

3 May 1985

Details of the 5th 'Polymer Colloids' Gordon Research Conference together with the Application Form (which should be photocopied to enable it to be submitted in duplicate) appear within. The 1985 Annual Business Meeting will be held during this Conference.

The programme for the Plastic and Rubber Institute's 'Polymer Latex II' also appears within. David Bladley is a member of the Organising Committee. The PRI preprints extended abstracts of the papers to be presented at its Conferences and copies of the preprint book can be obtained from the Institute after the Conference from the PRI Publications Department, 11 Hobart Place, London SW1W 0HL, at £22 (including postage).

The 16th Annual Short Course on 'Advances in Emulsion Polymerization and Latex Technology' will be held at Lehigh University 3 - 7 June, 1985 (Information from Mohammed El-Aasser). The 8th European Short Course will be at Davos, Switzerland 19-23 August, 1985 (Information from Gary Poehlein).

The 30th IUPAC International Symposium on Macromolecules will be held in The Hague, Holland August 18-23, 1985. Emulsion polymerisation is not covered but there are sections on Water-Soluble Polymers and Polymers at Interfaces (including polymer adsorption). Information from QLT Convention Services, Keizersgracht 792, 1017 EC Amsterdam, Holland.

The 30th IUPAC Congress in Manchester, 9-13 September 1985 excludes polymers but includes colloids having a two-day symposium on 'Micellar Systems' with which Ron Ottewill has been much concerned. Information from Dr J.F.Gibson, Royal Society of Chemistry, Burlington House, London W1V 0BN.

Apart from scheduling a further symposium (for which the chairman has yet to be nominated) on emulsion polymerization for the A.C.S. Spring Meeting in New York in 1986 (April 6 -11), the Division of Polymeric Materials: Science and Engineering has a symposium on 'The Assessment of Particle Size Distributions' co-sponsored by the Division of Colloid and Surface Chemistry arranged for the 1985 Fall meeting at Chicago (September 8 - 13): the deadline for submission of papers for the latter meeting has just past, however. Abstracts (4 copies) for Spring 1986 meeting are due by 15 October and preprint copy by November 15, 1985. In absence of other information inquiries should be directed to the Division Chairman Dr R.A.Dickie, Scientific Research Laboratories, Ford Motor Co., Box 2053, 20000 Rotunda Drive, Dearborn, Michigan 48121.

Members should have received (and answered) a circular from Mohammed El-Aasser about the 1986 Annual Meeting which will be at the Johnson Foundation's Wingspread Conference Centre, Racine, Wisconsin June 30 - July 4, 1986. Any member who has not received this letter should let Mohammed know.

The 59th Colloid and Surface Science Symposium at Clarkson University, June 24-28, 1985 doubles as the 5th International Conference on Surface and Colloid Science. It has a massive programme with 708 Contributed Papers by 614 speakers arranged in up to 9 simultaneous symposia. Although Healy, Rowell and Iyklema seem to be the only members of the Group involved several of the symposia e.g. Colloidal Optics (6 sessions) including papers on light scattering, Colloidal Behaviour in Non-aqueous systems (3 sessions), Microemulsions (4 sessions), Flocculation (6 sessions), Mixed Surfactants (4 sessions), Micelles (3 sessions), and Dispersions (5 sessions) look likely to contain items of interest. Information from E. Rosenthal, Clarkson University, Potsdam, NY 13676 ((315)-268 4437).

The proceedings of the 1st Symposium on Polymer Colloids of the American Institute of Chemical Engineers, held at Houston, Texas in March, 1983 has been published under the editorship of Mohammed El-Aasser in a single issue of the Journal of Dispersion Science and Technology 5 (1984) Nos. 3 & 4. The publishers are Marcel Dekker, 270 Madison Avenue, New York, NY 10076, U.S.A. Abstracts of the contents listed below are appearing in Chemical Abstracts 102 (1985) Nos. 12, 14 etc.

J.W.Vanderhoff, M.S.El-Aasser, F.J.Micale, E.D.Sudol, C.M.Tseng, A.Silwanowicz, D.M.Kornfeld & F.A.Vicente
"Preparation of large particle size monodisperse latexes in space polymerisation kinetics and process development"

H.-C. Lee & G.W.Poehlein "Emulsion polymerisation in a seed-fed Continuous Stirred Tank Reactor"

W.Y.Chiu, M.-C.Tsai, & C.Chin "Particle size distribution in continuous emulsion polymerisation with free radical desorption"

C.I.Kao, D.I.Lee, & E.F.Stevens, "Kinetic studies of seeded emulsion polymerization of styrene under batch and continuous monomer addition conditions"

T.Makgawinata, M.S.El-Aasser, A.Klein, & J.W.Vanderhoff "Kinetic studies of semi-batch emulsion copolymerisation of 80:20 vinyl acetate-butyl acetate"

J.W.Vanderhoff, F.V.DiStefano, M.S.El-Aasser, R.O'Leary, D.M.Shaffer & D.L.Viscoli "Inverse emulsion polymerisation of acrylamide: polymerization kinetics and process development"

C.J.McDonald "Characterization of an acrylamide modified ethyl acrylate latex by Carbon-13 NMR spectroscopy"

B.Emelie, C.Pichot, & J.Guillot "Control of surface and structural properties in (Methyl Methacrylate-Butyl Acrylate) emulsion terpolymers"

A.I.Ranka, M.S.El-Aasser, & J.W.Vanderhoff "The influence of colloidal stability on Critical Pigment Volume Concentration (CPVC)"

S.M.Ahmed "Effect of agitation and the nature of the protective colloid on particle size during suspension polymerisation"

D.C.Sundberg "Grafting of styrene on to polybutadiene latices in batch and semi-continuous reactions"

B.Rocchetti, J.Guillot, & A.Guyot "Structure-property relationship in Acrylonitrile/Acrylate emulsion copolymers"

'POLYMER COLLOIDS' Edited by R. Buscall, T. Corner, & J. F. Stageman

This is a book recently (1985) published by Elsevier Applied Science Publishers, London at £38. pp. 324 + xli. ISBN 0-85334-312-8.

Titles and authors of chapter are:

1. Types of Polymerisation by the late M.W.Thompson (ICI Paints Division, Slough)
2. Mechanisms and Kinetics of Emulsion Polymerisation by G.W.Poehlein (Georgia Tech.)
3. Adsorption from Solution. I - Low Molecular Weight Ionic Adsorbates by R.O.James (Eastman Kodak, Rochester N.Y.)
4. Adsorption from Solution. II - Macromolecular Adsorbates by Th.F.Tadros (Plant Protection Division, ICI, Bracknell)
5. The Stability of Polymer Latices by R. Buscall & R.H.Ottewill (ICI Corporate Bioscience and Colloid Laboratory, Runcorn and University of Bristol)
6. Rheology of Polymer Colloids by I.M.Krieger (Case Western Reserve University)
7. Natural and Synthetic Rubber Latices by D.C.Blackley (London School of Polymer Tec)
8. Colloidal Aspects of Poly(vinyl chloride) Production Processes. by D.G.Rance (ICI Petrochemicals and Plastics Division, Wilton)

The first chapter is particularly valuable in its later section because it contains a review of many patents (mostly from ICI) which is not available elsewhere.

Proceedings of the Lyon 'Emulsion Copolymerisation and Copolymers' Symposium 1984

The papers presented have now been printed from camera-ready copy in double volume Supplement (no. 10/11) of 'Die Makromolekulare Chemie'. The bound volume will be sent post free if a remittance is sent with the order at DM 128 from Hthig & Wepf Verlag, Postfach 102869, D-6900 Heidelberg 1, West Germany or at U.S. \$ 40 from Hthig & Wepf, Room 227, 611 Broadway, New York, N.Y. 10012, U.S.A.

Provisional programme

Polymer latex II

Tuesday 21 May 1985

- 0900 Registration
- 0930 **Session A**
- 1 Factors determining the breadth of particle size distributions obtained in the emulsion polymerization of styrene
A S Dunn, S A Hassan (UMIST)
- 1000 2 Carboxylation and structure of latex particles with different monomer compositions
D Rahlwes, H G Vogt, D Kranz (Bayer AG, FR Germany)
- 1030 Coffee
- 1100 3 Kinetics of the surfactant-free emulsion polymerization of styrene
M C Wilkinson (Chemical Defence Establishment)
- 1130 4 Preparation of latices by the mini-emulsion process
M S El-Aasser (Lehigh University, USA)
- 1200 5 Simplifications to the theory of batch emulsion polymerization and copolymerization
M J Ballard (ICI Corporate Colloid Science Group)
- 1230 Luncheon
- 1400 **Session B**
- 6 Flocculation of aqueous concentrated latex dispersions containing adsorbed polymer layers
Th F Tadros (ICI Plant Protection)
- 1430 7 The effect of the addition of non-absorbing soluble polymer on the stability and rheology of polymer latices
D Belbin, R Buscall, C A Mumme-Young, J Shankey (ICI Corporate Colloid Science Group)
- 1500 8 Electrodeposition of cationic polyurethane latices
M S El-Aasser (Lehigh University, USA)
- 1530 Tea
- 1600 9 Characterization of the polymer-water interface in emulsion copolymer emulsions: application to acrylic latices
B Emelie (Centre National de la Recherche Scientifique/Norsolor Society, France)
- 1630 10 Latest developments in antioxidant systems for latex
M Renaud (Goodyear, France)
- 1700 11 Preparation and characterization of inverse emulsion polymers of acrylamide with ionic comonomers
C Pichot (Centre National de la Recherche Scientifique, France)
- 1730 Evening social function - a wine tasting
- 1930 Dispersal

Wednesday 22 May 1985

- 0900 **Session C**
- 12 Practical aspects of hydrodynamic chromatography for latex particle size measurements
A Rudin, C D Frick (University of Waterloo, Canada)
- 0930 13 Measurement of particle size distribution by autocorrelation spectroscopy
R W Lines (Coulter Electronics Ltd)
- 1000 14 Particle size distribution measurement of polymer latices using an integrated chromatograph
T Thornton, R Maley (Micromeritics Ltd)
- 1030 Coffee
- 1100 15 The use of electrical conductimetry in the examination of NR latices
A D T Gorton, T D Pendle (MRPRA)
- 1130 16 Permeability of heterogenous polymer latex films
M C Wilkinson (Chemical Defence Establishment)
- 1200 17 Viscoelasticity's contribution to greater knowledge about emulsion films
A Jouandeau (Metravib SA, France)
- 1230 Luncheon
- 1400 **Session D**
- 18 Leaching behaviour of NR latex films
K F Gazeley (MRPRA)
- 1430 19 Compounding modifications for improved NR latex thread
J L Collins, A D T Gorton (MRPRA)
- 1500 20 New applications of polymer latices
D C Blackley (London School of Polymer Technology)
- 1530 Tea
- 1600 21 Waterborne anticorrosive latex paints
W Gruber (Chemische Werke Huls AG)
- 1630 22 The development and future potential of aqueous urethane systems
C G Connolly, D R Karsa, D W Swale (Lankro Chemicals Ltd)
- 1700 Close of conference
- Conference Fee (including lunches and refreshments) £202 (PRI Members £167). Information from: Mr M.D. Shuttleworth, Plastics and Rubber Institute, 11 Hobart Place, London SW1W 0HL Telephone 01-245 9555. Telex 912881 CWUKTX G. Mark 'Attn PRI'
- There will be an opportunity for questions after each paper (subject to the conference running on time).

