dependent nucleation rates and aspect ratios, both properties increasing with increasing pH. Transition from Type II crystals to Type I crystals can be accomplished by lowering the system pH, this transition occurring in minutes, but Type I crystals do not change in days to Type II crystals by raising pH.

Decouling of Translation/Rotational Diffusion of Semi-dilute Rigid Rodlike Suspensions

J.K. Phalakornkul, A.P. Gast*, R. Pecora‡

Department of Chemical Engineering, Stanford University, Stanford, CA 94305-5 025
‡Department of Chemistry, Stanford University, Stanford, CA 94305-5080

Abstract:

We develop a theoretical framework for the general case (at an arbitrary time and arbitrary wavevector **k**) of the dominant decay rate consistently observed from dynamic light scattering (DLS) experiments of semi-dilute concentration of rodlike polymers. The decay rate is calculated from the expression of the dynamic structure factor according to the DSO II theory. [1] The decay rate is obtained as a power series in the scattering vector **k** to sixth order. Our analytical expression indicates that the indispensable information of polymer dynamics including cooperative diffusion, coupling between translational and rotational motions and self diffusions in perpendicular and parallel directions can be obtained from this dynamic mode. While the coefficient of $\mathbf{k}^2$ depends on the translational diffusion coefficient, the coefficients of $\mathbf{k}^4$ and $\mathbf{k}^6$ are the combined effects of translation, rotation and translational anisotropy.

Based on our theoretical framework, we analyse our DLS spectrum of the model system of poly-γ-benzyl,α-L-glutamate suspended in a good solvent to elucidate various dynamic behaviors of the rods, including the mutual diffuvisity and self diffusivities in the direction perpendicular and parallel to the long rod axis, as a function of polymer concentration. While extracting the cooperative or mutual translational coefficient from the measured diffusivity is straightforward, acquiring the self values is more complicated. Decoupling translation/rotation is a prerequisite. Previous work has identified the effects of translational-rotational coupling on the measured diffusivity both from a dilute suspension at long time, [2] and a semi-dilute suspension at short time. [3] However, to our knowledge, there has never been a successful separation. The failure lies upon the uncertain values of rotational mobilities experimentally measured by depolarised light scattering technique. [4] Here, we utilise transient electric birefringence technique (TEB) highly sensitive to optical anisotropy of asymmetric molecules. Once the translation is separated from the coupling, its anisotropy is measured from the same DLS spectrum. Furthermore, this mothodology provides important

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[1] M. Dio, T. Shimada, K. Okano, *J.Chem.Phys* **88** , 6 (1988).

[2] J.M Rallison and L.G Leal, *J.Chem.Phys* **74** , 9 (1981).

[3] P.S Russo and F.E Karass, *J.Chem.Phys* **80** , 10 (1984).

[4] L.M DeLong and P.S Russo *Macromolecules* **24** , 24 (1991).

insights into the self diffusivities in the two directions. We report a rapid increase in the translational anisotropy between 40 rods/L^3 and 100 rods/L^3 before it levels off at 2.5×10^{-12} m^2/s. Below 40 rods/L^3, the perpendicular and parallel self diffusion coefficients remain equal to their infinitely dilute values. Above 40 rods/L^3, we observe a gradual decrease in the parallel self diffusivity. The coefficient reaches 80% of its dilute value at 180 rods/L^3 concentration. The perpendicular self diffusion coefficient decreases rapidly to 20% of its dilute value once the concentration becomes 100 rods/L^3, and remains relatively constant up to the highest concentration in this investigation, 180 rods/L^3.

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.

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., submitted.

Ab initio calculations have been carried out for the addition of n-alkyl radicals to ethylene, with the aim of identifying levels of theory suitable for the reliable description of the mechanism and energetics of the propagation process in the free-radical polymerization of ethylene. For the calculation of absolute barriers, use of a method such as QCISD(T)/6-311G(d,p), together with MP2 basis set corrections to 6-311+G(3df,2p), and B3-LYP/6-31G(d) zero-point vibrational energy corrections, is recommended. For the calculation of Arrhenius frequency factors, the parameters required, i.e., geometries, fundamental frequencies, and rotational barriers, can be reliably obtained at much simpler levels of theory, such as UHF/6-31G(d) or even UHF/3-21G.

The penultimate unit effect in free-radical copolymerizations. J.P.A. Heuts, R.G. Gilbert and I.A. Maxwell. Macromolecules, submitted (MA960704M).

Based upon new insights into the dynamics of propagation reactions, a theoretical justification of the penultimate model in free radical copolymerization kinetics is proposed. It is suggested that the penultimate unit effect may contain a large steric contribution (a different penultimate unit may affect the frequency factor for propagation by a factor typically between 1 and 10), and that the effect on activation energies is generally small. This implies that the stabilization energy model, where only differences in activation energies play a significant role, is valid only under unusual circumstances. Furthermore, a possible explanation is given for the occurrence of both the implicit and explicit penultimate unit effects. It is shown that mainly systems in which there is a large difference in the sizes of the substituents of both monomers are expected to exhibit an explicit penultimate unit effect. Finally, it is shown that neither a purely enthalpic effect, nor the steric effect proposed here, provides an adequate explanation why, experimentally, only radical reactivity ratios less than unity are found.

First-principles prediction and interpretation of propagation and transfer rate coefficients. J.P.A. Heuts, Sudarko, R.G. Gilbert. Macromol. Symp., in press.

Propagation and transfer rate coefficients in free-radical polymerizations are calculated from first principles, using quantum calculations (both *ab initio* and semi-empirical) to determine geometries, frequencies, torsional potentials and energies of reactants and transition state, after which transition state theory yields the Arrhenius parameters. While activation energies can only be calculated for small species and with large computational resources, acceptable frequency factors (A) are obtained with relative ease *provided* that lower frequencies corresponding to torsions are treated as hindered rotors, not harmonic oscillators; this entails finding the torsional potential and exact evaluation of the corresponding partition function. Simple theory can be used to find A because this involves a ratio of partition functions of reactant and transition state, and because torsions (which are dominated by geometrical considerations) dominate A. A is determined by three modes in the transition state: rotation of the monomer about the forming bond, rotation of a "propylene"-group about the terminal C–C bond in the radical, and simultaneous bending of the two angles associated with the forming bond. Calculations on ethylene and acrolein give agreement with experiment. These studies explain some experimental observations. (i) Changing the penultimate unit gives a small but significant change in the torsion of two of the three modes dominating A, leading to a penultimate-unit effect of *ca.* a factor of 1–10. (ii) Deuteration affects the moments of inertia of the torsions, leading to changes in A in accord with experiment. (iii) A, but not the activation energy, changes predictably along a homologous series (e.g., methyl, ... , butyl methacrylate). (iv) For a given monomer, A's for transfer to monomer and propagation are similar.

Catalytic chain transfer for molecular weight control in the emulsion homo- and co-polymerization of methyl methacrylate and butyl methacrylate. D. Kukulj, T.P. Davis, K.G. Suddaby, D.M. Haddleton, R.G. Gilbert. J. Polym. Sci. Polym. Chem. Ed., submitted.

The behaviour of catalytic chain transfer in semi-batch emulsion polymerization has been studied for two monomers, methyl and *n*-butyl methacrylate. Two different catalytic chain transfer reagents were used with different water solubilities: cobaloxime boron fluoride (COBF) which was found to partition approximately equally between organic and aqueous phases, and tetra-phenyl cobaloxime boron fluoride (COPhBF) which was found to reside predominantly in the organic phase. The difference in hydrophilicity between the two transfer agents was found to affect the polymerization mechanism. COBF exhibited superior transfer behaviour in all cases, whereas the restricted mobility of the COPhBF had a deleterious effect on the efficiency of the transfer mechanism. The best results were achieved under monomer-flooded conditions using COBF. MALDI analysis shows catalytic chain transfer to be the mechanism dominating initiation and termination of chains, as none of the chains appear to have initiator fragment end-groups. Analysis of copolymers by MALDI reveals both molecular weight and composition data.

An experimental investigation on the evolution of the molecular weight distribution in styrene emulsion polymerization. C.M. Miller, P.A. Clay, R.G. Gilbert and M.S. El-Aasser. J. Polym. Sci., Polym. Chem. Edn., submitted.

Styrene *ab initio* emulsion polymerizations were conducted at 70°C in an automated reaction calorimeter. Two polymerizations were performed, one above and the other below the critical micelle concentration (CMC) of the surfactant, thus ensuring differing polymerization kinetics between the two: the system below the CMC gave large particles which were expected to follow pseudo-bulk kinetics, while that above the CMC gave small particles which were expected to follow zero-one kinetics. The evolutions of the molecular weight distributions (MWDs) were characterized by removing samples periodically during the course of the reactions and analyzing with gel permeation chromatography. Interpretation of the data used average molecular weights, the GPC MWDs, and the number MWDs, as functions of conversion. It was found that all of the number MWDs (plotted as ln(number of polymer chains) versus molecular weight of polymer chains) were concave-up at low molecular weights and become nearly linear at molecular weights ($\geq 3 - 4\times10^6$); this linearity is expected from theory. The slope of the high molecular weight region was consistent with theory for the dominant mode for chain stoppage: termination and transfer for the pseudo-bulk system and (predominantly) chain transfer to monomer for the zero-one system. The most likely explanation for the concavity of the number MWDs is a heterogeneity of radicals: some surface-anchored with sulfate end groups and others (with hydrogen end groups arising from transfer to monomer and/or re-entry) being more mobile. Thus, two types of termination are proposed: slow reaction-diffusion for the less mobile surface anchored chains, and rapid short-long (center of mass) termination for the more mobile hydrogen-terminated chains.

Molecular weight distributions in free-radical polymerizations. 2. Low-conversion bulk polymerizations. P.A. Clay, R.G. Gilbert, G.T. Russell, Macromolecules, in press (MA960367H).

The results are reported for low conversion bulk polymerizations of methyl methacrylate (up to 15% conversion) and styrene (up to 8%) at 50°C with AIBN as initiator. Conversion was measured gravimetrically as a function of time, and the time evolution of the full molecular weight distributions (MWDs) was determined by GPC. The rates of polymerization were approximately independent of conversion, for both monomers these average rates of polymerization varying as $[\mathrm{AIBN}]^{0.5\pm0.05}$. MWD data were analyzed as ln$P(M)$, where $P(M)$ is the pseudo-instantaneous number distribution; approximate analytic solutions for the MWD [Clay, P. A.; Gilbert, R. G. *Macromolecules* **1995**, *28*, 552] suggest that plots of ln$P(M)$ vs. M should show extensive linear regions if chain stoppage is by transfer and/or chain-length-dependent termination. The cumulative number distribution is approximately the GPC distribution divided by the square of the molecular weight; pseudo-instantaneous distributions were obtained by subtracting appropriately normalized cumulative distributions at successive conversions. All MWD data show ln$P(M)$ is linear in M for higher M, with the slope of this region being independent of conversion but increasing significantly with increasing [AIBN]. The data are quantitatively consistent with chain stoppage being both by transfer to monomer and by termination between long and short chains, long-long termination being too slow to be important. The data afford qualitative evidence both for and against the low-conversion termination rate coefficients being significantly dependent on chain length. Attempts to use the shape at low-M of plots of ln$P(M)$ to indicate whether termination occurs by combination or disproportionation were also inconclusive.

Critically-evaluated propagation rate coefficients in free radical polymerizations. I. Styrene and methyl methacrylate. R.G. Gilbert. Pure & Appl. Chem., in press.

Critically evaluated rate coefficients and confidence limits, with derived Arrhenius parameters and confidence ellipses, are reported for the propagation rate coefficients of styrene and methyl methacrylate at low conversion in bulk. Data were obtained by an IUPAC Working Party, using pulsed-laser polymerization in several laboratories, and obey the consistency criteria established for this technique. These results provide useful "benchmarks" for measurements of propagation rate coefficients by other workers and other techniques.

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, in press (MA9600567).

A methodology developed to obtain rate coefficients for entry and exit (desorption) in emulsion polymerizations was applied to systems stabilized electrosterically by a copolymer of acrylic acid and styrene embedded in a styrene seed particle. This was grown as a second stage procedure, by adding styrene and acrylic acid to a styrene seed and then polymerizing. Rate coefficients for entry (ρ) and exit (k) for subsequent homo-polymerization of the resulting latices with styrene were obtained from the time dependence of the approach to steady state using both chemical and γ-radiolytic initiation; the latter was used in relaxation mode, which measures k directly. Compared to the same latices with an electrostatic stabilizer, at pH 7 the electrosteric stabilizer greatly reduced both ρ and k. When ionic strength was increased, ρ increased relative to that found for electrosterically stabilised latex in the absence of added electrolyte. For electrostatically-stabilized latices, entry is supposed to occur by aqueous-phase propagation to a critical degree of polymerization z which then undergoes irreversible entry; the present data for electrostatically-stabilized latices support this model, including its prediction that ρ be independent of particle size, all other things being equal. The decrease in ρ in the electrosterically stabilized latices is ascribed to a "hairy" layer through which diffusion of a z-mer is slow, so that it may be terminated prior to actual entry. For electrostatically-stabilized latices, exit is supposed to occur by transfer resulting in a monomeric radical which exits by diffusing through the aqueous phase, this event competing with intra-particle propagation; the decrease in k in the electrosterically stabilized latices (also seen in other polymerically stabilized systems) can be interpreted by assuming that aqueous-phase diffusion is slower in the "hairy" layer.

* The following publications have appeared since the previous Newsletter:

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).

Contribution to the International Polymer Colloid Group Newsletter
May 1996

from

Finn Knut Hansen

University of Oslo, Dept. of Chemistry
P.O.Box 1033 Blindern, 0315 OSLO, Norway

The Loen meeting

The "Associating Polymers" meeting in Loen, Norway, held 25-30 June 1995 was a great success, both scientifically and socially. The symposium was the first meeting devoted entirely to "Associating Polymers" as such and was held at Hotel Alexandra in Loen which is situated in the Western part of Norway, between Bergen and Trondheim. The advantage with such a location is a good balance between scientific and social activities, and that the participants get to know each other better. The number of people attracted to the meeting was ca. 80. Because of the success of this meeting, a follow-up is proposed in 1998, arranged in France.

In Figures 1 and 2 some interesting statistics from the meeting is given. In Fig. 1 we have classified all the presentations according to polymer type, as far as this is possible (some presentations did not focus on particular polymers, and some considered several). It is interesting to note that PEO based and polysaccharide based polymers constitute the main interest and with approximately equal weight.

In Fig. 2 the contributions are classified according to applied measuring techniques (also here some have applied several techniques). As expected, rheology is still the most popular technique, with light scattering methods as second. It may be noted that several newer techniques such as SANS (Small Angle Neutron Scattering), PGSE-FT NMR (NMR diffusion measurements) and luminescence/fluorescence techniques are promising to give new insight. Among the techniques under the Misc. label are methods such as electron

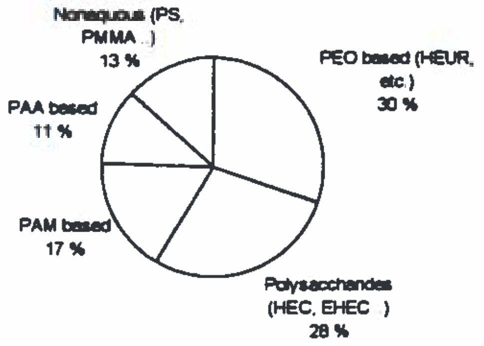

Figure 1. Presentations classified by polymer type(s).