GORDON CONFERENCE

The program for the 5th Gordon Research Conference on Polymer Colloids is attached together with an application form. Applications are to be filled out in duplicate and sent to Dr. Cruickshank at the address indicated on the form. Those selected as participants must pay the conference fee in full at least three weeks before the conference date, July 8, 1985. Attendance is limited to approximately 100 conferees, so get your applications in early. In addition to invited presentations, there will be an opportunity to present a limited number of short papers (10 minutes). The latter are expected to include new material, especially significant, early-stage results of general interest to the conference. Those interested in making short presentations are requested to send titles and a one paragraph summary of the work to R. A. Wessling or R. H. Ottewill before the conference.

General information on the Gordon Conferences and brief details of the other summer Conferences appear in Science 227 (1985) 1067-1106: issue of 1 March 1985.

Tilton School, Tilton, New Hampshire
July 8-12, 1985

Chairman: R. A. Wessling, Dow Chemical Company
Vice Chairman: R. H. Ottewill, University of Bristol

Monday July 8, 1985

Morning Session - 9:00 a.m.
Discussion Leader - I. M. Krieger, Case Western Res. Univ.

	<u>Speaker</u>	<u>Topic</u>
1.	W.B. Russel Princeton Univ.	The Nonequilibrium Statistical Mechanics of Concentrated Colloidal Dispersions
2.	R.H. Ottewill Univ. of Bristol	Behavior of Concentrated Latexes
Evening Session - 7:30 p.m. Discussion Leader - D. H. Clemens, Rohm & Haas Company		
3.	S.G. Croll Sherwin-Williams	Drying of Latex Paints
4.	J.W.S. Goossens Bayer AG	The Mechanism of Coagulation of Heat Sensitive Latexes

Tuesday July 9, 1985

Morning Session - 9:00 a.m.
Discussion Leader - D. I. Lee, The Dow Chemical Company

1.	J.W. Vanderhoff Lehigh University	Semi Batch Emulsion Copolymerization
2.	J. Guillot CNRS-Lyon	Emulsion Copolymerization of Acrylonitrile: Experiment and Simulation
3.	Shinzo Omi Tokyo Univ. of Ag & Tech.	Computer Modeling of Semi-Continuous Emulsion Polymerization and its Applications to Various Copolymerization Systems
Evening Session - 7:30 p.m. Discussion Leader - R. M. Fitch, S. C. Johnson & Sons		
4.	H. Ringsdorf Univ. Mainz	Polymeric Liposomes as Models for Biomembranes and Cells?
5.	J.H. Fendler Clarkson College	Kinetics and Mechanisms of Surfactant Vesicle Polymerizations

GORDON RESEARCH CONFERENCES

"FRONTIERS OF SCIENCE"

APPLICATION

Please complete this application and mail (in duplicate)
to the Director.
Deadline for Receipt of Application is Three Weeks
Prior to the Conference

Office Use Only:
Received: _____
Sent to Chairman: _____
Waiting List Letter: _____
Registration Mailed: _____
Registration Returned: _____

Conference on _____ Date: _____

(Name of Conference — Please Print)

Name: (Please Print) _____ Location _____

Organization: _____

Accommodations
(Room & Meals) For:

Business Address: _____

Applicant _____

(inc. dept., street & no.) _____

Spouse _____

City and State: _____

Zip Code _____

Child(ren) _____

(over 12 only)

IMPORTANT _____

Total _____

Please check if you have applied to another 1985 Summer Conference _____
Indicate your particular activities which justify favorable consideration of you as a participant in and contributor to this Conference. (Not required of speakers.) Applications are referred to the Conference Committee for review in accordance with the established regulations, and this information is essential.

FIXED CONFERENCE FEES — Summer, 1985 - NEW HAMPSHIRE

*FIXED FEES:

Conferee (double occupancy) \$275.00

Non-resident Conferee (meals, no room) \$235.00

Guest (room, meals) \$185.00

*Children must be at least 12 years of age to have accommodations (room and meals) at conference host site.

1. Full fixed fee charged regardless of time conferee attends Conference. Please note fees.

2. Fixed fee cannot be prorated or reduced for anyone (speakers, discussion leaders, conferees).

3. Non-resident conferees are expected to eat all meals in the Conference Dining Room and, therefore, the Fixed Fee for non-residents includes the full meal charge.

4. Refunds - See General Information under cancellations. PAYMENT:

The full fixed fee will be required IN ADVANCE of ALL PARTICIPANTS AND GUESTS. Attendance and/or accommodations will NOT be reserved unless this fee is paid 3 weeks prior to the Conference. Foreign participants will also be required to pay Gordon Research Conferences in advance in U.S. dollars payable through a U.S. bank. The full fixed fee is charged to all regardless of length of stay at a Conference.

The recording of lectures by tapes, etc. and the photography of slide material are prohibited. Printed reference to Gordon Research Conference papers and discussion is not permitted. Authors are requested to omit references to the Conference in any publication. Guests are not permitted to attend the conference lectures and discussion series. Each member of the Conference agrees to these regulations when registration is accepted.

Please return to:

Dr. Alexander M. Cruickshank, Director
Gordon Research Conferences

Gordon Research Center

University of Rhode Island

Kingston, Rhode Island 02881-0801

Tel: (401) 783-4011 or (401) 783-3372

Office—Summer Schedule

Colby-Sawyer College

New London, N.H. 03257

(603) 526-2870

Signature _____

Date _____

Telephone: Business _____

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RECEIPT OF THIS APPLICATION WILL NOT BE ACKNOWLEDGED
PLEASE DO NOT SEND PAYMENT WITH THIS APPLICATION

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POLYMER COLLOID RESEARCH PROJECTS WHICH HAVE RECENTLY
COMMENCED AT THE POLYTECHNIC OF NORTH LONDON

D. C. Blackley, London School of Polymer Technology,
The Polytechnic of North London, Holloway, London N7 8DB.

26 APR Recd

Several of the research students who have recently joined our research group are working in the area of applied polymer colloid science and technology. Two are investigating the possibilities of reinforcing the mechanical properties of thin films derived from rubber latices by incorporation of polymer particles derived from other polymer colloids. This project has considerable industrial relevance, in that it is frequently desirable to enhance the tear strength and puncture resistance (and to a lesser extent the tensile strength) of such films without at the same time increasing the elastic modulus significantly. Of particular industrial importance is the possibility of reinforcing films from partially-vulcanised rubber latices, rather than vulcanisable films from unvulcanised rubber latices. In this programme, we intend to investigate the effects of several characteristics of the added polymer colloid, such as particle size, chemical nature, crosslink density, glass-transition temperature, structure and morphology of the particle, and the presence of reactive functional groups at the particle surface. It will be particularly interesting to ascertain whether or not the structure of the polymer colloid particle has much effect upon ability to reinforce films derived from rubber latices.

We also have two new research students who are working on aspects of the pre-vulcanisation of natural rubber latex. Both of these students are carrying out their experimental work at the Malaysian Rubber Producers' Research Association at Brickerdonbury, near Hertford, but both are registered through us for higher degrees, and both are being academically supervised by us. One of these students is endeavouring to investigate the sulphur prevulcanisation behaviour of highly-purified natural rubber latex. We have recently completed two interesting programmes on the sulphur vulcanisation of conventional ammonia-preserved natural rubber latex, but the interpretation of the results has been to some extent confused by the presence of non-rubber constituents in the latex. The intention in the current programme is to repeat some of the earlier work using natural rubber latex in which the level of non-rubber constituents (other than water and ammonia) has been greatly reduced. We are attempting to achieve this reduction by treating the latex with protein-digesting enzymes, and subjecting the latex to multiple centrifugation. The second of these projects is concerned with investigating the possibility of prevulcanising natural rubber latex by heating with peroxides or hydroperoxides. This is an old idea which is being revived because of disquiet concerning the levels of nitrosamines and nitrosatables which may be present in articles produced from conventional sulphur-prevulcanised latices, for which an important source of nitrosamines and nitrosatables is thought to be the organic accelerators which are used to facilitate the reaction.

We also have a research student who has commenced an extended project concerned with the effects of synthetic water-soluble hydrocolloids upon the properties of polymer latices, in particular, natural rubber latex. Reference has already been made to work in this area in a previous contribution to the Polymer Colloid Group Newsletter. Our interest is primarily in effects upon properties such as mechanical stability, chemical stability, and viscosity, and also possibly upon creaming behaviour. We intend to investigate systematically the effects of polymer variables such as molecular weight, hydrophobe-hydrophile balance, and nature of hydrophobic and hydrophilic groups.

CONTRIBUTION TO THE POLYMER COLLOID GROUP NEWSLETTERS

by Françoise CANDAU

23 APR Recd

INSTITUT Charles SADRON (CRM/EAHP), CNRS-ULP Strasbourg
6, rue Boussingault, 67083 Strasbourg-Cedex, France

MODIFICATION OF POLYACRYLAMIDE MICROLATICES BY USING A SEEDING PROCEDURE

(C. Holtzscherer)

A seeding procedure has been applied to inverse polyacrylamide microlatices in order to increase the final polymer content, as high solid contents are usually required in most industrial applications. The seed dispersions were prepared by radical polymerization of acrylamide in inverse microemulsions stabilized by aerosol OT emulsifier. They were shown to consist of two species in equilibrium: polymer particles ($d \sim 40\text{nm}$) with a rather narrow size distribution and small AOT micelles ($d \sim 3\text{nm}$).

The principle of the seeding procedure is analogous to that commonly used in normal emulsion polymerization. It consists in swelling prepolymerized microlatex particles (seed system) with acrylamide followed by a second step polymerization. The structural changes resulting from the seeding procedure were investigated by means of quasi-elastic light scattering (QELS) and electron microscopy (EM) measurements.

In conventional emulsion polymerization, the stabilization of the system is achieved by addition of emulsifier to the seed latex. In the present case, the emulsifier is supplied by the AOT micelles present in the medium. This procedure allows a 50% increase of the monomer content with respect to the initial composition, without destabilization.

QELS experiments indicate that the added monomer dissolves into the latex particles rather than in the AOT micelles (Kelvin equation), as demonstrated by the large decrease of the diffusion coefficient D ($D = kT/3\pi\eta d_h$, d_h : hydrodynamic diameter of the particle, see figure 1 a,b). The volume swelling ratios vary from 3 to 15; the seed particles grow not only by monomer incorporation but also by coagulation and fusion with the reservoir micelles.

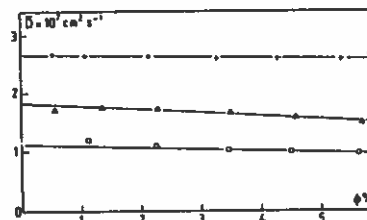


Fig.1: Variation of D with the volume fraction
a) seed latex, ($d_H = 30\text{nm}$)
b) swollen seed latex ($d_H = 43\text{nm}$)
c) final latex ($d_H = 70\text{nm}$)

The polymerization of acrylamide in the seed again produces a further growth of the particles (figure 1c).

The final size of the latex particles is shown to be quite independent of the seed particle composition and of the experimental conditions (i.e. $d \sim 70\text{nm}$) within the limits of this investigation. The size distribution of the particles is not strongly affected by the second or subsequent seeding stages. However, the structure of the final latices apparently is modified at very high dilutions, as evidenced by combined measurements of QELS and EM.

EXTENSION OF THE MICROEMULSION POLYMERIZATION PROCESS (C. Holtzscherer, Z. Zekhnini)

We are extending the inverse microemulsion polymerization process to systems containing different monomers and surfactants. We have thus prepared very highly stable latexes containing large acrylamide or sodium acrylate-acrylamide contents ($\sim 25\%$ overall composition) and relatively low emulsifier concentrations ($\sim 10\%$). The analysis of the microstructure and the composition distribution of the copolymers is presently investigated by ^{13}C NMR (in collaboration with F. Heatly, Manchester University, U.K.).