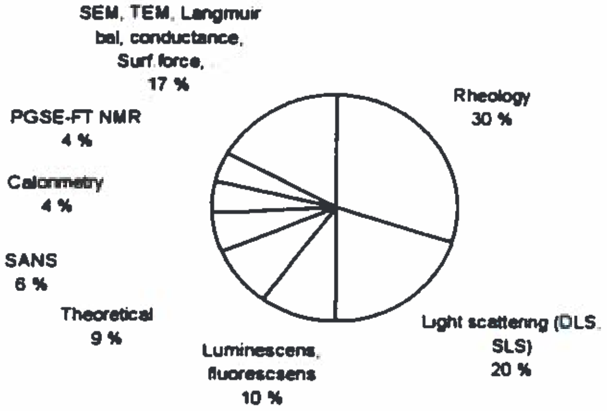

Figure 2. Presentations classified by measuring technique(s).

microscopy (SEM, TEM), Langmuir balance, conductance, surface force measurements and more. Some of these are described in the papers in this volume. Furthermore, the importance of understanding the thermodynamics (by e.g. constructing phase diagrams) in associative systems was stressed in several presentations. Such studies add considerably to the knowledge of the various association mečhanisms.

The proceedings from the meeting are published recently in Colloids and Interfaces.

The Polymer and Colloid Chemistry group in Oslo

The Polymer and Colloid Chemistry group in Oslo now consists of 4 professors, Nyström, Roots, Walderhaug and Hansen, and is organized in the Physical Chemistry Section. The group is working on both physical chemical properties of polymers in solution, their surface chemical properties by adsorption and phenomena at the liquid/solid, liquid/liquid and liquid/gas interfaces. Preparation and characterization of polymer particles is also a continuing interest, especially the influence of surfactants and adsorbed polymers on the polymerization process. The polymer types that are presently being studied are synthetic polymers such as copolymers based on poly(acylamide), poly(vinylalcohol), poly(styrene), and different block copolymers. In addition the group also work with modified polysaccharides such as hydrophobically modified cellulose ethers and chitosan (gelling systems), including interactions between polymer and surfactants and proteins.

In addition to the regular employees, the group now consist of 5 Ph.D. students and 4 master students.

Central experimental methods

The group is utilizing several techniques. The more central techniques are

Rheology (shear/viscosity, relaxation, oscillation)
Static and dynamic light scattering
NMR diffusion (PGSE-FT NMR)
Axisymmetric drop shape analysis (pendant and sessile drops)
Langmuir surface balance
Electrophoresis (by laser doppler method)
GPC

There are also several other instruments at the University of Oslo such as ESCA/XPS, TEM, SEM, etc. at our disposal. By utilizing a combination of several techniques we are able to extract more detailed information on the structure and dynamics of the polymer systems mentioned.

Recent papers

Below are published/to be publish papers from 1995-1996

F.K.Hansen, B.Nystrøm, H.Walderhaug and K.L.Børve,
Dynamic Interactions and Adsorption in Systems of Hydrophobically Modified Water-Soluble Polymers,
Makromol.Symp. 92, 345-354 (1995)

B. Nyström and B. Lindman,
Dynamic and Viscoelastic Properties during the Thermal Gelation Process of a Nonionic Cellulose Ether Dissolved in Water in the Presence of Ionic Surfactants.
Macromolecules, 28, 967 (1995).

H. Walderhaug, B. Nyström, F.K. Hansen, and B. Lindman,.
Interacteractions of Ionic Surfactants with a Nonionic Cellulose Ether in Solution and in the Gel State Studied by Pulsed Field Gradient NMR.
J.Phys.Chem., 99, 4672 (1995).

B. Nyström, H. Walderhaug, F.K. Hansen, and B. Lindman,
Rheological Behavior during Thermoreversible Gelation of Aqueous Mixtures of Ethyl(hydroxyetyl)cellulose and Surfactants.
Langmuir, 11, 750 (1995).

H. Walderhaug, B. Nyström, F.K. Hansen, and B. Lindman,
Surfactant-Polymer Interaction in Thermo-induced Gelling Systems of Ethyl(hydroxyethyl) cellulose (EHEC) Studied by NMR self-diffusion, Dynamic Light Scattering and Rheology.
Progr. Colloid Polym. Sci., 98, 51 (1995).

B. Nyström, K. Thuresson, and B. Lindman,
Rheological and Dynamic Light Scattering Studies on Aqueous Solutions of a Hydrophobically Modified Nonionic Cellulose Ether and Its Unmodified Analogue.
Langmuir, 11, 1994 (1995).

K. Thuresson, B. Nyström, G. Wang, and B. Lindman,
Effect of Surfactant on structural and Thermodynamic Properties of Aqueous Solutions of Hydrophobically Modified Ethyl(hydroxyethyl) cellulose.
Langmuir, 11, 3730 (1995).

F.K.Hansen and R.Myrvold,
The Kinetics of Albumin Adsorption to the Air/Water Interface Measured by Automatic Axisymmetric Drop Shape Analysis,
J.Colloid Interface Sci., 176, 408 (1995).

B. Nyström, H. Walderhaug, and F.K. Hansen,
Dynamic Light Scattering and Rheological Studies of Thermo-reversible Gelation of a Poly(ethylene oxide)-Poly(propylene oxide)-Poly(ethylene oxide) Triblock Copolymer in aqueous Solution.

Faraday Discussions, in press.

B.Nyström and H. Walderhaug,
Dynamic Viscoelasticity of an Aqueous System of a Poly(ethylene oxide)-Poly(propylene oxide)-Poly(ethylene oxide) Triblock Copolymer during Gelation.
J. Phys. Chem., in press.

B. Nyström, A.-L. Kjøniksen, and B. Lindman,
Effects of Temperature, Surfactant, and Salt on the Rheological Behavior in Semidilute Aqueous Systems of a Nonionic Cellulose Ether.
Langmuir, (submitted)

A.-L. Kjøniksen and B. Nyström,
Effects of Polymer Concentration and Cross-linking Density on Rheology of Chemically Cross-linked Poly(vinyl alcohol) near Gelation Threshold.
Macromolecules,(submitted)

K. Thuresson, B. Lindman, and B. Nyström,
Effects of Surfactants on Rheology of Water Soluble Polymers. An Investigation of the Effect of Hydrophobic Modification.
J. Phys. Chem., (submitted)

R.Myrvold, F.K.Hansen and B.Balinov,
Monolayers of some ABA Block-Copolymers at the Air-Water Interface
Colloids and Interfaces (in press)

A.-L. Kjøniksen and B. Nyström,
Dynamic Light Scattering of Chemically Cross-linked Poly(vinyl alcohol) during the Gelation Process.
Macromolecules, (submitted.)

H.Walderhaug, F.K.Hansen and B.Nystrøm,
Adsorption of a Hydrophobically Modified Water-Soluble Polymer to Polystyrene Latex Particles Studied by NMR Self-diffusion
(to be published)

INTERNATIONAL POLYMER COLLOIDS GROUP NEWSLETTER

Contribution
from

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

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

(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, Kalpakkum, Tamil Nadu, India

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Charge Number of Colloidal Silica Particles

Dispersions of ionic colloidal particles exhibit characteristic behavior at salt-free and low-salt conditions, due to strong electrostatic interparticle interactions. In spite of extensive studies, it is noteworthy that the number of electric charges on colloidal particles has not been given due attention.

This is an unfortunate situation, since the interaction in such ionic systems is expected to be largely determined by the Coulombic interaction, which is a sensitive function of the charge number.

There appear to exist three different attitudes regarding the colloidal charge number. In the first category, colloidal phenomena are discussed in terms of the analytical charge number N_a, which arises from the chemistry of the particle synthesis. This quantity may be determined by appropriate experimental methods such as conductometric titration. In the second, colloidal properties are discussed in terms of a theoretical framework using N_a and then, if a disagreement with the theory is found, an effective charge number N_e is introduced to re-scale N_a in such a way that reasonable agreement with observation is reached. In the third, the N_e is determined by independent experimental methods such as conductivity measurements and transference experiments. The second approach is encountered very often in the literature, particularly in computer-simulation work. This would be satisfactory, if the theory applied and the assumptions introduced were perfect, and if the resulting N_e could also be considered reliable, but even under such circumstances, we have at least two factors to be critically examined in the second approach, namely the theory (or the assumptions) and N_e. Unless either of the two is determined independently, the arguments become circular at best, and cannot be conclusive.

In this regard, there is a technical difficulty in preparing colloidal particles with various charge numbers while keeping other parameters (such as particle size) constant. This has hindered quantitative investigation of colloidal phenomena and hence precise estimation of the electrostatic interaction. Yamanaka et al. (J. Yamanaka, Y. Hayashi, N. Ise, T. Yamaguchi, submitted) found colloidal silica particles useful in the sense that the N_a can be varied with the quantity of added NaOH. Using conductivity measurements and conductometric titrations, the effective charge density, σ_e, in the absence of NaOH was determined to be 8×10^{-8} C cm^{-2} for a sample of a diameter of 0.11×10^{-6}m. The analytical charge density, σ_a, was found to increase with NaOH addition.

Comment on "Shear Modulus Titration in Crystalline Colloidal Suspension"

It was reported that the charge number of latex (strongly acidic groups) determined by conductometric titration did not agree with that measured by shear modulus titration (T. Pahlberg et al. *J. Colloid Interface Sci.*, 169, 85 (1995)). Based on the information of titration behavior mentioned in the preceding section, Yamanaka and Ise (*J. Colloid Interface Sci.*, in press.) demonstrated that the reported discrepancy can be ascribed to an overestimation of the strongly acidic group content by the conductometric titration, which was caused by coexisting weakly acidic groups on the latex particles. In other words, the total analytical charge number determined by the conductometric titration and the arguments of the degree of dissociation by the original authors cannot be accepted on the basis of elementary analytical chemistry.

Construction of a Two-Dimensional USAXS Apparatus

In order to facilitate structural studies of directionally oriented materials, Konishi et al. constructed a 2-dimensional ultra-small-angle X-ray scattering apparatus and investigated a single crystal of colloidal silica particles in dilute dispersions. It was composed of an X-ray generator (Rotaflex RU-H3R, Rigaku) and a Bonse-Hart camera in which two sets of two channel-cut single crystals of Ge were used to collimate the X-ray beam in both the horizontal and vertical planes (T. Konishi, E. Yamahara, and N. Ise, publication in preparation), as is shown in Fig. 1.

Fig. 2 shows a contour plot of rocking curves which corresponds to the intensity distribution of the (point-focus) direct beam in the detecter plane. The full width at half maximum is 17 sec of arc. Here we report two preliminary results on colloidal silica (radius: 560 A) dispersions. Fig. 3 is the USAXS profiles of the powder sample, in which the 2D-USAXS curve without desmearing can be compared with the desmeared 1D-USAXS data (T. Konishi et al. *Phys. Rev. B.* 51, 3914 (1995); *J. Am. Chem. Soc.* ***117*** , 8422 (1995)). The agreement between the two curves indicates that the desmearing procedures employed in the analysis of the 1D-USAXS data were satisfactory, since the smearing effect in the 2D-USAXS data is negligible.

Fig. 4 is a 2D-USAXS profile from the silica particles in a salt-free aqueous dispersion in a quartz capillary. Diffraction peaks were clearly seen, which indicate that an oriented colloidal crystal was formed in the dispersion. By analyzing the 2D-USAXS data in a similar way as used in crystallography, we determined the lattice structure to be bcc, the lattice constant to be 3800 A, and the [111] direction of the crystal to be parallel to the capillary axis. This confirms the previous conclusions obtained using the 1D-USAXS and indicates the importance of the interparticle attractive interaction.

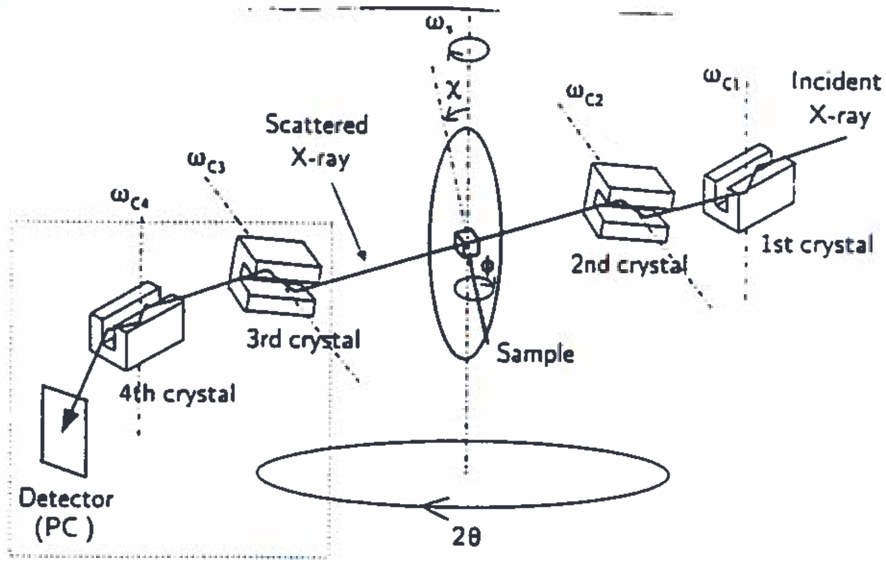

Fig. 1 The optical system of the 2-D USAXS

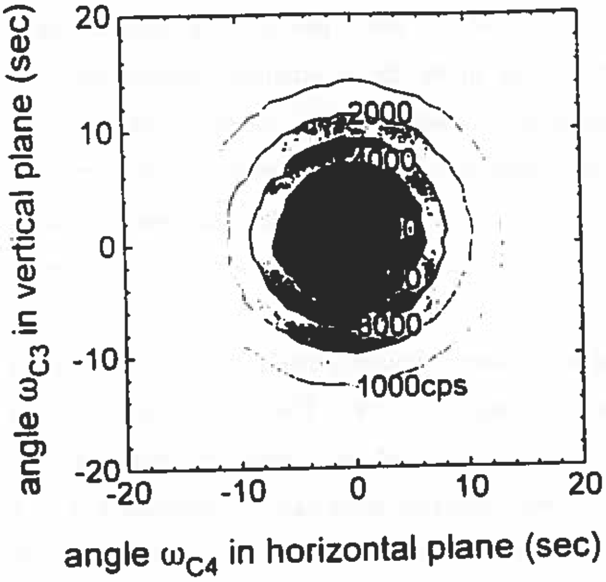

Fig. 2 Contour plot of the intensity of the direct X-ray beam (without sample) vs the rotation angles of the channel-cut crystals in horizontal and vertical planes.

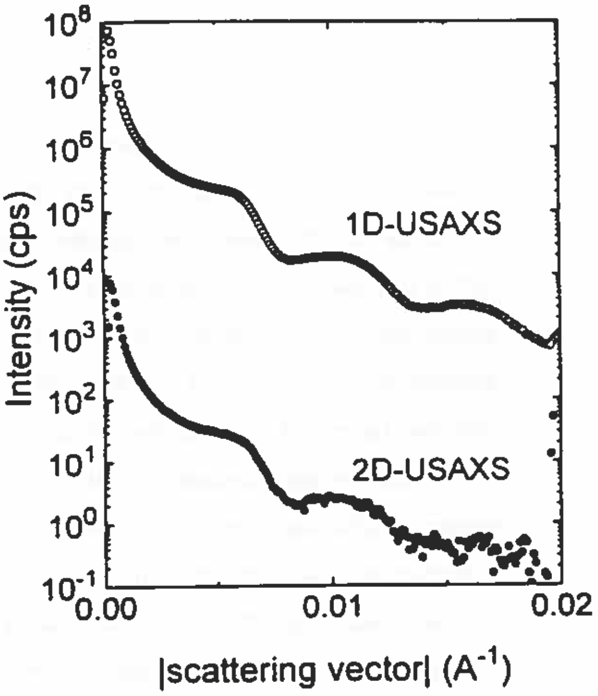

Fig. 3 1D- and 2D-USAXS curves for colloidal silica powder.