The copolymers present high intrinsic viscosities with a maximum ($[\eta] \sim 3700\text{cm}^3/\text{g}$) corresponding to a sodium acrylate content in the copolymer of about 40%. A systematic study of the latex stability as a function of various parameters is in progress.

REFERENCES

1. F. CANDAU, Y.S. LEONG, G. POUYET et S. CANDAU. "Synthesis and characterization of inverse polyacrylamide latices by microemulsion polymerization" dans Physics of Amphiphiles : Micelles, Vesicles and Microemulsions, V. DEGIORGIO et M. CORTI Eds., Amsterdam, (1985) p. 830.
2. F. CANDAU, Y.S. LEONG, G. POUYET et S. CANDAU, "Inverse microemulsion polymerization of acrylamide : characterization of the water-in-oil microemulsions and the final microlatices". J. Colloid Interface Sci., 101, 167 (1984).
3. F. CANDAU, Y.S. LEONG et R.M. FITCH, "Kinetic study of the polymerization of acrylamide in inverse microemulsion". J. Polymer Sci., Polymer Chem. Ed., 23, 193 (1985).
4. F. CANDAU, C. HOLTZSCHERER, "Microlatex inverses : Etude de leur formation et de leurs propriétés", J. Chimie Phys., (in press).

Agricultural University
Laboratory for Physical and Colloid Chemistry
De Dreijen 6
6703 BC Wageningen
The Netherlands

Electrokinetic and electrical conductance measurements on plugs of monodisperse polystyrene particles

Homodisperse polystyrene latices in the size range of 0.5–1.0 μm were condensed into concentrated plugs, with a porosity of ca. 0.40, by means of centrifugation. These plugs were inserted in a framing in which the current I resulting from an applied hydrostatic pressure difference across a plug, ΔP , is measured with two shortcircuited electrodes in direct contact with the plug. I appears to be time-dependent, due to electrode polarisation, which also creates a transient potential difference V between two additional electrodes in the two reservoirs. A plot of I vs. V appears to be linear over a long range. The slope of these lines is identical to the conductance of the system, extrapolation to $I=0$ produces the streaming potential V_s and extrapolation to $V=0$ the streaming current I_s . So in just one experiment three important parameters are obtained.

V_s and I_s are converted into ζ -potentials, assuming capillary geometry in the plugs. For negatively charged latex (prepared without emulsifiers according to the Kotera method, with $\text{K}_2\text{S}_2\text{O}_8$ as the initiator) the calculated ζ -potentials show a pronounced maximum as a function of the KCl concentration, just as was observed in electrophoresis experiments.

This phenomenon, in combination with the observation that the major part of the surface conductance takes place between the surfaces of the particle and the electrokinetic slipping plane, can be explained by assuming the presence of a "hairy layer" on the surface of the particles, the thickness of which varies with the ionic strength.

In order to assess the effect of varying the nature of the counterions, in a number of experiments the K^+ ions were substituted by tetraalkylammonium, TAA^+ ions. By also measuring the corresponding adsorption isotherms, it could be established that, contrary to the situation with K^+ as the counterion, the sum of the surface charge density, σ_0 , and σ_{TAA^+} is now close to the electrokinetically determined charge density σ_{ek} .

Recently, a maximum in ζ as a function of ionic strength has also been observed

for positively charged polystyrene particles, obtained by using azo-N,N'-dimethylene isobutyramidine hydrochloride as the initiator. Also in this case, the maximum occurs both in the plug experiments and during electrophoresis of the dilute suspensions.

This work has been done by Bijsterbosch, Van den Hoven, Van der Linde and Hidalgo-Alvarez.

Some Publications related to polymer colloids:

J. Papenhuijzen and G.J. Fleer.

"Preparation and Characterization of Polymer Single Crystals for Use as Adsorbent".

Journal of Colloid and Interface Science. 100 (1984) 561-570.

W. Norde

"Ion Participation in Protein Adsorption at Solid Surfaces".

Colloids and Surfaces 10 (1984) 21-31.

J. Lyklema

"Proteins at Solid-Liquid Interfaces. A Colloid-Chemical Review".

Colloids and Surfaces 10 (1984) 33-42.

A.G. v.d. Put, T.J.J. v.d. Hoven, B.H. Bijsterbosch.

"Measurements of electrokinetic phenomena and electrical conductances on plugs of monodisperse polystyrene particles". Proceedings of the 4th Conference on colloid chemistry, Eger '83. Conference Eds. J. Pintér and E. Wolfram, p. 3-6.

W. Norde

"Physicochemical aspects of the behaviour of biological components at solid/liquid interfaces" in "Microspheres and Drug Therapy, Pharmaceutical, Immunological and Medical Aspects". Chapter 3. S.S. Davis, L. Illum, J.G. McVie and E. Tomlinson, eds., Elsevier Science Publishers B.V. (1984) p. 39-59.

F.A.M. Leermakers, J.M.H.M. Scheutjens and R.J. Gaylord

"Modelling the amorphous phase of a melt crystallized, semicrystalline polymer: segment distribution, chain stiffness, and deformation". Polymer, 25, (1984) 1577-1588.

Contribution to Polymer Colloid Group News Letter
by Mamoru Nomura
Dept. of Industrial Chemistry, Fukui University, Fukui, Japan

(1).....Polymer Colloid Research in Fukui University:

1. Continuous Emulsion Copolymerization of Styrene and MMA---- Work and Paper preparation is in Progress.
2. Batch Emulsion Copolymerization of VAC and MMA-Part of this work was published in Bulletin of the Research Institute for Material Science and Engineering, Fukui Univ. 22, 49 (1984)
3. Development of a Simulation Model for Batch and Semi-Continuous Emulsion Copolymerization.
4. Professor T. Matsuo in Fukui Univ. has developed a Rapid Angular Light Scanning Photometer. He is now examining the particle formation in the very beginning of styrene emulsion polymerization.

(2)....."The 3rd Polymer Microspheres Symposium, Japan" held in November 8-10, 1984 in Fukui was very successful and gathered about 200 participants. In this symposium, 44 papers were submitted. Professor Vanderhoff was invited as a plenary lecturer and gave a fine lecture entitled "CORE-SHELL EMULSION COPOLYMERIZATION" The program is included in this Newsletter for reference which shows the industrial and academic activities in this field in Japan. Preprints will be provided. So contact M. Nomura, an organizer, in case somebody is interested. Papers are written in Japanese but figure captions are written in English.

Program:

- 01: Analysis of Emulsion Polymerization Using a Rapid Angular Scanning Photometer for light Scattering Measurement, T. Matsuo et al.(Fukui Univ.)
- 02: Desorption of Free Radicals from Polymer Particles in Emulsion Polymerization, S. Higasida, G.W. Poehlein(G.I.T.USA)
- 03: Living Radical Polymerization in Emulsion State, A. Yanagase et al.(Mitsubishi Layon Co.)
- 04: γ -ray Induced Non-soap Emulsion Polymerization in the presence of TiO2 Fine Powder, K. Saito et al. (Science Univ. of Tokyo)
- 05: Kinetics and Mechanism of Emulsion Polymerization of Ethyl Methacrylate, U.S. Satpathy, R.S. Konar (R.E. College, India)
- 06: Preparation of Aqueous Acrylic Dispersion by Non-aqueous to Aqueous Substitution of Dispersion Media and its Stability, M. Yabuta et al. (Kansai Paint Co.)
- 07: Emulsion Polymerization of Styrene & Acrylates with Modified Poly(vinyl Alcohol), K. Yuki et al. (Kuraray Co.)
- 08: Packing Structure of Particles in Polymer Latex Film, S. Hayashi et al. (Shinshu Univ.)
- 09: A Simulation Model for the Rate of Emulsion Copolymerization -Verification in Styrene and Methyl Methacrylate System, M. Nomura et al. (Fukui Univ.)
- 10: Investigation of Rate Constants in the Emulsion Copolymerization of Vinyl acetate and Methyl Methacrylate, M. Nomura(ibid)
- 11: Computer Modelling of Semi-continuous Emulsion Copolymerization Reactions, S. Omi et al. (Tokyo Univ. of Agric. & Techn.)
- 12: Control of Particle Size of Styrene-Acrylamide Copolymer Latexes, H. Kawaguchi et al.(Keio Univ.)
- 13: Preparation of Anionic and Amphoteric Latexes by Post-Reaction Treatment of Copolymer Latexes Containing Amide Group and Their Adsorption Desorption Properties, T. Arai et al.(Nihon Univ.)
- 14: Production of Anomalous Particles in the Process of Emulsifier-free Emulsion Copolymerization of Styrene and



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- 16
- 2-hydroxyethyl Methacrylate, S. Kamei et al. (Kobe Univ.)
 15: A Core-shell Latex with Copolymers of Vinylferrocene in the shell, N. Bessho (Japan Synthetic rubber Co.) M.S. El-Aasser et al. (Lehigh Univ.)
 16: Hydrosis of Dimethylaminoethyl Methacrylate in Emulsion Copolymerization, J. Hasegawa et al. (Nippon Zeon Co.)
 17: Galation of Nonaqueous solution of Polymers Having Tertiary Amino Group in the presence of Organic Peroxide, M. Okubo et al. (Kobe Univ.)
 18: Dynamic Properties of polymer Latex particles in Solution, S. Dosho et al. (Kyoto Univ.)
 19: Charged State of Polymer Latex Solution, K. Ito, N. Ise et al. (Kyoto Univ.)
 20: Flow Characteristics of Charged Polymer Latex Solution, K. Fujino (Mitsubishi Monsanto Co.)
 21: Study of Ordered Structure of Fluoropolymer Latex, T. Shimizu et al. (Daikin Industries Ltd.)
 22: Effect of the Hydrophilic-hydrophobic Nature of Latex Surface on the Adsorption of Water Soluble Polymers, K. Furusawa (Tsukuba Univ.)
 23: Surface Characterization of Carboxylated & HBMA-Copolymerized Latices, T. Suzawa et al. (Hiroshima Univ.)
 24: Surface Characterization of Polymer Latices Based on Homo- & Hetero-Coagulation, H. Tamai et al. (Hiroshima Univ.)
 25: Film Formation From Alkali Thickened Polymer Emulsion, M. Okubo et al. (Kobe Univ.)
 26: Morphology of Composite Polymer Emulsion Particles Consisting of Two Kinds of polymers Between which Ionic Bonding Interaction Operates, M. Okubo et al. (Kobe Univ.)
 27: Radiation-Crosslinking of Polymers in Latex Particles with Monofunctional monomers, K. Tsusima et al. (JAERI, Takasaki)
 28: Crosslinking of inter particles by Aldehyde, F. Yoshi (ibid.)
 29: Chemical Deposition Coatings From Anionic Polymer Micro-Emulsion onto Anodized Aluminum Plate, M. Okubo (Kobe Univ.)
 30: Microstructure of Coated Layer on Paper, S. Muroi, (Asahi Chemical Industry)
 31: Some Properties of the Films from Blend latices with Water Soluble polymers, S. Muroi et al. (Asahi Chemical Industry)
 32: Properties of Coatings Comprising of Microgel, A. Kashiwara et al. (Nippon Paint Co.)
 33: Applications of Polymer Latices in an Instant Color Photographic System, Y. Karino et al. (Fuji Photo Film Co.)
 34: Phase Transfer Catalyses Using High-Crosslinked particles with Pyridinium Groups, H. Kawaguchi et al. (Keio Univ.)
 35: Adsorption-Desorption and Separation Treatment by using the Dissociation properties of Carboxylated Latices, T. Arai (Nihon Univ.)
 36: Kinetic Studies of the Interactions between Functionalized Latices, S. Iwai et al. (Kyoto Univ.)
 37: Function of Proteins Immobilized onto Polymer Latices, H. Kitano et al. (Kyoto Univ.) S. Kunugi (Fukui Univ.)
 38: Immobilization of Trypsin onto Polymer Latex, Y. Aoki et al. (Kobe Univ.)
 39: Immobilization of α -Amyrase onto Latex Particles, F. Hosino H. Kawaguchi et al. (Keio Univ.)
 40: Immunologic Reactivity with Polymer Microsphere Having Different Surface Hydrophilicity as Carrier, M. Okubo (Kobe Univ.)
 41: Medical Applications of Immunolatex, T. Suzuta et al. (Tokyo Medical Univ.)
 42: Quantitative Analysis of Rheumatoid Factor with Soap Free Latex, T. Kuge, M. Nakagawa (Sekisui Chemical Co.)
 43: Preparation of Chemiluminescent Microspheres Applicable to the Measurement of Oxidative Microbicidal Activity of Phagocytes, S. Hosaka et al. (Toray Industries, Inc.)
 44: Phagocytosis of Latex Particles with Different Sizes and Different Surface potentials by Granulocytes, H. Kawaguchi et al. (Keio Univ.) M. Miyamoto et al. (Japanese Red Cross)

15 APR Recd

POLYMER COLLOIDS AT SYDNEY UNIVERSITY

Reporter: D. H. Napper

1. Influence of Monomer Solubility on Exit Rate Coefficients

Nomura and Harada have developed a quantitative theory for the rate of exit (desorption) of free radicals from latex particles. This theory is based upon the transfer-diffusion mechanism according to which the free radical activity of a growing polymer chain is transferred to a monomer molecule which subsequently diffuses out of the latex particle. The rate determining step in such a process can in principle be any (or all) of the following: the rate of transfer of free radical activity to monomer; the diffusion of the free radical to the particle surface; movement across the particle interface and diffusion away from the latex particle. In practice, it can be shown both theoretically and experimentally that for styrene, the last mentioned process is commonly rate determining. This arises from the low water solubility of the exiting free radical.

It would be predicted that the exit rate coefficient should increase with increasing solubility of styrene in the continuous phase. This can be accomplished by the addition of methanol. Relaxation studies show that the exit rate coefficient increases on the addition of methanol to the aqueous phase. However, a limiting value is reached. The limit is determined by the rate of chain transfer to monomer and can be accurately predicted from the latter. The results clearly demonstrate a transition in the rate determining step for the exit process.

2. k_p and k_t for Methyl Methacrylate Emulsion Polymerizations

A combination of dilatometric rate and relaxation studies, when coupled with quantitative ESR measurements, allow k_p and k_t to be determined over a wide range of emulsion polymerization conditions. The results show that k_p for methyl methacrylate decreases exponentially below the monomer concentration corresponding to the glass transition point, although the decrease is not as dramatic as predicted by recent free volume theories. The value of k_t in emulsion systems can be profoundly reduced by chain entanglements to the point where residual termination (i.e. termination arising from the propagation process) is the dominant mechanism for bimolecular termination. Recent theories appear to describe the variation in k_t with weight fraction of polymer satisfactorily.

[3 MAY Reed

1 - Kinetic studies in styrene-methyl acrylate emulsion copolymerization (W. RAMIREZ)

In view of preparing model polymer colloids for structuration studies, a program has been initiated to investigate the kinetics of emulsion copolymerization of the styrene (s)-methylacrylate (MA) system, with SDS as emulsifier and $K_2S_2O_8/Na_2S_2O_5$ as initiator system. As it was recently observed in styrene-acrylonitrile, different azeotropic compositions can be obtained according to the monomer to water phase ratio; that is quite well predicted owing to a simulation program taking into account of the actual reactivity ratios ($r_s = 0.75$, $r_{MA} = 0.17$), and of the partition coefficients of each monomer between aqueous and organic phase (monomer solubility in water: 0.3 g/l(s); 56 g/l(MA)). Colloidal characterization of these batch copolymer latexes is currently investigated, particularly to determine the composition of the polymer-water interface.

2 - Emulsifier-free copolymerization studies (J-L. GUILLAUME) -

Soapless emulsion copolymerization of styrene (s) and butyl acrylate (BuA) have been carried out at various comonomer feed compositions, using two types of initiator. When using $K_2S_2O_8$, it was observed that the monomer composition does not affect the final particle size distribution, presumably because of i) a slight change of the comonomer composition in the aqueous phase even when the organic phase becomes richer in butyl acrylate, ii) a similar rate of copolymerization inside the particles. Molecular weight and surface characteristics of latexes were found to sharply change (but in opposite direction) at high butyl acrylate content, which might be related to a change in the overall copolymerization rate.

When using a carboxylic initiator (4,4' azobis cyanopentanoic acid) results in the formation of fully-covered carboxylic latexes in the same size range but less stable. From carboxyl-end group titration in latexes as function of conversion, it is found that a large part of the initiator residue attached on the polymer is buried inside the particles during the initial flocculation period. It was determined that one third of the initiator residue is actually fixed on the polymer and that there is one

19

end group per polymer chain, indicating that growing chains could terminate by transfer, an assumption which implies to precise the S/BuA termination step.

Based on these results, it was attempted to calculate the average radical number per particle, the polymerization rate and the molecular weight. More information on the copolymerization reaction mechanism within the polymer particle is necessary to derive quantitative predictions.

3 - Structure-properties relationships in emulsion copolymers (X.Z. KONG)

As a part of a study to investigate the structure-properties relationships in emulsion copolymers, it is proposed to examine the effect of the particle morphology on the mechanical characteristics by using a micromechanical device which allows to measure the dynamic shear moduli and $\tan \delta$ as function of temperature and of frequency.

Abstract of a paper to be submitted in Polymer. "A comparison of micromechanical properties of latex films obtained from different emulsion copolymerization pathways" (J-Y. CAVAILLE - C. JOURDAN - X.Z. KONG - J. PEREZ - C. PICHOT - J. GUILLOT).

The real and imaginary parts of the dynamic shear modulus (G' and G'' respectively) and the internal friction ($\tan \delta = G''/G'$) of different Butyl Acrylate (BuA) - Vinyl Acetate (VAc) copolymer films were measured (1) as a function of temperature (from 100 K to 340 K), (2) and of frequency (from $5 \cdot 10^{-5}$ Hz to 5 Hz).

In a first part, emulsion copolymerisation process is described: the concentration gradient (BuA/VAc) in particles is well controlled and may vary from 0 (constant composition, corrected batch process) to very high values (core-shell structure). Moreover, different average compositions from 0 % to 100 % have been used in the case of conventional batch copolymerisation process. Finally, a simple blend of the two emulsion homopolymers has been used in order to obviate the presence of copolymer chains.

In a second part, micromechanical properties of these different films were investigated in the temperature -frequency range corresponding to glass transition of each polymer, except in one case where only one transition is observed (corrected batch process). These results were compared and discussed in correlation with the polymer morphology.

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4 - Abstracts of two papers to be published in the preprint booklet of the Polymer Latex II conference organized by the Plastics and Rubber Institute (London, 21-22 May 1985).

CHARACTERIZATION OF THE POLYMER-WATER INTERFACE IN EMULSION COPOLYMERS : APPLICATION TO N-BUTYL ACRYLATE COPOLYMER LATEXES (B. EHELIE , X.Z. KONG, C. PICHOT)

In order to characterize the polymer-water interface, the soap titration method has been used to determine the molecular adsorption area (A_s) of an emulsifier probe (SDS) onto butyl acrylate copolymer latexes with methyl methacrylate or vinyl acetate. Various phenomena were found to interfere in the surface morphology such as : complexation or grafting when nonionic surfactants are used as emulsifiers -presence of strongly adsorbed oligomers in carboxylated latexes- penetration of the surfactant. Results also support the assumption that particle structuration might take place during batch copolymerizations of systems having wide difference in the reactivity ratios and the water solubility between the two monomers.

PREPARATION AND CHARACTERIZATION OF INVERSE EMULSION POLYMERS OF ACRYLAMIDE WITH IONIC COMONOMERS (C. PICHOT, C. GRAILLAT, V. GLUKHIKH, M-F. LLAURO)

Copolymers of acrylamide (Am) with various amounts of sodium acrylate (NaA) or methacrylate ($NaMA$) were prepared by inverse emulsion polymerization at 40°C in xylene (or toluene) with a blend of surfactants as emulsifying system and AIBN as oil soluble initiator. Monomer reactivity ratios of the two systems have been determined under basic conditions. The particle size analysis of the inverse emulsions as a function of the conversion was investigated through different methods. Inverse copolymer latexes obtained by different polymerization processes were also characterized in terms of molecular properties (chemical composition-distribution of ionic groups-intrinsic viscosity).

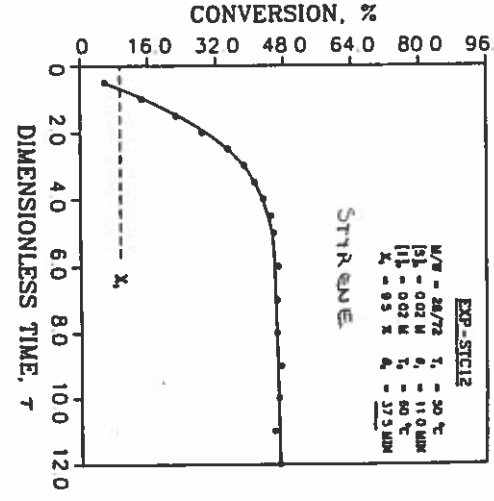
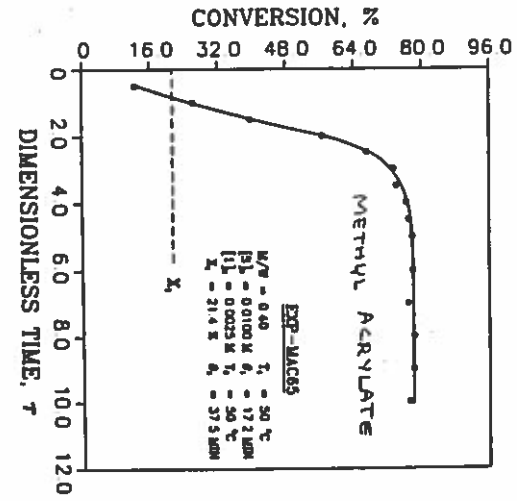
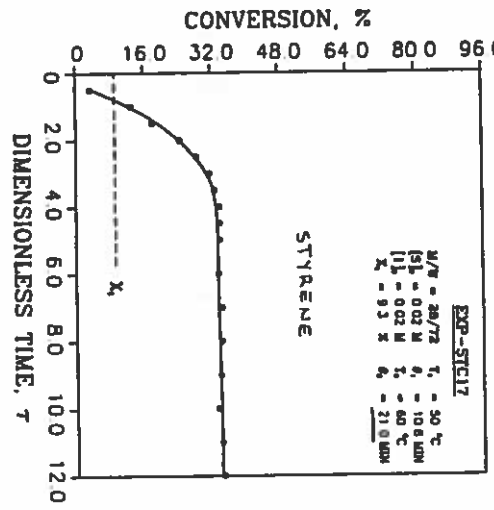
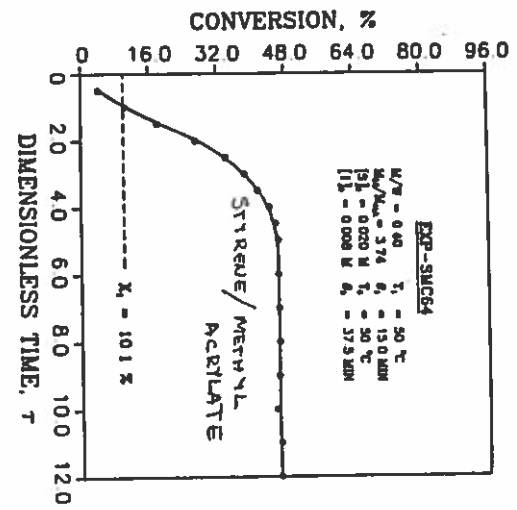
**STUDY OF EMULSION POLYMERIZATION TRANSPORT PHENOMENA
IN A CONTINUOUS REACTOR SYSTEM**

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117 APR Reed

Continuous reactor systems comprised of a pre-tubular reactor followed by one or more stirred-tank reactors (CSTR's) can serve as the basis for efficient commercial processes. They can also be used as effective research tools for studying reaction kinetic phenomena. H. C. Lee has just completed a PhD dissertation which involved emulsion polymerization of styrene and methyl acrylate in a tube-CSTR continuous system with and without the presence of chain transfer agents (CTA's).