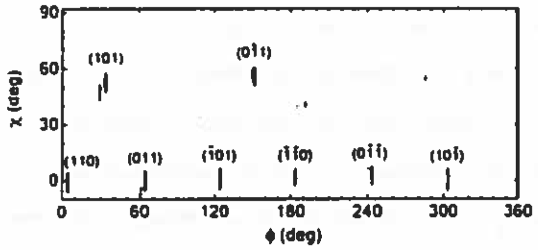

Fig. 4 Contour plot of the 2D-USAXS intensities vs the rotation angle (χ and ϕ) of the sample (capillary) for a single colloidal crystal of silica particles formed in a salt-free aqueous dispersion at 2.51 vol%. The χ is the angle of the sample in the plane at the right angle to the X-ray beam and the ϕ is that about the capillary axis. The scattering angle 2θ was 118 sec. For each peak observed, the corresponding diffraction planes are indicated by Miller indices.

Monte Carlo Simulation using the Sogami Potential: Phase Separation and Void Structure

Tata and Ise carried out Monte Carlo (MC) simulations for various values of charge density (σ) and salt concentration (C) with an aim to understand the experimental observations *viz.*, coexistence of stable void with ordered/disordered structure and the closest interparticle distance $2D_{exp}$ being less than the average spacing $2D_0$ which are unambiguous evidences for existence of long range attraction in the interparticle interaction (B.V.R. Tata and N. Ise, *Phys. Rev.B* in press).

Sogami potential $U_s(r)$ (*J. Chem. Phys.* 81, 6320 (1984)) which has the long range attraction in addition to short range repulsion has been chosen to be the interparticle interaction. The simulations for the first time revealed a homogeneous to inhomogeneous transition when σ was varied. Beyond a critical charge density interparticle distance became smaller than that expected for a homogeneous dispersion and voids appeared in the bulk of the dispersion. This phenomenon can be understood from the shape of the Sogami potential. The simulation results were found to be in excellent agreement with reported observations.

Constant volume simulations were performed to simulate aqueous dispersions of latex spheres having particle diameter d = 1100A and volume fraction ϕ = 3%. The equilibrium structural properties viz., pair correlation function $g(r)$, coordinate averaged pair correlation function $g_c(r)$, and first peak height of the structural factor S_{max} were calculated using particle coordinates. Fig. 5 shows the $g(r)$, $g_c(r)$ and projections of the corresponding simulation cells for dispersions with different charge densities. Notice from the figure that dispersion with $\sigma = 2 \times 10^{-7} C/cm^2$ was bcc-like ordered and homogeneous as the interparticle separation $2D_s$, obtained from the position of the first peak in $g(r)$, is same as $2D_0 (2D_0 = 3^{1/2} 2[2/n_p]^{1/3})$. On the other hand for dispersions with high σ the first peak in $g(r)$ shifted to smaller r implying $2D_s < 2D_0$. This suggests that the dispersion could be inhomogeneous. The corresponding projection of the MC cell confirmed this and showed presence of dense ordered/disordered regions coexisting with one or more voids. Thus it is clear from these results that a homogeneous dispersion turns inhomogeneous when σ was increased. In the inhomogeneous state voids coexisted with dense ordered/disordered regions where $2D_s < 2D_0$. The homogeneous to inhomogeneous transition is identified using S_{max} and is shown in Fig.6 It is clear from Fig. 6 that $2D_s < 2D_0$ whenever the dispersion is inhomogeneous and this explains the experimental observations of $2D_{exp} < 2D_0$. The addition of salt was found to lower the critical charge density where the transition takes place.

It should be mentioned that when the DLVO potential was used, the void formation could not be reproduced. The success of Sogami potential in explaining observations of voids and vapour-liquid condensation phenomena (B.V.R. Tata et al. *Phys.Rev. Lett.* **69**, 3778 (1992); *Phys. Rev. E.* **47**, 3404 (1993), A.K.Arora et al. *Phys. Rev. Lett.* **60**, 2438 (1988)) indicates that it is a more realistic choice than the DLVO potential in describing the properties of charged colloids. Further the present simulations clearly indicated that long range attraction is responsible for appearance of inhomogeneous structure in charged colloids.

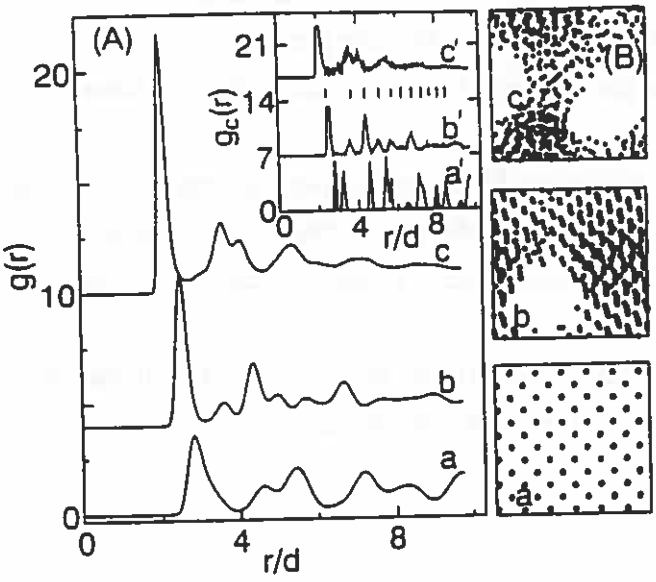

Fig. 5 (A) *g(r)* vs *r* for different charge densities at zero salt concentration. Curves *a,b* and *c* correspond to $\sigma = 2,4,6.8 \times 10^{-7}$ C/cm^2, respectively. The inset shows $g_c(r)$ vs *r*. The curves *a', b'* and *c'* correspond to the same parameters as those of curves *a,b* and *c*. Curves *b,c* and *b',c'* are shifted vertically for the sake of clarity. Vertical bars in the inset correspond to an ideal fcc lattice with $\phi = 4.52\%$ calculated from the first peak position of curve *b'*. (B) Projection of time averaged particle coordinates in the MC cell for parameters same as *a, b,* and *c*.

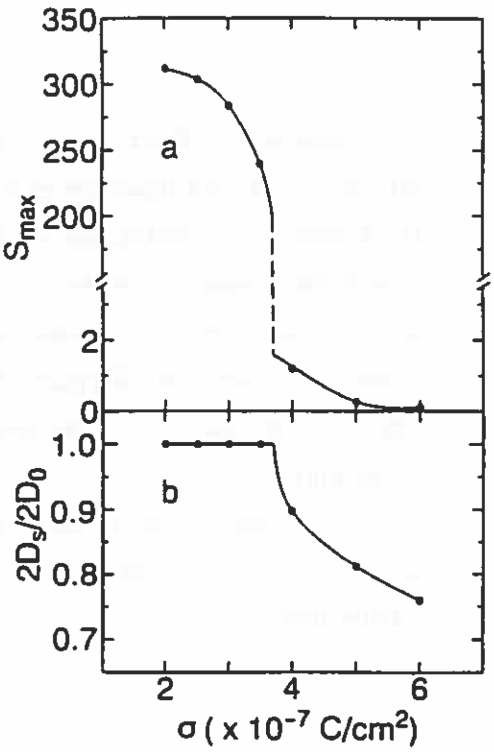

Fig. 6 Structural parameters (a) S_{max} and (b) the ratio $2D_s/2D_0$ as function of σ. The line drawn through the points is a guide to the eye.

Publication between October, 1995 and April, 1996

(1) H. Yoshida, N. Ise, and T. Hashimoto, Void Structure and Vapor-Liquid Condensation in Dilute Deionized Dispersions, *J. Chem. Phys.* **103**, 10146 (1995).

(2) N. Ise and H. Yoshida, Paradoxes of the Repulsion-Only Assumptions, *Acc. Chem. Res.* **29**, 3 (1996).

(3)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* in press.

(4)T. Konishi, E. Yamahara, and N. Ise, Characterization of Colloidal Silica Particles by Ultra-Small-Angle X-Ray Scattering, *Langmuir* in press.

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

(6)B. V. R. Tata and N. Ise, Homogeneous to Inhomogeneous Transition in Charged Colloids, *Phys. Rev. B* in press.

(7)T. Konishi and N. Ise, Orientation and Lattice Structure of Microcrystals of Colloidal Silica Particles in Dispersions Observed by Ultra-Small-Angle X-Ray Scattering, *Phys. Rev. Lett.* submitted.

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Light Scattering and Gel Inhomogeneities

A. MOUSSAÏD, H. J. M. SLOT and J. G. H. JOOSTEN*

Department for Physical, Analytical & Computational Chemistry, DSM Research, P.O. Box 18, 6160 MD Geleen, The Netherlands

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Light Scattering results on polyacrylamide networks show that the scattered intensity changes as different positions of a sample are probed. The scattered intensity from gels, measured by averaging through many different positions, was found to be much larger than the intensity scattered by the equivalent polymer solution. This excess arises from the frozen-in fluctuations due to the presence of cross-links. This additional structure in gels can be enhanced or reduced with conditions of preparation. Modeling a gel by a random network of springs is presented. The resulting scattering properties mimic real gel behavior.

KEY WORDS Light scattering, gels, polyacrylamide, nonergodicity, inhomogeneities, computer simulations

Contribution to the International Polymer Colloids Group Newsletter

by

Haruma Kawaguchi

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

Modifications of Hydrogel Microspheres

1 Magnetite-containing hydrogel microsphere

Mami Sakagawa, Yukio Ebisawa, Keiji Fujimoto and Haruma Kawaguchi

Monodisperse hydrogel microspheres were obtained by precipitation polymerization of acrylamide (AAm), methacrylic acid (MAc) and methylenebisacrylamide (MBAAm) in alcohol. Ferrous and ferric ions were absorbed into the dried hydrogel microspheres and then ammonia water was added to them in order to deposit magnetite in the microspheres. *In situ* formation of magnetite was confirmed by observation of ultrathin section of the composite microspheres by means of transmission electron microscopy and measurement of magnetic flux density of the microspheres. The magnetite-containing microspheres were used as seed particles for seeded polymerization of glycidyl methacrylate (GMA) and thus covered with poly-GMA to supress the leakage of ferric and ferrous ions from the microspheres. The product was used as a bioseparator after attaching biospecific fragments on the surface.

2 Partially hydrophobized hydrogel microspheres

Yoshiyuki Nakazawa, Sakurako Kawamoto, Keiji Fujimoto and Haruma Kawaguchi

The above-mentioned AAm-MAc-MBAAm terpolymer hydrogel microsphere was used as a seed for seeded polymerization of styrene (St). The resulting microspheres had raspberry-like surfaces with different sizes of poly-St doamins depending on the MBAAm concentrations. When this concentration was low, large domains were developed. The crosslinking density also affected the distribution of poly-St domains through the microsphere. Slightly hydrophobized microsphere, that is, the hydrogel microsphere bearing a very small amount of poly-St domains gave the least stimuli to cells.

3 Amphoteric hydrogel microspheres

Yasushi Ariyoshi, Mitsuhiko Kashiwabara, Hitoshi Okazaki, Keiji Fujimoto and Haruma Kawaguchi

Monodisperse reactive hydrogel microspheres were prepared by precipitation polymerization of p-nitrophenyl acrylate (NPA) with MAc and MBAAm in ethanol. The microspheres were converted to amphoteric ones by aminolysis reaction of the active ester of NPA units with ethylenediamine (EDA) or diethylenetriamine (DETA). The ratio of cationic to anionic groups (NH_2 to COOH) could be controlled by the amphoterization conditions although the possible range was limitted. EDA-coupled amphoteric microspheres shrank discontinuously around their isoelectric points. DETA-coupled amphoteric microspheres changed their size gradually with pH because DETA has amines with different dissociation constants. Contribution of both end groups of diamine to aminolysis caused additional crosslinking, which must be avoided to prepare highly volume-changable microspheres.

4 Protein-carrying hydrogel microspheres

Miwako Shidara, Keiji Fujimoto, and Haruma Kawaguchi

The above-mentioned reactive hydrogel microspheres can be used as a carrier for functional biocompounds because the immobilization can be carried out very easily and the microspheres themselves can be converted to bio-inert ones. Human immunoglobulin G (IgG) was immobilized directly onto the microsphere via the reaction between amine of IgG and on-surface active ester. It was confirmed from the transmission electron micrographs of gold colloid-stained microspheres that IgG was mostly immobilized near the surface of microspheres.

Recent Publications

*M.Kashiwabara, K.Fujimoto, H.Kawaguchi,
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INTERNATIONAL POLYMER COLLOIDS GROUP NEWSLETTER

Contribution from the Department of Chemical Engineering,
Yonsei University, 134, Shinchon-dong, Sudeamoon-ku, Seoul, Korea.

Reported by Jung-Hyun(Jay) Kim

Current researches accomplished in our laboratory include: (1) structural morphology developments in the interfacial phase of heterocoagulated composite particles : dynamic mechanical measurements. (2) the effect of morphologies on dynamic mechanical properties in heterocoagulated composite particles. (3) effects of the surface charge density on particle size distribution in seeded emulsion polymerization, (4) synthesis of low density organic aerogels.

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

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

The relationship between the morphology and the mechanical properties of films has been investigated. It has been shown that the miscibility of each phase, relative fraction of phase, characteristic size of the dispersed and continuous phase, degree of adhesion between phases and polymerization process (batch, semi-batch, etc.) could effect on the morphology of composite particles as well as the film properties being occurred as the particles coalesce into films.

In the present work, we present the model composite system intended to investigate the phase behavior during the network formation in the interfacial region between core and matrix phase. The morphology of this system is like that of core-shell structured latex particles encapsulated with thin small particle (SP) material layer having predetermined thickness. This article described the chain movement and the network formation behavior of the model composite particles using dynamic mechanical analysis. For that, composite particles having different type of shell structure were prepared. The nature of the interlayer was varied by changing the molecular structure of small particles : (a) conventional linear type (SP-L), (b) cross-linked type (SP-X), and (c) reactive type capable of forming crosslinked structure (SP-R). The linear chains of SP-L can interdiffuse with LP and SP, this makes impossible to maintain its interfacial domain structure, while crosslinked chains of SP-X cannot perform interdiffusion. However, reactive chains of SP-R crosslinked each other, which could form crosslinked network structure after chain interdiffusion, thus they maintained their domain structure.