The tubular reactor, with effluent conversion of about 10%, was used to produce a seed for the CSTR. CTA, when used, was fed directly to the CSTR; bypassing the tube. Monomer conversion of 10% in the tubular reactor completes the particle nucleation phase and experimental measurements confirm that no new particles are nucleated in the CSTR. The experimental conversion data shown for four runs in Figure 1 clearly indicate that the tube-CSTR is a stable reactor system. The limit-cycle oscillations often observed with CSTR systems are eliminated. Similar data for stable CSTR operation with seed particle feeds have been published for vinyl chloride (Berens) and MMA (Gonzales).



When a CTA such as CCl_4 is added to the CSTR the conversion (reaction rate) decreases in proportion to the amount added. This is shown in Figures 4-8 and 4-14 for low and high conversion runs. Figure 4-20 shows that the polymerization rate results can be plotted on a single straight line if the rate ratio R_p/R_{p_0} is used. R_{p_0} is the rate observed when no CCl_4 is used. Figure 4-18 shows that average particle size and the breadth of the particle size distribution are reduced when CCl_4 is added to the CSTR.

The rate reduction observed when CCl_4 is added is undoubtedly caused by enhanced transport of free radicals out of the latex particles into the aqueous phase. This results in a reduction in $\langle \bar{n} \rangle$, the average number of free radicals per particle.

A series of primary mercaptans, C_2 , C_4 , C_6 and C_{12} were also employed in Lee's experiments. These mercaptans were added in the same molar ratio to the monomer and the conversion-time profiles in the CSTR are shown in Figure 4-24. The C_2 mercaptan caused a very significant reduction in rate whereas the C_{12} mercaptan has almost no effect. The conversion-time curves for C_4 and C_6 mercaptans are intermediate between these two extremes. Rate data, as a function of the number of carbon atoms in the mercaptan, is shown in Figure 4-25. The dashed line in Figure 4-25 is R_{p_0} . The particle size distributions are shown in Figure 4-26 for the runs with C_2 , C_4 and C_{12} mercaptans and Figure 4-30 shows the variation of $\langle \bar{n} \rangle$ and k'_d with the number of carbons in

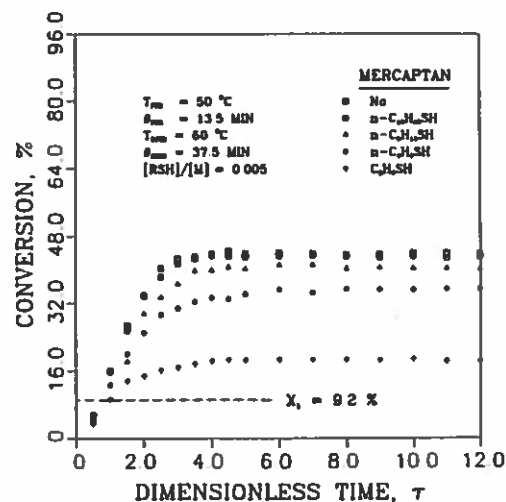


Figure 4-24. The Effects of Addition of Mercaptans with Different Chain Lengths on the Course of Styrene Emulsion Polymerization in a Seed-fed CSTR.

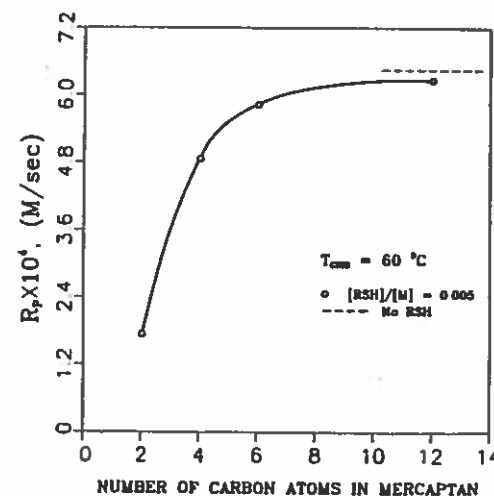


Figure 4-25. The Effects of Addition of Mercaptans with Different Chain Lengths on the Rate of Styrene Emulsion Polymerization in a Seed-fed CSTR.

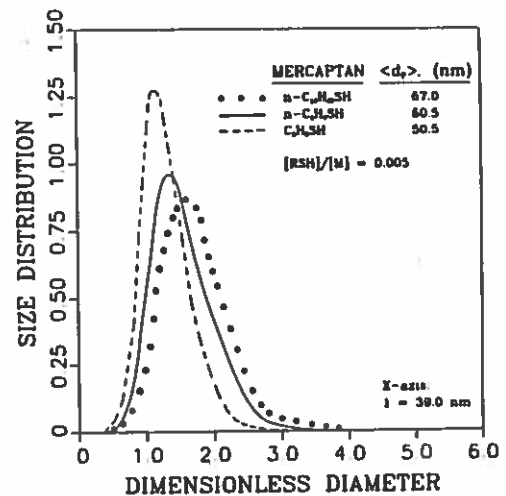


Figure 4-26. The Effects of Addition of Mercaptans with Different Chain Lengths on the Product PSD of Styrene Emulsion Polymerization in a Seed-fed CSTR.

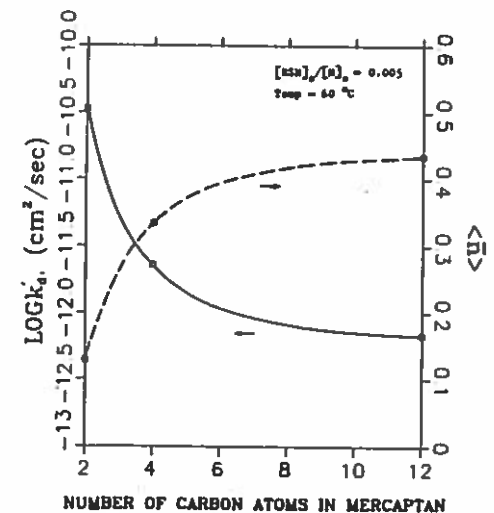
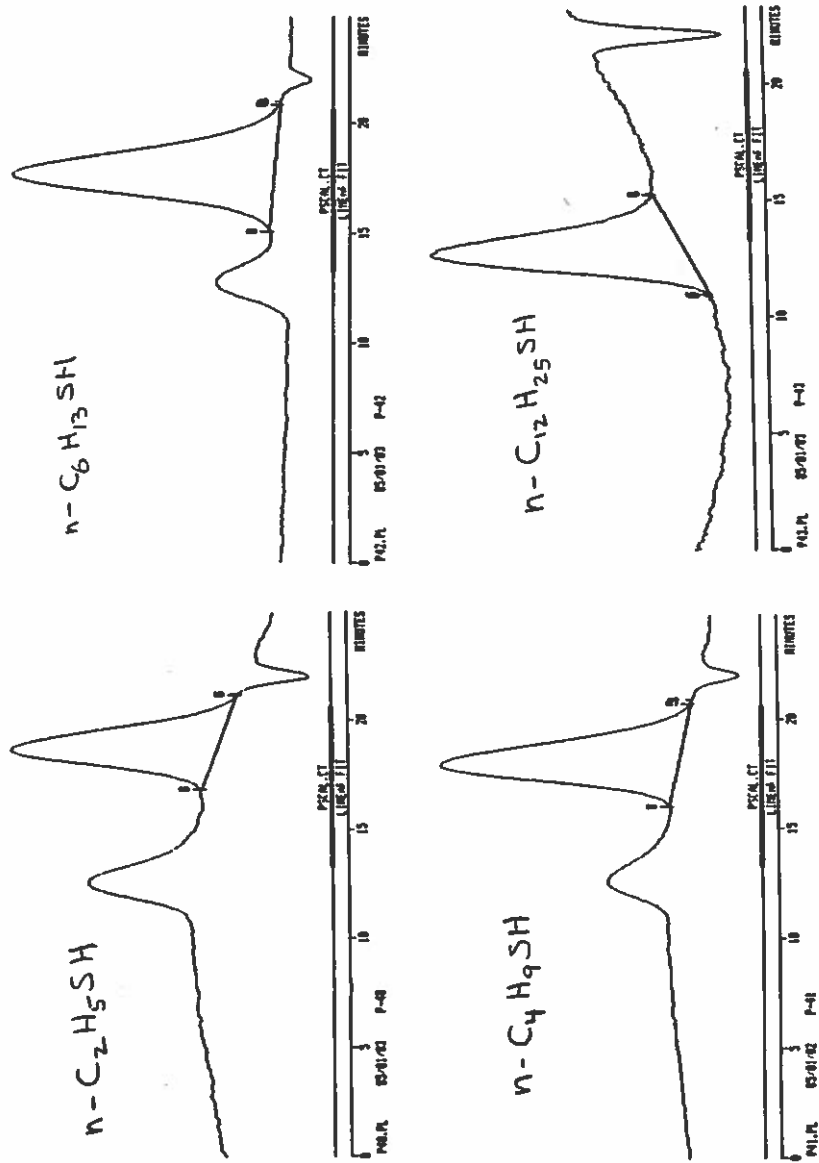


Figure 4-30. The Effects of Addition of Mercaptans with Different Chain Lengths on k'_d and $\langle \bar{n} \rangle$ for Styrene Emulsion Polymerization in a Seed-fed CSTR.

FIGURE 2
GPC CURVES FOR
DIFFERENT MERCAPTANS



25

the CTA. The parameter k_d' is a rate coefficient for the so called radical desorption from particles.

There are at least two possible explanations for the results shown in Figures 4-24 through 4-30. Since chain transfer activity of the mercaptans is nearly independent of the number of carbon atoms the observations must be caused by different rates of desorption of the mercaptan radicals from the particles or by a change in water solubility which limits mass transfer of the higher molecular weight mercaptans from the monomer droplets to the particles.

We believe that the GPC curves for the various runs indicates that the latter factor is most important. The GPC trace for the product latex in the C_2 runs show two distinct peaks. Presumably the high molecular weight peak is due to the polymer formed in the tubular reactor which contained no mercaptan. The GPC results for the C_4 and C_6 mercaptans also show two peaks with corresponding increases in the fraction of low molecular weight material reflecting higher CSTR conversions. The GPC result for the C_{12} run has only one peak at high molecular weight indicating that not much of the C_{12} mercaptan is being transported to the reaction site in the particles.

THE EFFECTS OF LATEX COALESCENCE

and

INTERFACIAL BONDING ON LATEX FILM PROPERTIES

18 APR Reed

D. I. Lee, J. G. Galloway, E. F. Stevens

Designed Latexes and Resins

Dow Chemical U.S.A.