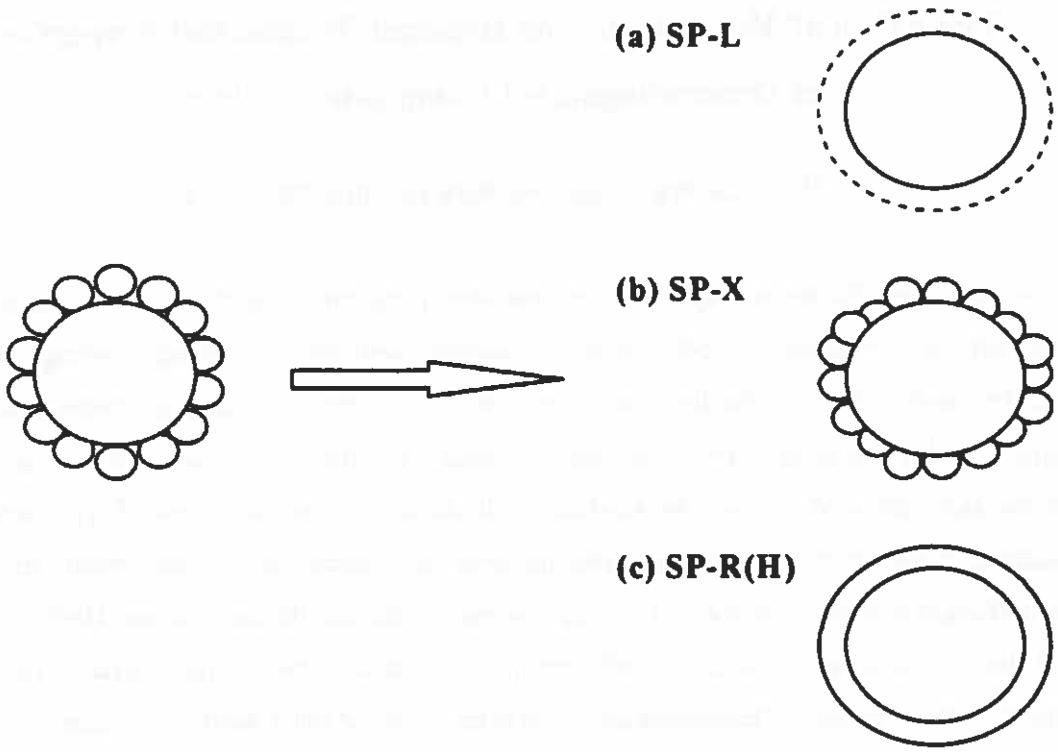

Fig. Development of shell region morphology of heterocoagulated composite particles.

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The Effect of Morphologies on Dynamic Mechanical Properties in Heterocoagulated Composite Particles

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

In this work, the heterocoagulated particles were prepared using two kinds of particles of different sizes, small negative(SP) and large amphoteric particles(LP), taking advantage of their opposite surface charge in the dispersion state. In order to vary compatibility between small and large particles, two kinds of small particles were used. : Poly(methyl methacrylate-butyl acrylate-acrylic acid) and poly(styrene-butyl acrylate-acrylic acid) particles (SP-M and SP-S). Dynamic mechanical properties of heterocoagulated particles were measured as a temperature to verify their changes in micro-morphology by using dynamic mechanical thermal analyser(DMTA).

In the case of using SP-M as SP, only one main relaxation, which corresponded to LP was shown in tan d spectra of heterocoagulated particles. On the other hand, in the case of using SP-S as SP, two main relaxation process, which corresponded to those of LP and SP-S were shown in tan d spectra. This results were interpreted from the better compatibility between LP and SP-M than between LP and SP-S. Due to good compatibility between LP and SP-M, the volume diffusion was expected to occure during the annealing process perfomed at 70 ℃ for 24h.

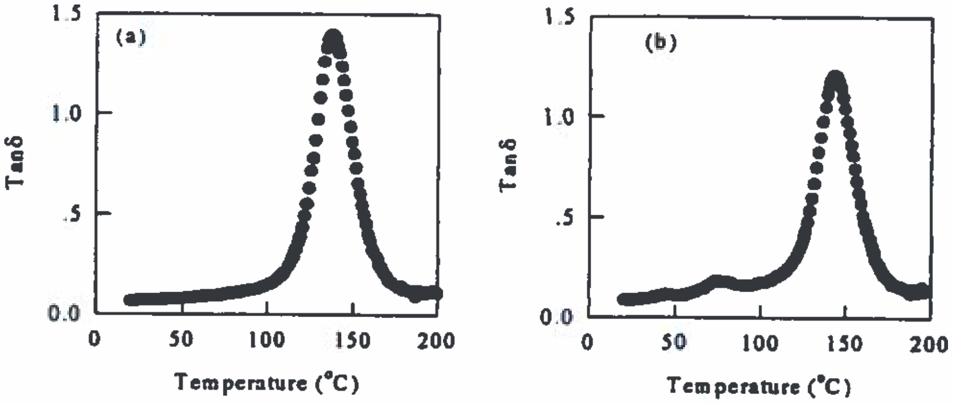

Fig. Tan δ vs. Temperature of heterocoagulated particle.

(a) small particles : poly(methyl methacrylate-butyl acrylate-acrylic acid)

(b) small particles : poly(styrene-butyl acrylate-acrylic acid)

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Effects of the Surface Charge Density on Particle Size Distribution in Seeded Emulsion Polymerization

In-Woo Cheong, Jung-Hyun Kim

The characteristics of the seed particle(i.e. total surface area, amount, number density, surface charge density, etc.) are important factors in seeded emulsion polymerization. Experiments and mathematical modeling were carried out in order to investigate the effect of the amount and the surface charge density of seed particle on particle size distribution in the emulsifier-free seeded emulsion polymerization of methyl methacrylate

Mathematical model based on DLVO theory and limited coagulation mechanism was developed. The physical factors that influence the adsorption rate of oligomeric radicals onto seed particles were the electrical repulsion and reversible diffusion between seed particles and oligomeric radicals. Assumptions applied to the model were 1) no heterocoagulation occurs between the percursor and the seed particle, 2) only oligomer with chain length j_{crit} can precipitate and form precursor particle, 3) the adsorption rate of oligomeric radical is diffusion controlled.

Styrene seed latex was prepared by using two stage shot process. In shot process sodium styrene sulfonate(NaSS) was used to control the size and the surface charge density of seed latex particle. Emulsifier-free seeded emulsion polymerization of MMA was carried out in batch and no swelling condition. In seeded emulsion polymerization, the seeds with various surface charge density(13.5-59.0$\mu C/cm^2$) were used. Reaction temperature was 50 ℃ and initiation was redox system with KPS and $NaHSO_3$. The surface charge density was measured by titration method. The particle size and its distribution were measured by capillary hydrodynamic fractionation. The fractional conversion and the rate of polymerization were determined by gravitational method.

The highly charged seed particle have influence on the secondary particle formation and the low rate of polymerization during seeded emulsion polymerization due to the low adsorption rate of oligomeric radicals in aqueous phase.

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Synthesis of Low Density Organic Aerogels

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

Sol-gel polymerizations have largely involved the hydrolysis and condensation of metal alkoxides to form inorganic aerogels or xerogels. Recently, organic modifications of the traditional sol-gel process have led to hybrid materials knowns as ormosils, ormocers, or ceramers. In these systems, the reactive components are soluble metal alkoxides and functionalized oligomers or polymer molecules(e.g. polytetramethylene oxide).

While the above synthetic approaches incorporate organic monomers, oligomers, or polymer molecules into a traditional sol-gel polymerization, our research has focused on extending the sol-gel concept to the polymerization of multifunctional organic monomers, exclusively. The aqueous polycondensation of resorcinol with formaldehyde is a proven synthetic route for the formation of cross-linked gels that can be dried into aerogels or xerogels.

The ultrastructure and properties of organic aerogels are analogous to their inorganic counterparts. In general, these materials have a continuous porosity, an ultrafine cell/pore size (≤ 50 nm), high surface area (400-1000 m^2/g), and a solid matrix composed of interconnected colloidal-like particles or polymeric chains with characteristic diameter of 10 nm. This ultrastructure and the low Z (atomic number) composition are responsible for the unique optical, thermal, electrical, and acoustic properties of organic aerogels.

Resorcinol reacts with formaldehyde under alkaline conditions to form mixtures of addition and condensation products. The major reactions include: (1) the formation of hydroxymethyl(-CHOH) derivatives of resorcinol. (2) the condensation of the hydroxymethyl derivatives to form methylene ($-CH_2-$) and methylene ether ($-CH_2OCH_2-$) bridged compounds, and (3) the disproportionation of methylene ether bridges to form methylene bridges plus formaldehyde as a product.

The resorcinol-formaldehyde gels are converted into aerogels by supercritical extraction with carbon dioxide. Because water is not miscible with liquid CO_2, the aquagels are first exchanged with an organic solvent (e.g., acetone), and then processed insides a temperature-controlled pressure vessel. The critical point of carbon dioxide (Tc=31°C; Pc= 7.4Mpa) is low enough that no polymer degradation takes place during the drying operation.

This work demonstrates that organic based aerogels can be successfully synthesized from the resorcinol with formaldehyde. The solid content is the major variable controlling the structure and properties of organic aerogels. It affects the density, surface area, and porosity of these materials. This ultrastructure determines the mechanical, acoustic, optical, thermal, and electrical behavior of organic aerogels.

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The suitability of scanning angle reflectometry for colloidal particle sizing

[1] E.A. van der Zeeuw, [1] L.M.C. Sagis, [1,*]G.J.M. Koper,
[2] E.K. Mann, [1] M.T. Haarmans and [1] D. Bedeaux

[1] *Leiden Institute of Chemistry, Leiden University,*
Gorlaeus Laboratories, PO Box 9502, 2300 RA Leiden, The Netherlands.
[2] *Institut Charles Sadron, Rue Boussingault , Strasbourg.*

We investigated the suitability of reflectometry as a sizing method for polystyrene latex particles. This technique, where the particles are adsorbed at a quartz/water interface, involves the analysis of the reflection around the Brewster angle of light polarized in the plane of incidence [1]. A computation of a full reflectivity curve containing about 20 datapoints, taking into account all electromagnetic interactions, is extremely complex and may take up to 100 hours on an Indy R4600 computer (Silicon Graphics, Mntn View, CA). To use the complete electromagnetic theory [3]. for analysis of experiments therefore is impractical. We analyzed the experimental reflectivity curves using an approximate theory (*free-sphere* model), which neglects all electromagnetic interactions between different particles and their images in the substrate. To assess the errors introduced by neglecting these interactions, we have calculated reflectivity curves using the full electromagnetic theory for this system, and analyzed them with the *free-sphere* model. We found that the diameters determined with the *free-sphere* model deviate at most 2% from the actual values. The surface coverage determined with the *free-sphere* model is systematically smaller than the actual coverage. The difference can be as large as 15% at a coverage of 9%. We also show that size-polydispersity of the sample plays a minor role in the analysis of the data. This compares well to what has been found experimentally using bimodal mixtures of latex particles [2]. The usefullness of the *free-sphere* model, is demonstrated by measurements in which polystyrene latex particles are swollen by an organic solvent that is miscible with water [4].

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Contribution to IPCG Newsletter

by

Dr. Peter A. Lovell

Polymer Science & Technology Group, Manchester Materials Science Centre
University of Manchester & UMIST, Grosvenor Street
Manchester, M1 7HS, United Kingdom
tel: +44 161 200 3568; fax: +44 161 200 3586
e-mail: pal@umist.ac.uk

UK Polymer Colloids Forum

The UK Polymer Colloids Forum continues to be well supported and we now have over 220 people registered with the Forum. Please let me know by e-mail or fax if you would like to register and be added to the mailing list.

I am organising the fourth meeting of the Forum which will take place from 23-24 September 1996 at Keele University. I am pleased to say that for the first time we have two non-UK guest speakers, Alain Guyot of CNRS and Jenci Kurja of Eindhoven. You should find details of the provisional programme near the front of this issue of IPCG Newsletter.

General Observations Concerning the Design of Particles for Rubber-Toughening Plastics

I have now carried out research into the design and preparation of pre-formed particles for rubber-toughening acrylic polymers, epoxy resins and unsaturated polyester resins. This has involved not only emulsion polymerisation to prepare the particles, but also detailed studies of the mechanical properties and deformation mechanisms of the materials prepared by dispersing the particles into the polymer to be toughened. The work was completed towards the end of last year and I am now in a position to give some general observations which constitute, to some extent, "rules" for design of toughening particles prepared by emulsion polymerisation.

Matrix Ductility: Rubber-toughening is a method by which the ductility inherent in a polymer can be realised. However, if the polymer is inherently non-ductile, rubber-toughening can only provide a limited increase in absolute toughness. For example, the ability to toughen a crosslinked resin is increasingly restricted as the crosslink density of the resin increases. Whilst the toughness of high T_g epoxy resins and unsaturated polyester resins can be enhanced by substantial factors using rubber-toughening, the absolute values of toughness remain low and fall in what most people would consider the "brittle" regime.

Particle size: Well known to be an important factor from studies of more conventional rubber-toughened plastics prepared via phase separation routes. The situation is no different with pre-formed particles. Each polymer to be toughened requires a certain minimum particle size, which for example is ~0.2 µm for acrylics and ~0.3 µm for piperidine-cured DGEBA epoxy resin.

Particle structure: Our work has very clearly demonstrated the importance of particle structure. An outer layer of rigid (high T_g) polymer is essential to successful recovery of the particles from the latex (by spray drying or coagulation) in an agglomerated powder form that is readily redispersed to individual particles by blending with the polymer/resin to be toughened. The outer layer also needs to be designed such that it is miscible with and/or reactive towards the polymer to be toughened – a strong interface is necessary to facilitate stress transfer from the polymer to the particles. The internal structure of the particles is important. Use of three-layer particle structures comprising a core and shell of rigid polymer with an inter-layer of rubbery polymer offers a degree of freedom in particle design that is not available with two-layer particles which simply comprise a rubbery core and a rigid polymer shell. By increasing the size of the rigid polymer core within a three-layer particle, the modulus and yield stress of the toughened material can be increased. The extent to which these properties can be enhanced in this way depends upon the mechanism by which the polymer fractures. When fracture proceeds via shear yielding induced by particle cavitation, increasing the size of the rigid polymer core ultimately reduces the thickness of the rubbery inter-layer to a point (40-50 nm thickness in our work on epoxy resins) at which the cavities formed within it are unable to dilate (due to the constraints imposed by the rigid polymer on either side), thus limiting the extent of shear yielding and leading to a reduction in toughness. However, for materials which fracture via crazing, this is not a limitation and increasing the size of the rigid polymer core can lead to increases in toughness if the core itself undergoes crazing during the fracture process; the ultimate limitation then becomes reduction of the compliance of the particle to a point at which it no longer acts as a stress concentrator. Finally, if transparency is required in the toughened material, then each layer in the particle must have a composition that gives a refractive index which matches that of the matrix polymer (at the temperature and wavelength of light associated with the application).

Grafting and Crosslinking: Use of monomers such as allyl methacrylate to achieve grafting between layers is well established. Unreacted allyl groups from formation of a preceding layer undergo reaction with the monomers used to form the subsequent layer, thereby providing grafting (and good transfer of stress) between layers. Each layer, except the shell of rigid polymer, needs to be crosslinked in order to ensure that the integrity of the particle is retained during isolation and blending of the particles, and, for toughened thermoplastics, during subsequent moulding. The level of crosslinking in the rubbery layer needs to be optimised. By increasing the degree of crosslinking in this layer, particle cavitation can be delayed. This provides a means of increasing the yield stress and toughness, since more energy can be stored before the localised yielding processes are triggered. The limitation here is that a degree of crosslinking of the rubber will ultimately be reached at which the material will fracture before cavitation of the particles (and the ensuing yielding mechanisms) can occur, in which case the material will show brittle behaviour again. As mentioned above, the outer shell polymer needs to be grafted to the layer below it but not crosslinked, since crosslinking restricts mixing with the matrix polymer to be toughened. If simple physical mixing of the shell polymer with the matrix polymer is the means of achieving the interface, then in order to ensure a thick interfacial region (i.e. a strong interface) the polymer chains which constitute the particle shell should have a degree of polymerisation greater than that of the matrix polymer.

High-Performance and Environmentally-Friendly Adhesives

Research Assistant: Mr. John Garrett
Sponsor: EC Brite Euram Project joint with Jowat, Lobers & Frank Gmbh (Germany), Evode Ltd. (UK) and the University of Bielefeld (Germany)

This collaborative research project is now into its final year. Our part in the project has concerned research into reactive acrylic latexes as environmentally-friendly replacements for solvent-based contact adhesives. The results, unfortunately, are subject to publication restrictions at the present time but will be summarised in a future issue.

Contribution to IPCG Newsletter

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

Chain Transfer to Polymer in Emulsion Polymerisations

This is a topic which has always been an interest of mine and has great bearing on the properties of many emulsion polymers and latexes. I am embarking on a new, major effort to determine unequivocally the chemistry of chain transfer to polymer and "protective colloid" in emulsion polymerisations of acrylic monomers and vinyl acetate. The ultimate objective is to gain, through knowledge of the chemistry, a fundamental understanding of the effects of polymerisation conditions upon polymer and latex properties.

At present I have one research student (Mr. Nasir Ahmad) who in September 1995 began work on studies of chain transfer to polymer in acrylate polymerisations, supported by the Pakistan High Commission and ICI Acrylics. The NMR aspects of the project are being done in collaboration with Dr. Frank Heatley of the Chemistry Department at the University of Manchester.

Complementing the current project, I have just received confirmation of a new fully-funded grant from EPSRC for a two-year study of chain transfer to polymer and grafting to water-soluble polymers in emulsion polymerization of vinyl acetate, which also will be carried out in collaboration with Frank Heatley. Another new project, expected to begin in September, concerns studies of chain transfer to hydroxyethylcellulose in acrylate emulsion polymerisations and is to be sponsored by EPSRC and Zeneca Resins.

Contribution to the International Polymer Group, Newsletter

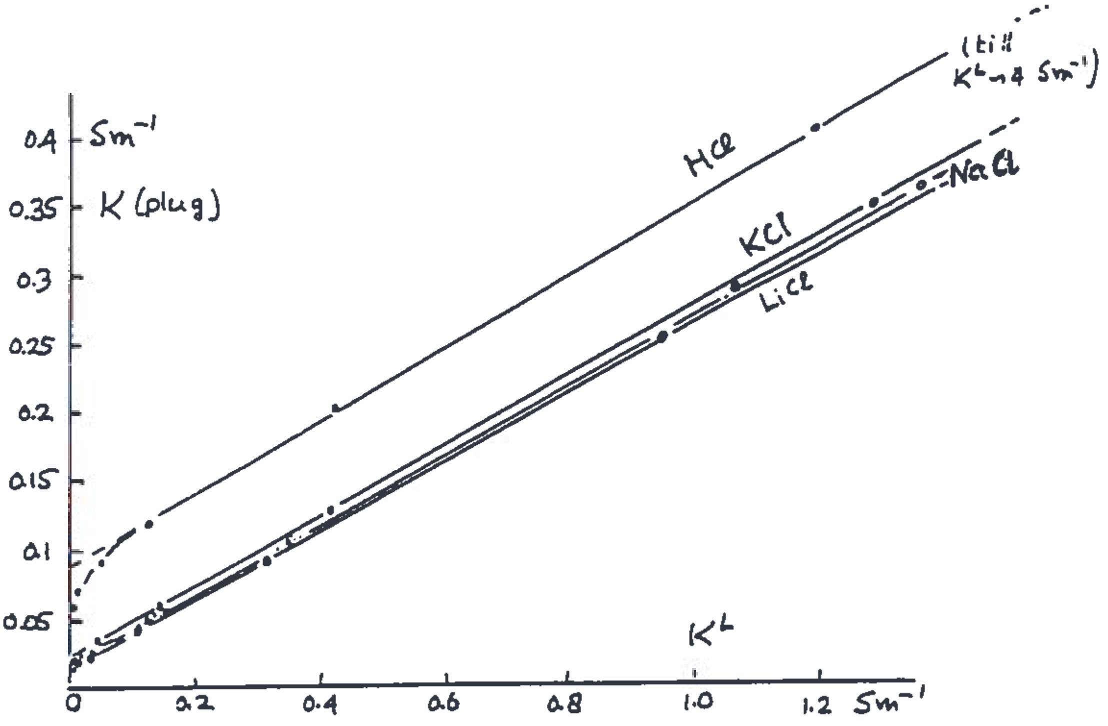
ELECTROKINETIC PROPERTIES OF PLUGS

J. Lyklema, M. Minor and A. van der Linde

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

In the previous Newsletter we reported on flow, electro-osmosis, streaming potentials and the conductivity of plugs, composed of densely packed polystyrene latices, carrying negative sulfonic acid charges. We demonstrated that the conductivity K(plug) as a function of the conductivity of the dialysate K^L was a straight line with a finite intercept.

This work has now been extended to include the effect of the nature of the counterion (cation). Figure 1 gives results for four different cations. The same trend is recovered as before, but there is also a pronounced lyotropic sequence.



The linearity finds its origin in eq [1] of our previous report. From this equation one can derive that to a good approximation

$$K(\text{plug}) = [1 + 3\varphi f(0)]K^{L} - \frac{3\varphi f(0)}{2a} K^{\sigma} \qquad [1]$$

where φ is the volume fraction of the plug (0.61 in our case), K^L the bulk conductivity, K^σ the surface conductivity, a the particle radius and $f(0)$ is a parameter depending on the packing and on the Dukhin number $Du = K^\sigma / aK^L$; according to O'Brien and Perrins $f(Du = 0) \approx 0.4$.

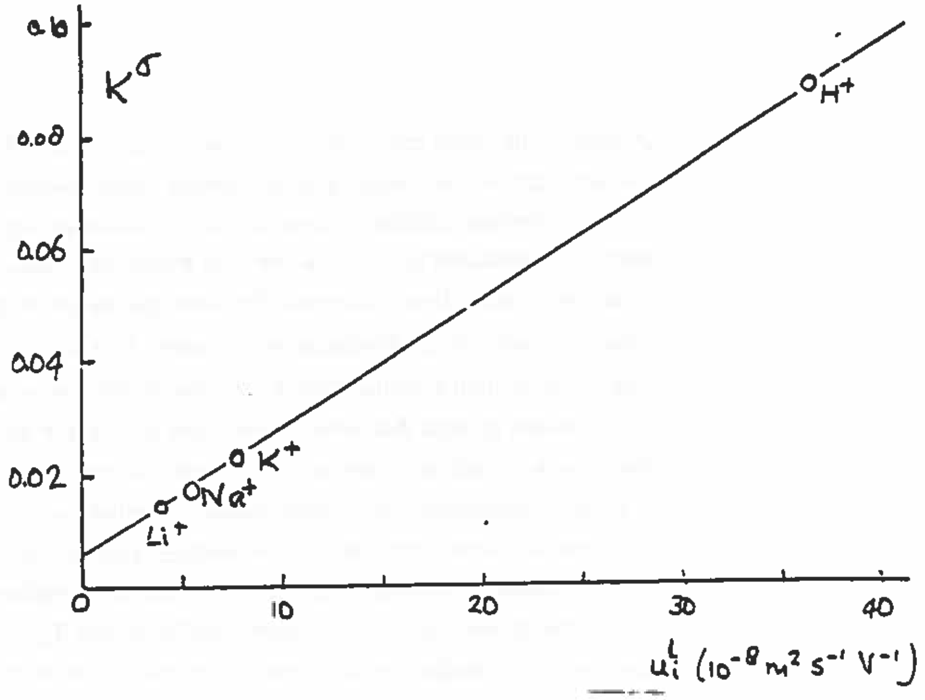
Equation [1] agrees with the observation in fig. 1 that the slope is only determined by the volume fraction and, hence, independent of the nature of the counterion. On the other hand, the intercept is proportional to K^σ and therefore it does depend on the nature of the counterion. From this plot, K^σ can therefore be obtained by extrapolation and compared with theoretical models.

There are two contributions to K^σ, a diffuse and a non-diffuse one, $K^{\sigma d}$ and $K^{\sigma i}$, respectively:

$$K^\sigma = K^{\sigma d} + K^{\sigma i} \qquad [2]$$

For $K^{\sigma d}$ Bikerman has derived an expression; it appears that $K^{\sigma d}$ consists of an ionic transport term, linearly depending on the ionic mobilities in bulk u_i^L and an electro-osmotic contribution, which does not depend on u_i^L. $K^{\sigma i} \approx \sigma_i^i u_i^i$, the product of the charge in the stagnant layer and the tangential mobility of the ion that may be present there, and which is probably proportional to u_i^L. Summing up, it follows that [2] contains two terms proportional to u_i^L and one, the electro-osmotic one, that is independent of it.

A plot of K^σ as a function of u_i^L is given in fig. 2



The intercept is, as predicted, independent of the nature of the counterion. For the other ions the relationship appears to be about linear. This has some consequences, because the slope contains the diffuse (~ electrokinetic) and the stagnant layer (~ Stern-layer) charge. It may perhaps be concluded that these remain constant and this may, in turn, have its consequences for the interpretation of the slip process.

THE UNIVERSITY OF SYDNEY
POLYMER COLLOIDS GROUP
Reporter: DH Napper

Macromol. Symp. 98, 911–915 (1995)

COILS, GLOBULES AND SINGLE CHAIN GLASSES

Donald H. Napper

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

Abstract: The cyclic coil-globule-coil transitions for poly(N-isopropylacrylamide) tethered to an interface exhibit unexpected phenomena. Two, not the predicted single,coil-to-globule transitions can be observed: the one that is predicted occurs in worse than θ-solvents whereas the other is observed in better than θ-solvents. The latter phenomenon appears to be associated with the the formation of n-clusters, first postulated by de Gennes. The chains in their globular form were found to undergo an entropy driven entanglement process that prevents reversible swelling in the globule-to-coil transition and leads to hysteresis in the layer thickness. Single chain glasses of polystyrene prepared by microemulsion polymerisation display physical properties different from those of multichain glasses including a higher conformational temperature, larger free volume and a predominantly exothermic rather than an endothermic DSC scan near T_g. These observations have been attributed to the occurrence of cohesional entanglements.

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

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).

JOURNAL OF COLLOID AND INTERFACE SCIENCE 174, 162–165 (1995)

The Fractal Aggregation of Latexes Sterically Stabilized by Hydrophilic Chains

SONG NIAN YAO,[1] PENG WEI ZHU, AND DONALD H. NAPPER[2]
School of Chemistry, The University of Sydney, New South Wales 2006, Australia

The fractal dimensions of aggregates of latex particles coated by poly(ethylene oxide) (PEO) have been measured in worse-than-θ-solvents for different electrolyte concentrations and temperatures. For the lowest molecular weight PEO studied (2×10^4), the measured fractal dimension of 2.1 was almost independent of temperature over the range studied. The value corresponds to partially reversible cluster aggregation, which leads to relatively compact aggregates. For the highest molecular weight PEO studied (6×10^5), the fractal dimension decreased significantly (from 2.4 to 1.7) with temperature, signifying the generation of more ramified aggregates. The results obtained for this hydrophilic polymer contrast markedly with those previously published for the aggregation of latexes coated by the hydrophobic polymer poly(*N*-isopropylacrylamide), which becomes hydrophobic as a result of a coil-to-globule transition.

Key Words: fractal; aggregation; latexes; steric stabilization; hydrophilic chains.

Contribution to the IPCG Newaletter June,1996

Masayoshi Okubo
Department of Chemical Science and Engineering, Faculty of Engineering,
Kobe University, Kobe 657, Japan
Phone 81-78-803-1142, Fax 81-75-803-1169
e-mail okubo@appchem.chme.kobe-u.ac.jp

Publications(1996)

(1) **"Production of micron-sized monodispersed cross-linked polymer particles having hollow structure"**, Masayoshi Okubo, Hideto Minami, Tsuyoshi Yamashita, *Macromol. Symp.*, **101**, 509-516(1996)

4 μm-sized monodispersed cross-linked polymer particles having hollow structure were produced as follows. First, 1.7 μm-sized mono-dispersed polystyrene (PS) seed particles produced by dispersion polymerization were dispersed in ethanol/water (7/3, w/w) solution in which divinylbenzene (DVB), benzoyl peroxide (BPO), poly(vinyl alcohol), and toluene was dissolved. The PS seed particles were swollen with DVB, toluene and BPO maintaining high monodispersity throughout the dynamic swelling process where water was slowly added continuously. And then, the seeded polymerization of the (toluene/DVB)-swollen PS particles was carried out.

(2) **"Control of hollow size of micron-sized monodispersed polymer particles having a hollow structure"**, M. Okubo, H. Minami, *Colloid Polym Sci*, **274**, 279-284(1996)

Micron-sized monodispersed cross-linked polymer particles having one hollow in the inside were produced by the seeded polymerization for the dispersion of (toluene/divinylbenzene)-swollen PS particles prepared utilizing the dynamic swelling method which the authors proposed. In order to control the hollow size, the weight ratio of toluene/PS was changed in the range of 5~20. The hollow size increased with an increased in the weight ratio. Even if benzene and xylene were used in place of toluene, similar hollow particles were produced, though the hollow size was affected by their solubility in water.

(3) **"Thermodynamics of high swelling of polymer particles with a large amount of monomer utilizing the dynamic swelling method"**, M. Okubo, T. Yamashita, M. Shiozaki, *J. App.Polym. Sci.*, **60**, 1025-1031 (1996)

Recently, we suggested a novel swelling method to make polymer seed particles absorb with a large amount of monomer prior to the seeded polymerization for preparing monodispersed polymer particles having diameter above 5 μm, which was named "the dynamic swelling method". In this article, the thermodynamic background of this method was discussed theoretically and experimentally.

(4) **"Production of submicron-sized multihollow polymer particles having high transition temperatures by the stepwise alkali/acid method"**, M. Okubo, A. Ito, A. Hashiba, *Colloid polym Sci*, **274** ,(5), 1-5 (1996)

Submicron-sized multihollow styrene-methacrylic acid (92.6/7.4, molar ratio) copolymer particles having high transition temperature above 100°C were produced by using the stepwise alkali/acid method proposed by the authors. Theoriginal particles were prepared by emulsion copolymerization of styrene and methacrylic acid. The effects of pH, temperature and time in the alkali treatment process as the first step on the multihollow structure were clarified under the same acid treatment conditions.

(5) **"Adsorption behaviors of emulsifiers and biomolecules on temperature-sensitive polymer particles"**, M. Okubo, H. Ahmad, *Colloid Polym Sci*, **274**, 112-116 (1996)

Adsorption and desorption behaviors of emulsifiers and biomolecules on the two kinds of temperature-sensitive composite polymer particles were compared. One (I) was produced by seeded emulsion copolymerization of dimethylaminoethyl methacrylate and ethylene glycol dimethacrylate with 0.17 µm-sized polystyrene seed particles. The other (II) was produced by seeded emulsion copolymerization of N-isopropylacrylamide (NIPAM) and N, N'-methylenebisacrylamide with 0.36 µm-sized styrene-NIPAM copolymer particles. The amount of adsorption at temperatures above each lower critical solution temperature (LCST) was found to be much higher for I than II. In both cases, at temperatures below the LCST, almost lactalbumin hydrolysate molecules adsorbed above the LCST were desorbed but the desorptions of adsorbed egg albumin and lysozyme molecules were not so high. The adsorption and desorption were reversible for both particles and the efficiency was more excellent for I than II. From these results, it is concluded that the adsorption/desorption of protein onto the temperature-sensitive polymer particles is controllable by changing the temperature below and above the LCST of the shell layer and the sensitivity is based on the surface property of the composite polymer particles.

(6) **"Production of core-shell composite polymer particles utilizing the stepwise heterocoagulation method"**, M. Okubo, Y. Lu, *Colloids Surfaces A: Physicochem. Eng Aspects*, in press

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.