Midland, MI 48674

A B S T R A C T

The effects of latex coalescence and interfacial bonding on the mechanical properties of latex films have been extensively investigated using a series of model latexes. It has been found that the tensile strength of latex films increases with increasing gel content (i.e., crosslinking) of latex polymers up to about 75%, then it decreases with further increase in gel, while the elongation of latex films decreases steadily with increasing gel content. This finding has suggested that latex coalescence is severely retarded above a gel content of about 75% and that the limited coalescence of latex particles at higher crosslinking puts a severe constraint on the possibility of increasing the strength of latex films by crosslinking the latex polymers. This limitation in the structure-property relationship of latex systems has been alleviated by controlling the interfacial bonding of latex particles during film formation. In addition to the effect of latex coalescence, this paper describes the effect of interfacial bonding on the strength of latex films, based on hydrogen and ionic bondings of carboxylic groups at the interface and their ionic crosslinking with multi-valent ions such as Zn^{++} . It also describes the development of self-curable latexes based on unique chemistry.

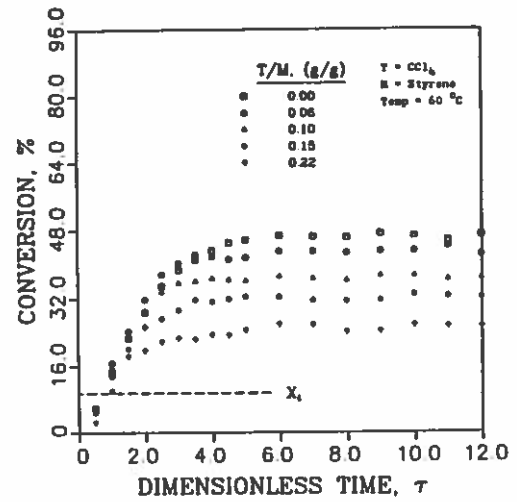


Figure 4-8. The Effects of Increasing CTC Concentration on the Course of Styrene Emulsion Polymerization in a Seed-fed CSTR. Temp. = 60 °C.

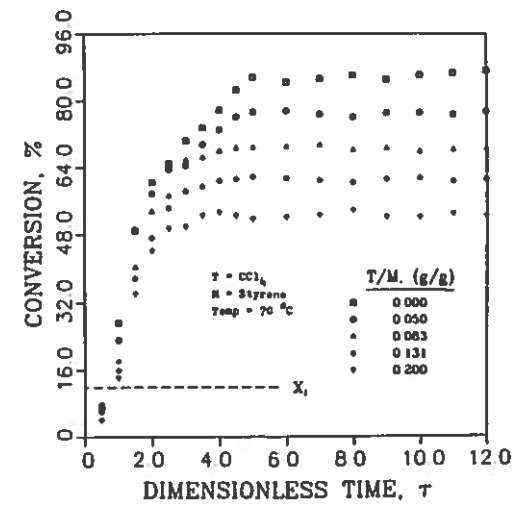


Figure 4-14. The Effects of Increasing CTC Concentration on the Course of Styrene Emulsion Polymerization in a Seed-fed CSTR. Temp. = 70 °C.

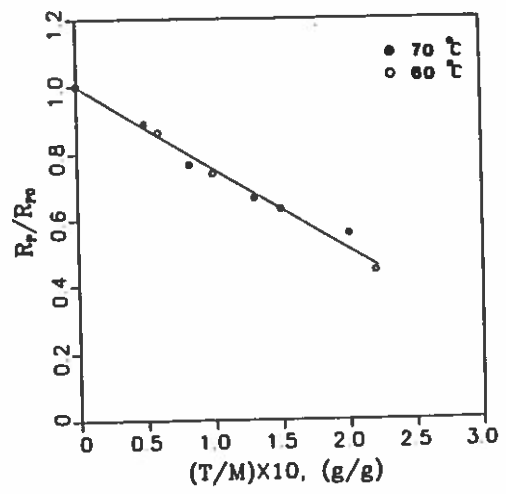


Figure 4-20. The Effects of Increasing CTC Concentration on R_p/R_{p0} for Styrene Emulsion Polymerization in a Seed-fed CSTR. $R_p/R_{p0} = 1.0 - 2.454(T/M)$.

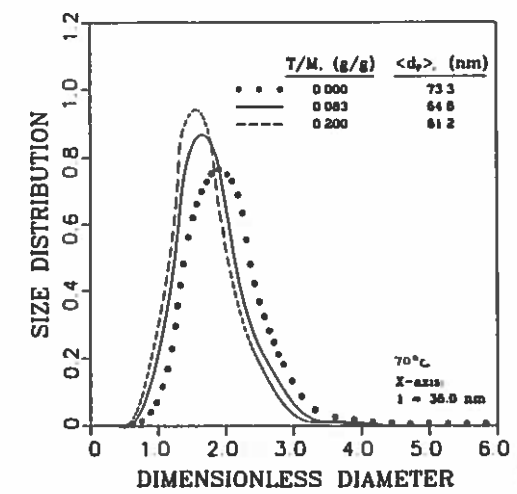


Figure 4-18. The Effects of Increasing CTC Concentration on Product PSD of Styrene Emulsion Polymerization in a Seed-fed CSTR. Temp. = 70 °C.



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April 11, 1985

29
17 APR Recd

POLYMER COLLOID GROUP NEWSLETTER

Spring 1985

The work reported on earlier has been completed and two papers accepted by the Journal of Applied Polymer Science as per the attached two abstracts.

Prof. Richard D. Gilbert and I have started a new PhD student, Mr. M. B. Taylor in our Fiber and Polymer Science program at the School of Textiles. He will work on the kinetics and other details of the inverse emulsion polymerization of water soluble monomers. It is hoped that this work will lead to very high molecular weight polymers. Gamma radiation will be used for the initial studies.

Vivian
Vivian T. Stannett
Camille Dreyfus Laboratory

30
RADIATION INDUCED EMULSION POLYMERIZATION
OF VINYL ACETATE IN A PILOT PLANT REACTOR

PART I: RECYCLE FLOW REACTOR

R. R. Challa, J. H. Drew, V. T. Stannett and E. P. Stahel
Chemical Engineering Department
North Carolina State University
Raleigh, NC 27695-7905

ABSTRACT

A number of successful radiation polymerizations of vinyl acetate in emulsion have been carried out in a modular stainless steel flow pilot plant. In a recycle mode, the system was utilized for extremely accurate kinetic measurements and experimental verification of model restrictions such as plug flow, lack of post irradiation effects and differential reactor behavior. Experimental conditions were explored to minimize contaminant, primarily oxygen, inhibition and the tendency for this formulation, essentially an adhesive, to build up on the reactor walls. Industrial scale-up of such a prototype system appears attractive.

RADIATION INDUCED EMULSION POLYMERIZATION
OF VINYL ACETATE IN A PILOT PLANT REACTOR

PART II. KINETICS

R. R. Challa, J. H. Drew, E. P. Stahel and V. Stannett
Chemical Engineering Department
North Carolina State University
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ABSTRACT

The recycle flow reactor pilot plant, described in Part I of this series has been used to study some kinetic and other features of the emulsion polymerization of vinyl acetate. In particular the dependence of the rate on the emulsifier concentration was determined and found to be 0.38 ± 0.09 . Separate batch experiments were in reasonable agreement as 0.29 ± 0.10 . The effects of temperature, dose rate and agitation rate were also determined and were in agreement with most of the literature values.

Cationic emulsifiers were found to work well with the system in contrast to most chemical initiators. The molecular weights of the polymers were measured before and after hydrolysis and reacylation. They were consistent with chain transfer to monomer being the principle termination mechanism and with chain branching.

To: Polymer Colloid Group Newsletter

26 APR Reed

From: John Ugelstad

"Magnetic" particles.

At SINTEF we have continued our work on improvements of "magnetic" particles and have established cooperation with different biological and biomedical institutes around the world where the applications of the particles are being investigated. The particles prepared up to now have especially been made for use in selective separation of cells, viruses and organelles.

1. Preparation of "magnetic" particles (M450)

The preferred method of preparation of the "magnetic" particles is the one where magnetic iron oxides are formed by an in situ process inside the pores of preformed macroporous monosized particles. The iron oxides in this case form small grains distributed all through the particle. This tends to diminish the "magnetic memory".

The particles prepared in this manner have a surface area of $\approx 100 \text{ m}^2/\text{g}$. As stated earlier this is a disadvantage in the way that one has to apply a large amount of antibody, most of which is inactive as it is hidden within the pores of the particles.

The particles which we now market are particles where we have filled the pores and covered the surface with a polymer. These particles denoted M 450 have a diameter of 4.4-4.5 μm , a density of $\approx 1.5 \text{ g/cm}^3$ and a surface area of 3-5 m^2/g obtained by the BET method. These particles are sufficiently hydrophobic to allow physical adsorption of the antibody. They do however have sufficient -OH groups on the surface to also allow chemical coupling.

2. Coupling of antibody to particle.

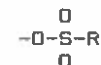
2.1 Physical adsorption.

In accordance with what is found by a number of authors studying adsorption of proteins on polymer surfaces we find that the particles bind irreversibly about 3 mg of antibody per gram.

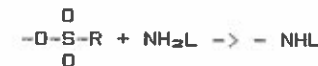
this amount is very strongly attached to the surface and cannot be removed by normal washing procedures. The amount of antibody bound may seem somewhat low taken into account that we have a surface of 3-5 m^2/g . It should be noted that this value is obtained by adsorption of N_2 . The geometric surface of the particle is only $\approx 1 \text{ m}^2/\text{g}$.

2.2 Chemical Coupling.

Coupling with chemical bonds have been concentrated on coupling via -OH groups on the surface which in a first step are converted to tosyl or tresyl esters (paratoluene sulfonic acid-, 2,2,2- trifluoro ethane sulfonic acid ester):



In the next step the solution of affinity purified antibody is added and binding takes place by reaction with amino groups on the protein:



The reaction with the tresyl ester is much faster and leads to the binding of slightly more antibody. It turns out however that the antibody bound via the tosyl ester is more active in binding to the antigen (1). Most interesting it turns out that while the reaction between the antibody and the tresyl ester appears as a rapid direct reaction it was possible to experimentally demonstrate the two step mechanism of the reaction with the tosyl ester. The antibody is in a first rapid reaction adsorbed physically to the particles. This is followed by a relatively slow chemical coupling of the antibody. It should be noted that even in the case that we operate with hydrophilic surfaces with a high density of -OH groups the tosylation reaction may be expected to render the surface hydrophobic.

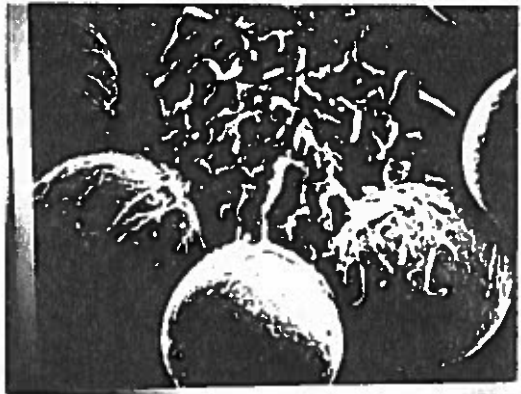
Whether we have a physical binding or a chemical binding of the antibody to the particles we should preferentially have the antibody bound with the Fc part oriented towards the particle surface and the antigen binding Fab parts oriented outwards. The acid treatment involved in the affinity purification of the antibody may be expected to lead to an increase in the hydrophobicity of the Fc part of the molecule. This may in turn give a more favorable orientation by physical adsorption and explain a more favorable orientation and a higher activity of the antibody by use of tosyl ester than by use of tresyl ester.

3. Application of the particles in cell separation.

In addition to the use of the magnetic particles for removal of neuroblastoma cells from bone marrow (2 - 5) the

particles have more recently been applied for removal of β -lymphoma cells and for selective separation of T-lymphocytes from bone marrow and peripheral blood.(6,7). Likewise the particles have been proven to be effective in selective separation of hepatocytes (8,9). The selective removal of T-cells from bone marrow is of great interest as it may allow allogenic bone marrow transplantations to take place. It will be evident that one in this case, because of the high percentage of T-cells in the bone marrow must have very selective magnetic particles with very low non-specific binding to cells. This requirement seems to be fulfilled with the new compact magnetic particles (M-450). In the case of the hepatocytes it was found that one could selectively remove > 99.9% of hepatocytes leaving the majority of the .1% of cells one wanted to study in the serum.

The picture below shows magnetic beads bound to a hepatocyte cell.



A mouse monoclonal antibody directed against surface antigens of the hepatocyte cell type to be removed is attached to the cells in a separate step. The particles have been activated by an immuno purified sheep antimouse JgG. During the mixing of the particles with the hepatocyte cell mixture the cells with the monoclonal antibody attached to them finger-like protrusions from the cell enfold the magnetic particles. No such binding occur with non-labelled cells.

4. Magnetic particles with shell and core structure.

The most recent magnetic particles we have produces are particles with the same inner structure as M 450 but with a shell of pure polymer around them. The structure is as indicated:

The rFe_2O_3 is distributed as fine grains in the inner particle. The outer shell of polymer may be formulated to have -OH groups, -COOH groups or -NH₂ groups on the surface. Up to now we have produced such particles which have an inner diameter of 3.5 μm and an outer diameter of 4.5 μm . These particles have been made on request of the European "Molecular Biology Laboratories" in Heidelberg which wanted uniform magnetic particles with a reduced magnetic interaction between the particles. EMBL apply our particles for selective extraction of organelles and viruses (10).

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**SYNTHESIS OF AMPHIPHILIC POLYMERS AND
THEIR APPLICATION IN EMULSION POLYMERIZATION**

by

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INTRODUCTION

In emulsion polymerization most of the polymeric surface active materials used have been primarily block copolymers with ethylene oxide as the hydrophilic moiety. It was therefore considered of interest to study the behavior in emulsion polymerization of graft copolymers as particle stabilizers. The action of two of these are described in this paper.

In the synthesis of the two graft copolymers, N-vinylpyrrolidone was chosen as the grafting material. One of the backbone monomers was p-methylstyrene, the other backbone was created through the reaction of commercial poly(vinyl alcohol) with allylamine. Both synthesis are described in the experimental section. These graft copolymers were then subsequently used in the emulsion polymerization of styrene, methyl methacrylate and acrylonitrile.

EXPERIMENTAL

a) Synthesis of poly(p-methylstyrene-g-N-vinylpyrrolidone (Surfactant A))

In this study N-vinylpyrrolidone was chosen as the grafting agent because of the slow polymerization rate of N-vinylpyrrolidone in benzene with AIBN as initiator¹. This gave us more control in the building of the grafts on the backbone.

First of all the p-methylstyrene was polymerized to the desired chain length with the help of mercaptan as the chain transfer agent in toluene solution at 60°C with AIBN as the initiator. Some backbone methyl groups could be activated using t-butyl hydroperoxide and cuprous chloride in the presence of another monomer. However, owing to the difficulty in removing the cuprous/cupric salts from the solution, a method by chain transfer to polymer was adopted instead. For this method partial bromination of the methyl groups of the backbone with N-bromosuccinimide (NBS) in carbon tetrachloride solution and benzoyl peroxide as initiator created bromomethyl groups along the backbone. The bromines can be further substituted with mercapto groups directly or with sodium salts of 3-mercapto-propionic acid in hexamethylphosphoric triamide (HMPT). The latter method was adopted over the first because of the unwelcome odor formation in the first one. The efficiency for the substitution of bromine with carboxylic group in HMPT was 97.11% according to the elemental analysis. A mole ratio of sodium 3-mercapto-propionate to bromine of 2 to 1 was used, however, to achieve this almost quantitative substitution.

The final step in the reaction involved the polymerization of N-vinylpyrrolidone (in excess) in the presence of the mercapto derivative of poly(p-methylstyrene). The initiator employed was AIBN at 70°C, and the reaction was carried out in toluene solution. A separation of the crude reaction mixture indicated that approximately 60% of the N-vinylpyrrolidone had homopolymerized. The graft copolymer was purified by continuous extraction with methyl ethyl ketone. After dissolving it in tetrahydrofuran, the polymer was precipitated from hexane. The composition evaluation by elemental analysis of the graft copolymer indicated that there was a graft to backbone weight ratio of 13:1. This surfactant A had a CMC of 8.6×10^{-2} mol/l. Cloud point of the 0.5% aqueous solution was above 100°C.

b) Synthesis of poly(vinyl alcohol-g-allyl-amine-g-N-vinylpyrrolidone (Surfactant B))

Two commercial poly(vinyl alcohol) samples (100 percent hydrolyzed) of molecular weights of $M_n = 14,000$ and $25,000$ were purified by reprecipitation to remove additives and low molecular weight fractions. These purified PVA samples were

dissolved in distilled water in a round bottom 3-neck flask. After purging with nitrogen the freshly distilled (N₂ purged) allylamine was transferred to the flask, followed by a dilute nitric acid solution of ceric ammonium nitrate. The grafting reaction was allowed to proceed for one hour, then stopped by letting air into the flask. Co-grafting was verified by IR analysis of the product. The flask with its content was then flushed with nitrogen, and the N-vinylpyrrolidone added together with another 10 ml of the ceric ammonium nitrate in dilute nitric acid. The grafting reaction was allowed to proceed for one hour, after which time the mixture was poured into 2 liters of acetone to precipitate the graft copolymer. This surface active material with its allylamine units as the anchoring moieties and the N-vinylpyrrolidone branches as the stabilizing moieties was used as the surfactant in acrylonitrile polymerizations.

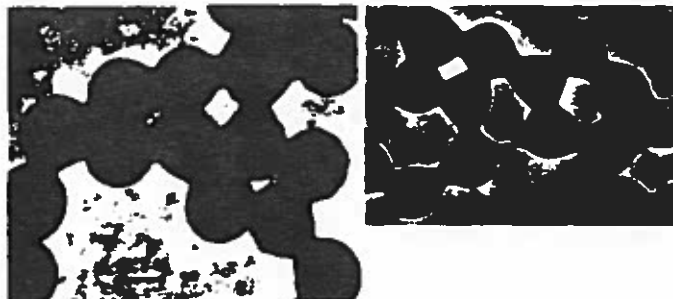
RESULTS AND DISCUSSION

The polymerizations of the three monomers studied, styrene, methyl methacrylate and acrylonitrile were carried out at 60°C. The following table shows the concentrations of ingredients needed for these reactions, and for the creation of a stable latex.

Monomer	Water	K ₂ S ₂ O ₈	Surfactant	
			A	B
Acrylonitrile	100	800	1	24
MMA	100	600	2	70
Styrene	100	300	1	28

concentration imparts by weight

The surfactant A yielded acidic latices, which is assumed to be due to the fact that the pyrrolidone ring opening² creates a γ-amino acid at the 60°C reaction temperature in the presence of the mildly acidic medium produced by the induced decomposition of potassium persulfate. In styrene as well as MMA polymerizations it was found that the rate as well as the number of particles formed was directly proportional to the surfactant A concentration. The minimum concentration of surfactant needed in case of styrene was found to be 28g/100g monomer. This produced a latex with $N = 1.09 \times 10^{13}$ particles/cm³ water, a number average particle diameter of 160nm, and a D_w/D_n 1.02. The electron micrographs were clear, and no difficulties were encountered in the preparation of the microscope grids. The removal with water of the excess surfactant became difficult with a surfactant charge of 40g/100g monomer and higher. The minimum concentration of the surfactant A needed in MMA polymerization for the formation of a stable latex was very high, 70g/100g monomer. The electron microscope latex analysis showed the latex particles to be quite homogeneous, the 80g/100g monomer charge latex had a D_w/D_n of 1.03, with $N = 1.22 \times 10^{13}$ and a number average particle diameter of 125 nm. It should be mentioned here that in order to prepare the electron microscope pictures of any clarity and particle separation, a tedious process of surfactant removal had to be carried out which included centrifugation and serum replacements. The electron microscope pictures for both the polystyrene (I) and poly(methyl methacrylate) (II) latices are shown below.



I

II

It is obvious that the attraction of the surfactant A to the poly(methyl methacrylate) particles is very strong, which suggests some interaction between the poly(vinylpyrrolidone) branches and poly(DMA), since a strong interaction between the backbone poly(p-methylstyrene) and poly(DMA) is most unlikely. A study is currently underway to provide a conclusive answer to this phenomenon.

The acrylonitrile polymerizations in the presence of surfactant B produced extremely stable latexes. The minimum concentration of surfactant required to achieve stability was 24g/100g monomer, in a monomer to water ratio of 1:8.

CONCLUSIONS

N-vinylpyrrolidone can be successfully employed to create poly(N-vinylpyrrolidone) branches on poly(p-methylstyrene) and poly(vinyl alcohol-g-allylamine) backbones. The resulting surface active polymers, surfactants A and B can be successfully used as latex stabilizers in emulsion polymerization of styrene and methyl methacrylate (Surfactant A) and acrylonitrile (Surfactant B).

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Poly(styrene-*b*-(vinyl alcohol))
As A Polymeric Surfactant

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INTRODUCTION

There are many advantages of using nonionic polymeric surfactants. These include the inherited advantages of nonionic surfactants such as better stability in the presence of mild acids, bases, and electrolytes. Hydrophilic properties can be easily adjusted for oil/water or water/oil emulsions, and the surfactants are compatible with most polymers. Polymeric surfactants have the added advantages of excellent mechanical stability, better oxidation resistance, and they do not have to be removed from the base polymer, thus reducing the production cost. Therefore, a good nonionic polymeric surfactant is highly desirable. There are relatively few categories of commercially available polymeric surfactants. Poly[(ethylene oxide)-*b*-(propylene oxide)] block copolymers are widely used, but are relatively low in molecular weight. Poly(vinyl alcohol) has relatively high molecular weight, but is only effective in stabilizing poly(vinyl acetate) latices. In this study, the main objectives were to prepare a block copolymer with nonionic nature for stabilizing latices, and to develop an understanding of the mechanism which allows stabilization to take place.

In this study, a di-functional initiator, 4-(*t*-butylperoxycarbonyl)-3-hexyl-6-(7-*t*-butylperoxycarbonyl)heptyl) cyclohexene, was used to synthesize poly(styrene-*b*-(vinyl acetate)) in a two-stage polymerization. The amphipatic block copolymer, poly(styrene-*b*-(vinyl alcohol)), was obtained by hydrolyzing poly(styrene-*b*-(vinyl acetate)) in a dioxane-aqueous sodium hydroxide mixture. This block copolymer dispersed very well in a water-dioxane mixture and was used as a polymeric surfactant. This process is novel for the preparation of block copolymers of styrene and vinyl acetate.

Dispersion polymerizations of styrene, vinyl acetate, and methyl methacrylate were carried out using poly(styrene-*b*-(vinyl alcohol)) as the protective colloid. Very stable vinyl monomer latices were obtained. The kinetics of the dispersion polymerization of styrene in the presence of poly(styrene-*b*-(vinyl alcohol)) and the particle sizes of the resulting latices were studied in detail.

EXPERIMENTAL

Synthesis of Poly(styrene-*b*-(vinyl acetate))

A di-functional initiator, 4-(*t*-butylperoxycarbonyl)-3-hexyl-6-(7-*t*-butylperoxycarbonyl)heptyl) cyclohexene (D-S606 from Pennwalt Corporation), was used to synthesize poly(styrene-*b*-(vinyl acetate)) in a two stage polymerization. Solution polymerization was used for the preparation of polymeric initiators and for the preparation of block copolymers. Both benzene and toluene were used as solvents. The polymerizations were carried out in 8 oz. bottles. The general recipes for the preparation of polystyrene initiators and for block copolymer synthesis are shown in Tables I and II. Selective solvent extraction was used to separate the block copolymer from polystyrene and poly(vinyl acetate) homopolymers.