Contribution to the IPCG Newsletter May, 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

Main activity of our group is on colloidal crystals, their morphology, crystal structure, crystal growth and effect of external fields such as an gravitational field, electric field, and centrifugal field. Two years ago, kinetic analyses of the colloidal crystal growth have been started under microgravity by using aircraft and rocket. On January 1996 T. Okubo moved from Kyoto to the *Gifu University* as full professorship. On april 1st, Associate Professor Akira Tsuchida and Research Technician Kazuo Takezawa joined our group. Cooperative work with the groups of Professors M. Stoimenova(Institute of Physical Chemistry, Sofia, Bulgaria), M. Antonietti(Max-Planck Institute of Colloids and Interfaces, Teltow, Germany), N. Nemoto(Department of Applied Physics, Kyusyu University) and K. Kaji(Institute of Chemical Research, Kyoto University) is now in progress on the colloidal crystals.

Publications(1996)

(1)"**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.

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

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.

(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)"**Importance of the Electrical Double Layers in Structural and Diffusional Properties of Deionized Colloidal Suspension**", T. Okubo, *Colloids Surfaces* in press.

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.

(5)"**Static and Dynamic Light-scattering of Colloidal Crystals of Monodispersed Polystyrene Spheres**", T. Okubo and K. Kiriyama, *Ber.Bunsenges.Phys.Chem.* in press.

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.

(6)"**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.

(7)"**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($l_{obs} \approx d_{eff} \approx l_0$). 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.

(7)"**Structural and Dynamic Properties of Colloidal Liquids and Gases of Silica Spheres(29 nm in diameter) as Studied by the Light Scattering Measurements**", T. Okubo, A.Tsuchida and K.Takezawa, Ber.Bunsenges.Phys.Chem., submitted.

Static and dynamic light-scattering measurements are made for colloidal-liquids and -gases of silica spheres, 29 nm in diameter, in the exhaustively deionized aqueous suspension and in the presence of sodium chloride. Single broad peak is observed in the light-scattering curve and the liquid-like and gas-like distributions have been observed. The nearest-neighboured interparticle distances of colloidal liquids estimated from the peaks of the structure factor, 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($l_{obs} \approx d_{eff} \approx l_0$). This relation support definitely the electrostatic interparticle repulsive interaction. Two dynamic processes have been extracted separately from time profiles of autocorrelation function of colloidal liquids from the non-negative least square analysis. Decay curves of colloidal gases are characterized by the single translational diffusion coefficients(D), which are always lower than the calculation from the Stokes-Einstein equation using true diameter of spheres and increase 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 liquids and gases.

Contribution to IPCG Newsletter from Laboratoire de Chimie des Procédés de Polymérisation (LCPP-CNRS) (*) and Unité Mixte CNRS-bioMérieux Lyon-France

(submitted by J. Guillot and C. Pichot)

(*) **New address: LCPP/CNRS/CPE. Bat. 308, BP 2077, 43 Av du 11 Nov 1918- 69616, Villeurbanne Cedex- france (fax: (33)72 43 17 68)**

A) Dispersion polymerization with poly(ethylene oxide) macromonomers P. Lacroix-Desmazes, A. Guyot (LCPP-CNRS)

The use of poly(ethylene oxide)-based macromonomers as stabilizers in dispersion polymerization of styrene in hydroalcoholic media has been studied. The formation of the particles has been detailed and the predictions of the final particle size from a simple mechanistic model are compared with the experimental results. The nucleation is very fast and it is completed within 0,1% of styrene conversion. Moreover, the rate of polymerization depends strongly on the partitioning of styrene between the serum and the particles. A simulation has been developed to determine the partitioning of styrene and ethanol during the polymerization. Otherwise, most of the copolymers formed in situ remains soluble in the serum, and a fraction of adsorbed species takes part in the stabilization mechanism. Various factors which influence the incorporation of macromonomers at the surface of the particles have been studied: the structure and concentration of the macromonomer, the polarity of the reaction medium, the styrene concentration, among others. High incorporation yields (close to 100%) and high grafting density have been obtained in favorable conditions.

B) Styrenic Reactive Surfactants in Acrylic Emulsion Polymerization O. Soula, A. Guyot (LCPP-CNRS)

Our first objective in this thesis is the synthesis of new copolymerizable surfactants called surfmers, their characterization and the measurement of their surfactant properties. The surfactants have the following basic structure :

The chosen values for n are 1 and 6, for m, 17 and 45, for X, OCH3, OH and OCH2CH2CH2SO3-Na+. The study will include the kinetics of the comsumption of the acrylic monomer and the surfmer, as well as the surfmer incorporation in the latex particles and the colloidal properties of the particles.

C) High Solid Content Multi-sized Emulsion Copolymerization of Styrene, Butyl Acrylate and Methacrylic Acid. F. X. Chu, C. Graillat, J. Guillot and A. Guyot (LCPP-CNRS)

Latices with bi- and tri-modal particle size distribution were prepared by introducing some additional surfactants (or a second seed) during the semi-continuous emulsion polymerization of styrene, butyl acrylate and methacrylic acid. The polymerization was investigated by following the variation of the particle size, the size distribution, the number of particle , the Tg of particle and the total conversion at different steps of the polymerization process. The results show that bimodal and trimodal PSD polymer latices can be obtained by this method, and that the secondary generation of particles is greatly influenced by the nature and the amount of additional surfactants (or the second seed) as well as the moment when they are introduced. High solid content (>65%), low viscosity and coagulum free latices have been obtained through this method. The rheology of the latices was studies as a function of the particle size and size distribution. The maximum packing fraction of particles was calculated by Krieger-Dougherty equation. It was found that the maximum packing (or highest solid) occurs at the wt. fraction 80% of large particle in total solid for both bimodal and trimodal latices. For characterizing the particle size and size distribution of multi-sized polymer latices, a method was developed by combining the quasielastic light scattering (QELS) with a centrifuge. This method has been compared with other techniques such as transmission electron microscopy, QELS, sedimentation and capillary hydrodynamic fractionation.

D) Copolymerisation with depropagation. a-methylstyrene(αMSt)-MMA in Emulsion. F.Martinet, J.Guillot (LCPP-CNRS)

Several objectives are sought: comprehensive study of the effect of depropagation on kinetics, microstructure, molecular weight distribution (MWD) and thermomechanical properties (Tgís) of the copolymers.
First, solution and bulk copolymerisations were investigated to know the effect of α-MSt content and temperature on rate constants Kp, reactivity ratios Rij and glass transition. Modelling and simulation software have been developpped for N monomers, including depropagating one. Safe quantitative connections between experimental parameters and copolymerisation, as well as copolymer features were obtained.
However, molecular weights and yields were generally quite low ; so, the very hight level of compartimentalisation provided by Emulsion process was required to increase both molecular weight and copolymerisation rate. Furthermore, α–MSt led to very small particle size and the smaller the higher is the α-MSt content , i.e. very high number of particles per volume unit, Np ; which allowed to accurately investigate kinetics (kp, (), microstructure, MWD, glass transition behaviour of systems with quite high α-MSt contents. At moderate temperatures, i. e. , up to 80/85 ∞C molecular weights are high enough to lead to a definite increase of Tgís within a reasonable polymerisation time. Tgís up to 140/145 ∞C can be obtained with optimising conditions.

The software has been completed to include specific features of such emlsion Copolymerisations : Np, (radical desorption, gel effect,and allows a global and comprehensive overview of the many interconnected parameters involved in such complex polymerising systems. For instance, the effect of molecular weight distribution on glass transition - which is, of course, a limiting factor in α-MSt copolymerisations can be quantified, in good agreement with experimental data. The software has revealed a useful tool to improve polymerisation process: optimisation of semibatch, controlled composition reactor, e.g.
Next step of the work is the grafting copolymerisation onto polybutadiene seeds, which are beeing characterised, now.

Publications are in progress to be published :

*Copolymerisation with depropagation. α-methyl styrene / MMA Copolymerisation I - Solution Copolymerisation in toluene : Kinetic investigations and modelling - F. Martinet, J. Guillot. to be published in J. App. Polymer Sci.

* Copolymerisation with depropagation α-methyl styrene / MMA Copolymerisation- II - Bulk Copolymerisation in toluene: Kinetic, microstructure, glass transition investigations- F. Martinet, J. Guillot. to be published in J. App. Polymer Sci.

* Copolymerisation with depropagation. α-methyl styrene / MMA Copolymerisation III - Emulsion Copolymerisation : Modelling and experimental kinetics, microstructure, molecular weight distribution and glass transition behaviour- F. Martinet, J. Guillot. to be published in J. App. Polymer Sci.

E) Efficiency of Thiols as Chain Transfer Agent (CTA) in Emulsion Copolymerisation- I. Barudio, M.L. Nesti, J. Guillot (LCPP-CNRS)

In contrast with bulk and solution polymerisation, thiols appear to have a much lower CTA efficiency in Emulsion polymerisation. We tried to understand, on a quantitative basis, this unusual behaviour from kinetic, colloidal and MWD experimental data obtained in copolymerisation in the presence of various thiols. If the particle size does not seem to be significantly affected, the average number of radical per particle, ($\tilde{n}$ is generally decreased and, as a consequence, the rate of polymerisation, Rp.
Thiols of various molar mass have been used : C4 , C12 , C16 in Emulsion styrene/butyl acrylate and vinyl acetate/butyl acrylate copolymerisations, in batch and semicontinuous processes. In batch, C4SH has a much higher efficiency than C12SH, and aboveall C16SH, on limiting molecular weights, but (is also more decreased. It has been experimentally found that kinetics, MWD and even Tgis are affected according a regular depedence on amount and bulkiness of the thiol. An explanation is a diffusion limitation, above all in batch : heavy RSH have significantly much lower transport coefficients than the monomers and tend to accumulate, this way, in the droplet phase, up to relatively high conversions. That is corroborated by the different observed behaviour in semicontinuous process, wherein a lower amount of such CTA have a higher efficiency, owing to a fast diffusion directly towards the polymer particle phase, in the absence of monomer droplets.

To quantify the connections between the characteristics of thiols – or similar CTA – and emulsion kinetics, microstructure, MWD and properties (Tgís), a software has been developped, which takes into account radical desorption, gel effect (on the basis of Stockmayer-OíToole approach) and which assumed, in addition, that diffusion phenomena can occur with heavy compounds such as RSH or even bulky monomers, mainly at the water-droplet interphase. Agreement between predictions and experimental data are satisfactory and allowed to estimate, e.g., transport coefficients. The possibility of reaction of CTA in the water phase has been also included in this modelling. It is noteworthy that this software simulates kinetics, microstructure, MWD(and the GPC diagramme), Tgís (and the glass transition DSC/DTA themogramme) and gives, to a large extent, a global overview on the polymerising system. For instance, the effect of MWD on Tgís can be correctly computed in terms of chain-end effect : higher flexibility of the terminal dyads.

Publications to be submitted:

* The effect of thiol Chain Transfer Agents on the kinetics of Emulsion Copolymerisations and Microstructure of Latex. Modelling
I. Barudio, J. FÈvotte, J. Guillot. to be published in J. Appl. Polym. Sci.

* The effect of thiol Chain Transfer Agents on Emulsion Copolymer Properties : Molecular Weight Distribution and Glass Transition. Control of the MWD
I. Barudio, J. FÈvotte, J. Guillot. to be published in J. Appl. Polym. Sci.

F) Emulsion Copolymerisation of Styrene an n-Butyl Acrylate in the Presence of Acrylic and Methacrylic Acids: Eft of pH on reaction kinetics and carboxyl group distribution- A. Martins dos Santos, T. F. McKenna and J. Guillot (LCPP-CNRS)

The batch emulsion copolymerisation of styrene (STY) with n-butyl acrylate (BA) in the presence of acrylic (AA) and methacrylic acids (MAA) has been investigated. Values of reaction rate and conversion observed at different pH were compared with the results of a model simulation. The effect of pH on the glass transition temperature (Tg) of the polymers was also investigated, as was its effect on the distribution of the carboxyl groups at different positions within the emulsion system (surface and core of particles, and in the aqueous phase). Three methods were used to measure the number of carboxyl groups: conductimetry, organic phase potentiometry, and titration with solution of sodium hydroxide in methanol.

G) Suspension Copolymerisation of Styrene and n-Cyclohexyl Maleimide Stabilised with Polyvinyl Alcohol: Optimisation of Particle Size Distribution

W. Ramirez , T.McKenna, A. Guyot. (LCPP-CNRS)
Current address: Industrias Resistol SA, Grupo di Investigaciones, Bosque di Ciruelos 99, Mexico DF 11700, Mexico.

Abstract. A set of polyvinylalcohol (PVA) samples with different hydrolysis rates and molecular weights were used to stabilise the suspension polymerisation of styrene and its copolymerisation with n-cyclohexyl-maleimide. The stability of the monomer droplets was studied using turbidity measurements, and is related to the surface tension of the PVA solution in water, Optimal stability corresponds to PVA with a moderate hydrolysis rate (80-88%) regardless of the molecular

weight. However, during the polymerisation some reversible aggregation was observed when the molecular weight of the PVA is not high enough.

H) Development of Sensors for Copolymerisation Process Control in dispersed media (LCPP-CNRS) .

An continuous and strong effort is devoted to the development of reliable sensors for the accurate estimate of overall conversion and particle size, as well as for other reaction parameters measurements such as pH, free emulsifier. So far, we have mostly worked with on-line control pH and on-line conversion sensors : density, ultrasonic velocity and above all heat balance ; the latter beeing now one of the most reliable and simple sensor for emulsion copolymerisation.
The objective is to equipped the reactors with appropriate sensors, preferably on-line ; but safe off-line are also investigated, of cours. Indeed, all pertinent variables do not actually need to be continuously provided to control device and softwares, for an ´ intelligent manufactoring of emulsion copolymers.

Hereafter are some publications related with this rather new field of investigation, at LCPP.

Computer-Aided Parameter Estimation and On-line Monitoring of Emulsion and Solution Polymerisation Reactors.
G. Fèvotte*, I. Barudio* , T. F. McKenna** (*)LAGEP-URA CNRS D1328, (**)C.N.R.S. - L.C.P.P.

The production of polymers is a complex process that produces material of which the quality is highly sensitive to operating conditions. Much work has been done in the past on the development of reactor models - models which are often highly complex, and can require any number of parameters and pseudo-constants. Currently, work also tends to focus on the development of sensors such as calorimetry and on-line density measurements in order to follow the evolution of conversion and the macromolecular properties of the polymer being produced.
The project discussed here represents an effort to adapt these techniques by using two process computers and specially adapted non-linear algorithms (computer 1) for overcoming uncertainties in the data used by on-line computer models (computer 2) to monitor, control and modify polymer properties, e.g. glass transition temperature and molecular weights. The emulsion and solution copolymerisation of styrene and butyl acrylate is treated as an example.

Joint Use of Calorimetry, Densimetry and Mathematical Modelling for Multiple Component Polymerisations .T. F. McKenna, G. Fèvotte, C. Graillat, and J. Guillot (LCPP-CNRS)

A study of the joint use of calorimetry, densimetry and gravimetry combined with mathematical modelling are presented with an eye to the application of these techniques as on-line estimators of the state of multi-component polymerisations. Model equations are presented to demonstrate the need for on-line estimates of individual monomer conversion, and how this data can be used to estimate such polymer properties as the molecular weight distribution, glass transition temperature and copolymer composition.

Calorimetry can be used to estimate the overall amount of heat generated during the course of reaction, however it is necessary to obtain a good estimate of the enthalpy of any feeds being introduced at temperatures lower than that of the reactor as this can be a major source of error in the on-line evaluation of the energy balance equations. Densimetry is a difficult tool to master, and requires three to four significant figure precision in the estimate of density values in order for it to provide reliable on-line results. Gravimetric measurements are easy and reliable, and can be used in conjunction with either of the above-mentioned methods in systems involving more than one monomer. An important contribution of this paper is the discussion of problems related to the on-line use of these techniques - a discussion which is all but absent from the current scientific literature.

A sensitivity analysis was performed, and revealed that density measurements played a more determining role in the precision of joint estimation techniques than did either of total amount of heat generated during the reaction or the overall conversion of monomer.

Emulsifier-free emulsion copolymerization of styrene with two different amino-containing cationic monomers

1/ Kinetic studies- *F. Ganachaud, F. Cornier, A. Elaïssari and C. Pichot* (Unité Mixte CNRS-BioMérieux) (submitted to J. Appl. Polym. Sci.)

Kinetics of emulsifier-free emulsion copolymerization of styrene were investigated in the presence of two amino-containing monomers, Amino Ethyl Methacrylate Hydrochloride (AEMH) and Vinyl Benzyl Amine Hydrochloride (VBAH), and using 2,2'-azobis (2-amidinopropane) dihydrochloride (V50) as a cationic initiator. At first, partition coefficient of AEMH and VBAH in water-styrene mixture were measured, indicating a strong hydrophilicity for both monomers; kinetics of solution homopolymerization, as followed by ^1H NMR, in water provided high $k_p/k_t^{1/2}$ values, 4.0 and 1.75 $(l.\ mol^{-1}.\ s^{-1})^{1/2}$ for AEMH and VBAH respectively. The two monomers were found to affect similarly the kinetics of emulsion copolymerization of styrene: i) the overall polymerization rate and particle number dramatically increased with functional monomer concentration; ii) the average radical number ($\bar{n}$) was only dependant upon the particle volume, reaching a 0.5 value for particle size below 100 nm; iii) The molecular weight of polymer samples decreased with the functional monomer concentration, revealing the strong activity of VBAH and AEMH in chain transfer. Polymerization mechanism in the presence of both VBAH and AEMH was discussed, referring to the coagulation nucleation mechanism to explain the formation of a large particle number. Using the method proposed by Gilbert et al, transfer rate constants were determined for each monomer (around 10 $l.\ mol^{-1}.\ s^{-1}$) and styrene ($4.5\ 10^{-2}\ l.\ mol^{-1}.\ s^{-1}$).

Adsorption of Labelled (Polythymidylic Acid) Oligonucleotide onto Cationic and Anionic Latex Particles (submitted to J. Colloid Int. Sci.)

A. Elaïssari[1†], J. P. Chauvet[*], M. A. Hallé[†], O. Decavallas[†], C. Pichot[†], and Ph. Cros[‡]

†UMR-103 CNRS-bioMérieux
** UMR-117 CNRS-ENS de Lyon*
‡Laboratoire des Sondes Nucléiques bioMérieux
ENS de Lyon; 46. Allée d'Italie 69364 Lyon cedex 07 - FRANCE

The adsorption of polythymidilic acids onto latex particles was investigated using a series of polymer latexes prepared by emulsifier-free emulsion copolymerization of styrene and vinylbenzylamine hydrochloride. In addition, for comparison a sulfate charged polystyrene latex was used to estimate the contribution of hydrophobic forces to the adsorption process.

The adsorption was performed using a labelled oligonucleotide (polythymidylic acid, 35 bases : Fluorescent-dT35) with a view to elucidating some general principles of oligonucleotide adsorption. It was found that the adsorbed amount of oligonucleotide is strongly dependent on the charge density of the positively charged latex particles, indicating that electrostatic forces play a major role in the adsorption process. The contribution of hydrophobic forces was estimated using the various maximal adsorption amounts obtained at pH 5.2 for all latexes and extrapolated to zero charge density. Desorption of the oligonucleotide was also examined by fluorescence measurements analyzing both the supernatant and the latex particles after washing, using front face method.

Adsorption of Single Stranded DNA Fragments onto Cationic Aminated Latex Particles (submitted to Langmuir)

François Ganachaud,[†] Abdelhamid Elaïssari,[†] Ali Laayoun,[‡] Christian Pichot,[†] and Philippe Cros[‡]*
† Unité mixte CNRS-BioMérieux
‡ Laboratoire des sondes nucléiques BioMérieux
Ecole Normale Superieure de Lyon, 46, Allée d'Italie
69364 Lyon Cedex 07, FRANCE

A study of the adsorption behaviour of oligodeoxyribonucleotide (ODN) onto polymeric supports has been performed on the interactions of polythymidylic acid in the presence of aminated latex particles. Due to the presence of cationic surface charges on the particles and the polyelectrolyte character of the oligodeoxyribonucleotides, it was observed that the electrostatic forces play a major role in the adsorption process. Strong adsorption was clearly evidenced together with a high affinity. A decrease in the adsorption was observed upon raising the pH. The contribution of hydrophobic forces was estimated using the various adsorption isotherms at various pHs, and extrapolating these results to zero surface charge density (s=0) and to zero zeta-potential ($\zeta=0$) of the latex particles. The physico-chemical approach is focused on the conformation of the adsorbed oligodeoxyribonucleotide by investigating the effect of ODN chain length on the maximum adsorbed amount on the latex particles. It was found that the ODN adsorbs in a flat conformation irrespective of ODN nature so long as the support was oppositely charged.

Structures of Adsorbed and Grafted Single-Stranded DNA Fragments onto Positively Charged Latex Particles: a Small-Angle Neutron Scattering Study

A. Elaïssari,$ J. Y. Chevalier,# F. Ganachaud,$ L. Auvray,§ A. Laayoun, C. Pichot,$ P. Cros**

$ Unité mixte CNRS-BioMérieux

** Laboratoire des sondes nucléiques, BioMérieux ENS, 46, Allée d'Italie 69364 Lyon, France*

 # LMOPS-CNRS BP 24, 69390 Vernaison, France

§ Laboratoire Léon Brillon, CEN Saclay, 91191 Gif-sur Yevette, France

Adsorption and covalent binding of polythymidylic acid (single-stranded DNA fragment) onto aminated cationic deuterated polystyrene latex particles have been investigated as a function of pH and ionic strength. The adsorption results confirmed that the driving forces on the adsorption were the electrostatic interactions between negative charges of the oligonucleotide (ODN) and positive ones of the cationic latex particles. In addition, the influence of the ODN length on the adsorbed amount has been studied. Covalent binding of the ODN on the latex particles was also examined in order to demonstrate the predominant effect of electrostatic interactions on the conformation of the ODN at low surface coverage. Small-angle neutron scattering (SANS) was used to determine the hydrodynamic thickness of adsorbed and grafted polythymidylic acid. The results showed that the hydrodynamic thickness of adsorbed or covalently grafted oligonuceotide on the latex particles is small reflecting that ODN was in a flat conformation whatever the fixation mode.

Synthesis and Characterization of Hydrophilic Amino Functionalized Polystyrene Latexes - *D.Duracher, F.Cornier, A.Elaïssari, C.Pichot* (Unité Mixte CNRS)

Monodisperse cationic latexes were synthesized by precipitation polymerization at 70°C of styrene, N-isopropylacrylamide (NIPAM), N-N methylenebis-acrylamide and aminoethyl methacrylate hydrochloride (AEM) using 2,2'-azobis (2-amidinopropane) dihydrochloride as cationic initiator. Particle in the size range 100-600 nm can be controlled via the amount of NIPAM monomer introduced in the first stage of " batch " polymerization; the incorporation of the amino cationic charges was performed using a shot addition of a NIPAM-AEM mixture at high conversion. Latexes were then characterized as regards to particle size and distribution, surface charge density (using a colorimetric titration method), particle morphology (using atomic force microscopy) and finally by electrophoretic mobility. The surface amino groups concentration originated from the functional monomer was found in between 12 - 25 mmole/g polymer. Using coagulation kinetics at room temperature allowed one to determine the critical concentration coagulation values of the different latex particles; the results have been discussed with respect to the surface charge density and actual thickness of the hydrodynamic layer.

Research on "Polymer Colloids" at the Laboratory of Forest Products Chemistry

Per Stenius

Laboratory of Forest Products Chemistry, Department of Forest Products Technology,
Helsinki University of Technology, Vuorimiehentie 1a, FIN-02150 Espoo, Finland,
Tel +358 (9)0 451 4233, fax +358 (9)0 451 4259, email per.stenius@hut.fi

It has been several years since I last contributed to the Polymer Colloid Group Newsletter; thank you for allowing me to stay on in spite of this silence. In 1991, on being offered a chair at the Department of Forest Products Technology at Helsinki University of Technology, I decided to leave the Institute for Surface Chemistry in Stockholm and to move back to Finland. Thus, beginning from the autumn, 1991, I have been engaged in building up both education and research in colloid chemistry at the department, with emphasis on aspects of interest in pulping, papermaking and printing. My laboratory now has 12 graduate students and is relatively well equipped; you will find full information on the Internet (look at http://www.hut.fi/HUT/Forestpc/index.html).

The major part of our work is concerned with the properties of cellulose fibre surfaces, which have been studied using ESCA, potentiometric titration, polyelectrolyte and polysaccharide adsorption, enzyme treatment and contact angle measurements. The objective of these studies are firstly, to obtain a comprehensive understanding of the surface properties of these rather complex fibres and secondly, to understand the interaction forces between these fibres and how they affect the properties of paper. Abstracts of several papers (published and recently submitted) are enclosed.

We have also been investigating the formation of complexes between cationic starch and anionic surfactants as well as the structure of films formed by such complexes. Abstracts of two papers are enclosed.

In a recent thesis work, the adsorption of PEO/PPO block copolymers on talc was investigated. An abstract of the thesis (papers have not yet been submitted for publication) is enclosed.

We have also recently started studies of the structure and chemistry of latex/kaolin coating films using ESCA, confocal microscopy and contact angle measurements.

ELSEVIER

Colloids and Surfaces
A: Physicochemical and Engineering Aspects 88 (1994) 277–287

COLLOIDS
AND
SURFACES A

Potentiometric titration of unbleached kraft cellulose fibre surfaces

Janne Laine [a,*], Lars Lövgren [b], Per Stenius [a], Staffan Sjöberg [b]

[a] Laboratory of Forest Products Chemistry, Department of Forest Products Technology, Helsinki University of Technology, Vuorimiehentie 1 A, 02150 Espoo, Finland
[b] Department of Inorganic Chemistry, University of Umeå, S-901 87 Umeå, Sweden

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Abstract

The surface properties of unbleached kraft cellulose fibres in the pH range 2–8 have been investigated using a high precision potentiometric titration method. The pulps were digested in various ways, varying both digestion time (level of residual lignin) and the amount of excess alkali. Titrations were made at constant ionic strength (0.1 M NaCl). The results were evaluated by assuming the existence of different types of acidic groups in the surface and adjusting their intrinsic stability constants and the capacitance of the electrical double layer to obtain the best possible fit to experimental data. Fitting was done using the error square sum minimising program FITEQL, version 2.0. Distribution diagrams were calculated with the program SOLGASWATER. It was found that the amount of acidic groups decreases with increasing digestion time, while the amount of excess alkali is not important. The pulps contain two types of acidic groups that dissociate in the pH range 2.5–7.5 (intrinsic stability constants $pK \approx 3.4$ and $pK \approx 5.5$). The pK value of the stronger acid agrees with what could be expected for uronic acids in hemicellulose (xylan), while the amount of the weaker acid correlates directly with the amount of lignin in the pulps.

Keywords: Potentiometric titration; Unbleached kraft cellulose fibre

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CELLULOSE (1994) 1, 145–160

Surface characterization of unbleached kraft pulps by means of ESCA

JANNE LAINE* AND PER STENIUS
Laboratory of Forest Products Chemistry, Department of Forest Products Technology, Helsinki University of Technology, Vuorimiehentie 1 A, 02150 Espoo, Finland

GILBERT CARLSSON AND GÖRAN STRÖM
Institute for Surface Chemistry, Stockholm, Sweden

The effect of digestion conditions (amount of effective alkali, digestion time) on the surface compositions of unbleached softwood (*Pinus sylvestris*) kraft pulp has been investigated by electron spectroscopy for chemical analysis (ESCA). The quantities monitored were the angular dependence of the total O/C ratio, the relative amounts of carbons in different states of oxidation and the adsorption of Al and Ca ions to the carboxyl groups in the surface. Examination of the angular dependence of ESCA intensities shows that the concentration of alkyl carbon is high in a very thin surface layer and that it decreases linearly with decreasing kappa number. The concentration of alkyl carbon is decreased by extraction of the fibres with dichloromethane, but the amount remaining in the surface after extraction still decreases linearly with decreasing kappa number (i.e. it decreases with increasing digestion time). It is suggested that the observed enrichment of alkyl carbon in the outermost surface layers most probably is due to reprecipitation of lignin. In pulp that has not been extracted, there is also strong enrichment of extractives in the surface. This amount increases with increasing effective alkali but is relatively independent of digestion time. ESCA analysis of the Al and Ca bound to the carboxyl groups shows that the amount depends on digestion time; the results are consistent with the notion that the reprecipitated lignin contains carboxyl groups.

KEYWORDS: kraft pulp surface properties, ESCA, lignin, extractives, carboxyl groups

Nordic Pulp and Pap. [illegible]
Accepted for
publication, April 1996

The effect of ECF and TCF bleaching on the surface chemical composition of kraft pulp as determined by ESCA

Janne Laine and *Per Stenius*, Laboratory of Forest Products Chemistry, Helsinki University of Technology, Espoo, Finland

*Gilbert Carlsson** and *Göran Ström*, Institute for Surface Chemistry, Stockholm, Sweden

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Keywords: Kraft pulps, Bleaching, Totally Chlorine Free, Elemental Chlorine Free, ESCA, Surface chemical composition, Lignin, Extractives.

SUMMARY: Unbleached softwood (*Pinus sylvestris*) kraft pulp with kappa number 25.9 was bleached using sequences OZEP, OPZEP, ODEDED and DEDED. Both the bulk and surface concentrations of lignin and extractives were investigated after each bleaching stage. The surface content of lignin and extractives was analysed by ESCA (Electron Spectroscopy for Chemical Analysis). It was found that the enrichment of lignin in the surface layers of fibres, originated from wood fibres (remnants of middle lamella) or formed during cooking (reprecipitated), retards the bleachability of kraft pulp fibres. Especially, the fraction of surface lignin removed by oxygen and peroxide was much smaller than the total decrease in lignin content. On the other hand, the strong oxidant ozone removed a significant amount of lignin independent on lignins location in the fibres. The effect of chlorine dioxide on the surface lignin content depended strongly on the number of treatments. There are some indications that the low reactivity of surface lignin in the early stages of bleaching is due to low amount of free phenolic lignin units or to high amount of condensed structures in the surface lignin, or that the outer cell wall layers contain substantial amounts of lignin-carbohydrate complexes. Surface lignin played a significant role also with regard to brightness development during bleaching. It is suggested that the surface lignin is more coloured than the residual lignin in the other regions of fibres.

The large amount of extractives found in the fibre surfaces very likely is due to reprecipitation that has occured during bleaching or in the interstage water washing of the pulps. Surface content of extractives decreased considerably by an oxygen, and slightly by a peroxide treatment, while ozone and chlorine dioxide bleachings had only a minor effect. A tentative conclusion is that neutral substrates are of great importance to the amount of extractives on the bleached pulp fibre surfaces.

Holzforschung
■ ([illegible]) ■–■
1996

Characterization of Unbleached Kraft Pulps by Enzymatic Treatment, Potentiometric Titration and Polyelectrolyte Adsorption

By Janne Laine[1], Johanna Buchert[2], Liisa Viikari[2] and Per Stenius[1]
[1] Laboratory of Forest Products Chemistry, Department of Forest Products Technology, Helsinki University of Technology, Espoo, Finland
[2] VTT Biotechnology and Food Research, Espoo, Finland

Keywords
Kraft pulp (pine and birch)
Enzymatic treatment
Xylanase
Mannanase
Potentiometric titration
Polyelectrolyte adsorption
Carboxyl groups

Summary

The surface properties of unbleached softwood (*Pinus sylvestris*) and hardwood (*Betula verrucosa*) kraft pulps were modified by treating the fibre surfaces with specific xylanase and mannanase (*Trichoderma reesei*). The amounts and accessibilities of surface carboxyl groups in untreated and enzyme-treated fibres were analyzed using adsorption of cationic polyelectrolytes and high precision potentiometric titration. According to the potentiometric titration both softwood and hardwood pulps contained two types of acidic groups, one with $pK_1 = 3.3$ (uronic acid in xylan) and one with $pK_2 = 5.5$ (probably carboxylic group in lignin). The relative amount of the weaker acid in softwood and hardwood pulp was 10% and 20% of the total acid content, respectively. The ratio of the two acids in pulps was not changed by mannanase treatment, while xylanase treatment decreased the relative amount of the stronger acid. This indicates that the major part of the carboxylic groups are bound to xylan. Xylanase treatment removed about 30% of the xylan in both birch and pine pulps and, consequently, 22% of the acid groups in hardwood pulp but only 8% of the acid groups in softwood pulp. Hence, in softwood kraft pulp fibres the content of uronic acid side-groups in accessible xylan on the surfaces of the fibres is lower than on the hardwood fibres.

ELSEVIER

Colloids and Surfaces
A: Physicochemical and Engineering Aspects 89 (1994) 59–69

COLLOIDS AND SURFACES A

Interactions between carboxymethyl cellulose and cationic surfactants
1. Phase equilibria and surface tensions

Mari Barck *, Per Stenius

Laboratory of Forest Products Chemistry, Department of Forest Products Technology, Helsinki University of Technology, Vuorimiehentie 1 A, 02150 Espoo, Finland

Received 6 January 1994; accepted 11 March 1994

Abstract

The surface tensions and phase equilibria of carboxymethyl cellulose (CMC)/surfactant/water systems were investigated as a function of the charge density of the polymer, the chain length of the surfactants and the ionic strength.

No interactions were observed between CMC and non-ionic surfactants. In systems of CMC and cationic surfactants (tetraalkylammonium bromides) critical association concentrations are observed at concentrations well below the critical micelle concentrations of the surfactants. Associative phase separation occurs in extremely dilute systems when the charge ratio between the surfactants and the polymers is close to zero. The separated phase is a viscous gel phase containing 40–60% of water.

The properties of the systems can be qualitatively understood assuming that (a) the driving force for association of the surfactants with the polysaccharide chains increases as the hydrophobic chain length of the surfactant or the charge density of the polyelectrolyte increases, and (b) there is an associative interaction between the surfactant aggregates and the polysaccharide which decreases with increasing ionic strength.

[illegible] Cationic surfactants; Interactions; Phase equilibria; Surface tension

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ORIGINAL CONTRIBUTION

J. Merta
P. Stenius

Interactions between cationic starch and anionic surfactants

1. Phase equilibria and surface tensions

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Dr. J. Merta (✉) · P. Stenius
Laboratory of Forest Products Chemistry
Department of Forest Products Technology
Helsinki University of Technology
Vuorimiehentie 1A
02150 Espoo, Finland

Abstract The surface tensions and the phase equilibria of dilute aqueous cationic starch(CS)/surfactant systems were investigated. The degree of substitution of the CS varied from 0.014 to 0.772. The surfactants investigated were sodium dodecyl sulphate (SDS), potassium octanoate (KOct), potassium dodecanoate (KDod) and sodium oleate (NaOl). The concentrations of CS were 0.001, 0.01 and 0.1 w%.

Critical association concentrations (cac) occur at surfactant concentrations well below the critical micelle concentrations of the surfactants, except for KOct, KDod and NaOl at the lowest CS concentrations investigated (0.001 w%). The surface tensions of CS/surfactant solutions decrease strongly already below the cac. This is attributed to the formation of surface active associates by ion condensation. Associative phase separation of gels formed by CS and surfactant takes place at extremely low concentrations when the surfactant/polymer charge ratio is somewhat larger than 1. The gel is highly viscous and contains 40–60% water, depending on the concentration of electrolyte, the surfactant hydrocarbon chain length and the nature of the polar head of the surfactant.

The concentration at which the phase separation occurs decreases with increasing surfactant chain length and the concentration of simple electrolyte, factors that promote micelle formation. This indicates that the gels are formed by association of CS to surfactant micelles. When surfactant well in excess of charge equivalence is added, the gels dissolve because the CS/surfactant complexes acquire a high charge.

Key words Cationic starch – anionic surfactants – surfactant polymer interactions – surface tension of surfactant solutions – phase equilibria

Author	Marika Laurila		
Name of the thesis	Adsorption behaviour of nonionic surfactants and polyacrylate on talc		
Date	24.3.1996	**Number of pages**	78
Department	Faculty of Process Engineering and Materials Science Department of Forest Products Technology		
Professorship	Forest Products Chemistry		
Supervisor and examiner	Professor Per Stenius		

The aim of this work was to understand the adsorption mechanism of nonionic block copolymers of polyethylene oxide-polypropylene oxide-polyethylene oxide (PEO-PPO-PEO) on talc, and the competitive adsorption of the surfactant and polyacrylate (PAA). The influence of temperature, Ca^{2+}-ions and chain length of surfactant on the adsorption isotherms were studied using the serum replacement technique. The solution behaviour of the block copolymers in aqueous solution, such as micellization and clouding, was also investigated.

PEO-PPO-PEO adsorbed fairly well onto bare talc surfaces. The adsorption isotherms were described by a Langmuir type equation. The specific adsorption increased as the number of hydrophilic PEO or hydrophobic PPO units decreased, but also when the temperature increased, especially if the surfactant was rather hydrophobic (PEO/PPO<1). The surfactants adsorb mainly due to hydrophobic interactions of the PPO chain. The free energies of adsorption were quite low.

Due to their amphiphilic character, the surfactants self-assemble into micelles. However, there were two break points in the surface tension curve indicating changes in configuration below the critical micelle concentration. Increasing the temperature led to clouding and phase separation, which in most cases was reversible.

Adsorption of PAA depended strongly on pH. In the case of talc, the surface was negatively charged and the dissociation of the polymer was at a maximum. The free energy of adsorption of PAA was much lower than that of the surfactants. The amount of adsorbed PAA increased on raising the temperature. But it was dramatically decreased on adding $CaCl_2$. The shape of the isotherms was Langmuirial type at low concentrations and in its entirety resembled the low affinity type.

The free energy of adsorption of surfactant decreased in competitive adsorption, but the same amount of maximum adsorption was reached regardless of temperature. Some kind of desorption of PAA occured at higher temperatures, where the adsorbed amount of pre-adsorbed PAA was higher. For the surfactant of lower molecular weight the desorption of PAA did not occur, and the amount of adsorption was lower compared to bare talc, in which the free energy of adsorption was much stronger than for the surfactant of higher molecular weight. The addition of Ca^{2+} salt increased the adsorption of surfactant. Also the polydispersity influenced differently on the adsorption of surfactant: In the case of higher molecular weight surfactant the effect in competitive adsorption with PAA was much stronger. Besides the adsorption, the polydispersity had an effect on association behaviour at clouding temperature as well as the break points in the surface tension curve might be related to the broad molecular weight distribution.

International Polymer Colloids Group Newsletter
Spring 1996 Contribution

Polymer Research Group
University of New Hampshire
Durham, NH 03824 USA

Yvon G. Durant & Donald C. Sundberg

Emulsion Polymerization Kinetics in Phase Separated Latex Particles.

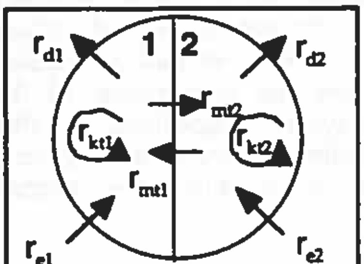

Figure 1.

Smith and Ewart (J. Chem. Phys., 16, p592 **1948**) presented the general equations for the calculation of the average number of radicals par particle. Later Stockmayer (J. Polym.. Sci., 24, p314 **1957**) and O'Toole (J. Appl. Polym. Sci., 9, p1291 **1965**) proposed very efficient ways of solving these equations under different conditions. This work needs to be modified for the case of multiphase systems. Here, we are considering the case of fully phase separated systems with only two phases and no gradient distribution in either phase. We need to keep track of 8 different events (in addition to propagation and transfer) occurring to the radicals within a particle, as displayed in figure 1. The following events can occur at a given rate (r) in each phase: entry (e), desorption to the water phase (d), termination (kt), and mass transfer to the other polymeric phase (mt). For a given volume of latex, we have N particles containing n and m radicals in phase 1 and 2 respectively, denoted $N_{n,m}$. Under steady state conditions, the rate at which a particle with n,m radicals is created is equal to the rate at which such a particle disappears. This balance can be expressed by the following equation.

$$N_{n,m}\left(r_{e1} + r_{e2} + r_{d1}n + r_{d2}m + r_{kt1}\frac{n(n-1)}{2} + r_{kt2}\frac{m(m-1)}{2} + r_{mt1}n + r_{mt2}m \right)$$
$$= N_{n-1,m}r_{e1} + N_{n,m-1}r_{e2} + N_{n+1,m}r_{d1}(n+1) + N_{n,m+1}r_{d2}(m+1) +$$
$$N_{n+2,m}r_{kt1}\frac{n(n+1)}{2} + N_{n,m+2}r_{kt2}\frac{m(m+1)}{2} + N_{n+1,m-1}r_{mt1}(n+1) + N_{n-1,m+1}r_{mt2}(m+1)$$

We have considered three solutions to this equation. The first one involve a Monte Carlo simulation of the physical events. The second solution consists of a Genetic Algorithm (GA), where the particle population constitutes the alleles of the chromosomes and the evaluation function is the differential between the two members of the above equation. The third solution involves the inversion of a sparse matrix of 1024 columns by 1024 rows. We have applied this model to Core-Shell, Inverted Core-Shell and Hemispheres structures.

Kyungwoo Lee and Donald Sundberg

The Effect of Copolymerization Variables on the Development of Latex Particle Development

The use of copolymers in the seed latex particle and comonomers in the second stage polymerization process introduce a number of additional considerations into the prediction and control of composite latex particle morphology. Among these are the effects of copolymer composition on the interfacial tensions, comonomer distribution among the organic and aqueous phases and its resultant effect on both interfacial tensions and new polymer composition.

There are few data sets in the literature for the effect of copolymer composition on surface tensions and even fewer for interfacial tensions. The available data suggest that the dependency of surface tension on composition is generally non-linear for random copolymers, while we had anticipated that it should be linear. We suspect that compositional drift during the preparation of the copolymer samples had the effect of creating some variation in the copolymer composition and that the polymer at the interface was not always that of the average composition. There appears to be a need to produce copolymers of carefully controlled composition to establish the needed relationships.

Monomer compositions in the aqueous and polymer phases during the polymerization are required parameters in the modelling of particle morphology. Equilibrium composition calculations are necessary at each incremental stage of the polymerization reaction and these rely on the interaction parameters between the monomers and the polymers in which they are soluble. Concentration dependent interaction parameters are valuable in this regard. We again find that the literature is sparse with regard to such data.

Because of the effect of copolymer composition on interfacial tension, one needs to be concerned with copolymer drift during the polymerization. Appropriate values of the reactivity ratios are necessary so as to calculate the distribution of copolymer composition during the reaction. We suggest that under equilibrium conditions, the copolymer with the greatest tendency to lower interfacial tension will be preferentially adsorbed at that interface and that such polymer may have come from early or late in the reaction, depending upon the reactivity ratios. Combined with the competitive adsorption of the comonomers at the same interface, this makes the calculations interfacial tensions reasonably complex.

The above effects have been combined in our equilibrium morphology analysis to allow predictions of latex particle structure for some copolymer systems.

A. VRIJ

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

Demixed Phases of Colloid plus Polymer Systems in a Common Solvent. Calculation of the Interfacial Tension

**A.Vrij, van 't Hoff Laboratory, Utrecht University, Padualaan 8,
3584 CH Utrecht, the Netherlands**

Abstract

An analytical formula for the interfacial tension of the (sharp) interface in a demixed (complex) system of colloid and polymer has been derived. The colloid and polymer are modelled as hard spheres and overlapping spheres, respectively. The treatment is based on a recent theory of Kalikmanov and Hofmans, in which the pair potential is modelled as a depletion potential.

For, e.g., a hard sphere with a diameter of 10 nm it gives an interfacial tension between, say, 0.015 and 0.055 mN/m (= dyne/cm) depending on the concentration and size of the polymer.

accepted for PHYSICA(A)

A. VRIJ

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

Langmuir 1996, *12*, 1127–1133

The Random Contact Equation and Its Implications for (Colloidal) Rods in Packings, Suspensions, and Anisotropic Powders

Albert P. Philipse

Van't Hoff Laboratory for Physical and Colloid Chemistry, Utrecht University, Padualaan 8, 3584 CH Utrecht, The Netherlands

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The experimentally observed asymptotic scaling $\phi(L/D)$ = constant, for the random packing volume fraction (ϕ) of rods with high aspect ratio (L/D), is shown to be the consequence of *uncorrelated* rod–rod contacts, the constant being equal to $\langle c\rangle = 5.4 \pm 0.2$ contacts per rod. The weak dependence of $\langle c\rangle$ on the particle shape accounts for the drastic decrease in random packing density going from spheres to thin rods. Moreover, $\langle c\rangle \approx 5.4$ is large enough for isotropic rod packings to be metastable "rod-glasses" with respect to a fully ordered nematic phase. In addition to rod packings, literature results on colloidal sediments, rheology, and percolation of random rods are (re)interpreted to conclude that uncorrelated pair contacts suffice to explain densities of a variety of (mechanical) thin-rod systems.

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Nonanalytical Concentration Dependence of Sedimentation of Charged Silica Spheres in an Organic Solvent: Experiments and Calculations

DOMINIQUE M. E. THIES-WEESIE,* ALBERT P. PHILIPSE,*,[1] GERHARD NÄGELE,† BARBARA MANDL,† AND RUDOLF KLEIN†

Van 't Hoff Laboratory for Physical and Colloid Chemistry, Utrecht University, Padualaan 8, P.O. Box 80.015, 3508 TB Utrecht, The Netherlands; and †Fakultät für Physik, Universität Konstanz, P.O. Box 5560, D-78434 Konstanz, Germany

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Sedimentation of charged silica spheres in ethanol has been studied as a function of ionic strength and volume fraction ϕ. It is shown for the first time by experiment that at very low ionic strength the normalized sedimentation velocity U/U_0 follows a remarkable ϕ dependence of the form $1 - p\phi^{1/3}$, which leads to a strong decrease in U/U_0 at very low concentrations. This dependence agrees with theoretical calculations of the sedimentation velocity. The calculated numerical coefficient p, however, is smaller than the experimental value. Both experiments and calculations show that addition of salt gradually changes the $\phi^{1/3}$ dependence to the linear ϕ dependence characteristic for hard spheres. The $\phi^{1/3}$ behavior for salt-free dispersions renders it very difficult to measure quantities at "infinite dilution."

Key Words: charged colloidal spheres; sedimentation.