Saponification of block copolymer

Poly[styrene-*b*-(vinyl acetate)] was saponified to poly[styrene-*b*-(vinyl alcohol)] by direct saponification. The direct saponification was done with gradual addition of aqueous KOH solution into the dioxane solution of the block copolymer under low heat. The extent of saponification was determined by the amount of KOH. Block copolymers were saponified to 100% and 88% for comparison.

Dispersion polymerization of vinyl monomers

The polymerization recipe is shown in Table III. This recipe follows the conventional emulsion polymerization recipe except dioxane was used to disperse poly[styrene-*b*-(vinyl acetate)] in the hydrolysis process. The surfactant solutions were prepared by dilution of the poly[styrene-*b*-(vinyl alcohol)] in water-dioxane mixture directly with water after the hydrolysis process without further purification.

RESULTS AND DISCUSSION

For a better understanding of emulsion polymerization system that is stabilized by the poly[styrene-*b*-(vinyl alcohol)], styrene monomer was chosen for the study on the following effects:

1. degree of hydrolysis of the block copolymer
2. polymeric surfactant concentration
3. polymerization temperatures
4. types of initiator
5. block copolymer molecular weight
6. dialysis

Two other monomers, methyl methacrylate and vinyl acetate, were also studied for their polymerization behavior when stabilized by the block copolymer, poly[styrene-*b*-(vinyl alcohol)]. As expected, these two monomers behaved differently from the styrene monomer, and they are discussed in a later section.

Two block copolymers were used as polymeric surfactants for the study of dispersion polymerization. The compositions of the two block copolymers (identified as Block I and Block II), their molecular weights, and the polystyrene polymeric initiators they originated from, are all listed in Table IV.

The degree of hydrolysis plays a very important role in determining the solubility of the poly(vinyl alcohol) homopolymer. This is also true for the poly[styrene-*b*-(vinyl alcohol)] amphipatic block copolymer. The solubility of the block copolymer in turn affects the ability of the block copolymer to function as a surfactant in stabilization of latices. The monomer conversion versus time curves for styrene polymerization in 88% and 100% hydrolyzed block I solutions are shown in Figure 1. The 88% hydrolyzed poly[styrene-*b*-(vinyl alcohol)] block copolymer has a higher solubility in water just like the 88% hydrolyzed poly(vinyl alcohol) homopolymer and lead to a more stable latex.

The amount of the polymeric surfactant used was varied from 1, 3 and 5 parts per 100 parts monomer. No apparent influence on the rate of styrene polymerization was observed.

The differences in the block copolymers and their polystyrene to poly(vinyl acetate) block ratios studied also have no apparent effect on the polymerization kinetics. The scanning electron microscopy studies show the difference in block copolymer lengths do affect the particle size. Although the system in general follows bulk kinetics.

The monomer conversion versus time curves for AIBN and potassium persulfate indicate that the use of AIBN results in higher rate of polymerization. This is due to the fact that the monomer soluble AIBN exists inside the particles.

The rate of styrene polymerization in a dialyzed polymeric surfactant solution was compared with the rate

of polymerization in a non-dialyzed polymeric solution. It was found that, in both solutions, the rates of polymerization were almost identical.

Under the exact same polymerization conditions as styrene, methyl methacrylate and vinyl acetate monomers were also polymerized in the polymeric surfactant solution of block I. After the addition of these two monomers into the polymeric surfactant solutions, very stable latices were formed for both methyl methacrylate and vinyl acetate. When polymerizations were carried out, the polymers produced started to precipitate out of the surfactant solution in particulate form. No stable latex was obtained. This is in contrast with the styrene latices which remained stable throughout the polymerization process.

The monomer conversion versus time curves for AIBN-initiated polymerizations of methyl methacrylate and vinyl acetate at 70°C are plotted in Figure 2. The figure shows that the rates of polymerization for both methyl methacrylate and vinyl acetate are faster than for styrene. This is partially attributed to precipitation of the polymers once they are formed. Poly(methyl methacrylate) and poly(vinyl acetate) are less compatible to the polymeric surfactant - poly[styrene-*b*-(vinyl alcohol)]. The polystyrene block in the polymeric surfactant lacks the compatibility with the oil phase (polymer/monomer mixtures) so the surfactant lost its anchoring ability to stabilize the latices. Therefore, the system can no longer be stabilized by the polymeric surfactant, and the polymers formed precipitated out of the surfactant solution. The precipitation of the polymers provided the driving potential for the polymerization process because the monomers can react with each other better without the hindrance of polymer in the particle.

The three different monomers studied; styrene, methyl methacrylate, and vinyl acetate, all gave stable emulsions before polymerization began. However, only the polystyrene latex showed stability throughout the polymerization process. This phenomenon is attributed to the use of poly[styrene-*b*-(vinyl alcohol)] block copolymer as a surfactant and can be visualized as follows: Prior to polymerization, the polystyrene block from the poly[styrene-*b*-(vinyl alcohol)] can be swollen to a different degree by all three monomers. The monomers act as diluents in the particles. The poly(vinyl alcohol) block of the block copolymer dispersed into water phase. As the polymerization process progresses, the amount of monomer in the latex particles is also reduced. Polystyrene chains are less compatible with poly(vinyl acetate) or poly(methyl methacrylate), but are more compatible with polystyrene and styrene monomer. Poly(vinyl alcohol) can only stabilize vinyl acetate emulsions because the residual poly(vinyl acetate) block can penetrate into the vinyl acetate particles, providing extra anchoring ability. Likewise, the extra penetrating ability of polystyrene chains into polystyrene particles enabled polystyrene particles in the latex to be stabilized throughout the polymerization.

The extra anchoring ability of the hydrophobic block of an amphipatic block copolymer, and its role in obtaining a stable latex, are very important in the study and utilization of amphipatic block copolymers as polymeric surfactants. An amphipatic block copolymer can therefore be custom made for a special monomer to be stabilized.

CONCLUSION

(1). A sequential initiator with cyclic perester peroxide and primary peroxide was used to synthesize poly[styrene-*b*-(vinyl acetate)]. The preparation of the block copolymers was carried out in a two-stage polymerization in a free radical system.

2). With the addition of dioxane, the poly(styrene-(vinyl alcohol)) aqueous solution from the direct hydrolysis process could be used as a polymeric surfactant solution. The polymeric surfactant solutions are used to study vinyl monomer dispersion polymerizations.

3). Very stable latices were obtained for styrene, methyl methacrylate, and vinyl acetate monomers. This indicates the poly(styrene-*b*-(vinyl alcohol)) could be used as an oil-in-water stabilizer.

(3). The anchoring ability of polystyrene chains of the poly(styrene-*b*-(vinyl alcohol)) was shown in the dispersion polymerization of styrene monomer. When compared with methyl methacrylate and vinyl acetate polymerizations, only in styrene polymerization were stable latices obtained. This is because polystyrene chains can penetrate the polystyrene particles better than other kinds of polymer particles.

(4). The dispersion polymerization of styrene monomer stabilized by poly(styrene-*b*-(vinyl alcohol)) followed bulk kinetics because of the large particle size. The particle sizes were over 1 micrometer. The systems were stabilized through steric stabilization.

(5). The particle sizes could be controlled by adjusting the polystyrene and poly(vinyl alcohol) block lengths and the concentration of the block copolymer.

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Table III
General Recipe
for Dispersion Polymerization

Material	Weight
Polymeric Surfactant	1-5
Monomer	100
Water	154
Dioxane	41
Initiator	1-0.5

* Polymerization temperature: 65-75°C

Table IV
Polystyrene Initiators, Molecular Weights,
and Saponification Numbers of
Poly(styrene-*b*-(vinyl alcohol)) that
Were Used as Polymeric Surfactants

	Block I	Block II
Polystyrene Initiator	PS-11	PS-2
Polystyrene M_n	34,000	20,300
Block Copolymer M_n	129,000	68,100
Saponification Number	471	453
Polystyrene : Poly(vinyl acetate)	1 : 2.76	1 : 1.92

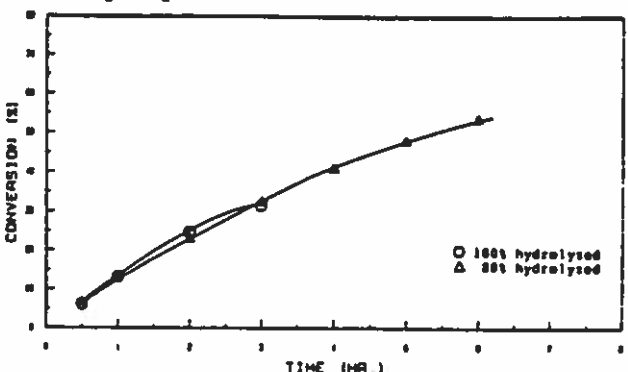


Figure 1. Effect of degree of hydrolysis of Poly(styrene-*b*-(vinyl alcohol)) on styrene dispersion polymerization (initiator: AIBN; temperature: 70°C; surfactant conc. 5 Phr monomer)

Table I
General Recipe for Solution Polymerization
of Polymeric Initiator

Material	Weight in grams	Moles
D-5606	5.0	0.0805
Styrene monomer	60.0	0.672
benzene or toluene	100.0	1.282

Polymerization temperature 65°C or 75°C
D-5606: initiator
4-(*t*-butylperoxycarbonyl)-3-hexyl
-6-(7-(*t*-butylperoxycarbonyl)-
heptyl(cyclohexane))

Table II
General Recipe for Block Copolymer Synthesis

Material	Weight in grams
Polystyrene Initiator	5.0
Benzene	30.0
Vinyl Acetate	10-20

Polymerization temperature : 96-110°C
Note: vinyl acetate to polystyrene initiator weight ratios: 4 to 1 and 2 to 1

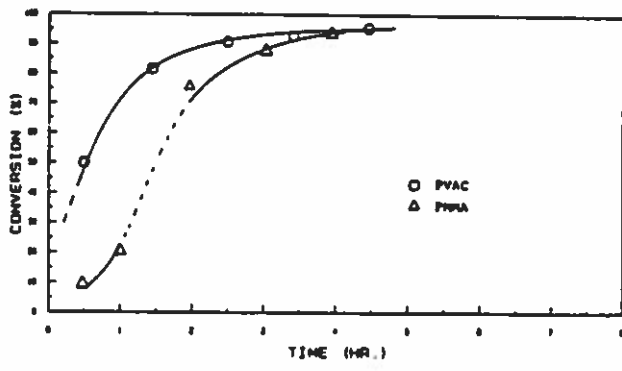


Figure 2. Conversion versus time curves for vinyl acetate and methyl methacrylate dispersion polymerization (stabilized by block I; temperature: 70°C; initiator: AIBN)

29 APR 85

SURFACE ACTIVITY AND STABILITY
PROPERTIES OF POLYMETHACRYLATE-G-
POLYETHYLENE OXIDE POLYMERS

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INTRODUCTION

It has been shown that polymeric surfactants with the stabilizing moiety grafted onto a strongly adsorbing backbone are very effective in stabilizing dispersions (1-3). The mechanism of stabilization has been described as steric stabilization in terms of the solution thermodynamics of the stabilizing moiety (4).

In this work we compare the stabilization and adsorption of PMMA-g-PEO polymeric surfactants with nonionic surfactants (alkoxylated nonylphenol-ethers, NP-EO_n). The two types of surfactants are expected to stabilize the dispersion (a latex) sterically in the same way. The adsorption behaviour, however, need not be the same since one type is a graft copolymer and of high molecular weight while the other is a block copolymer and of low molecular weight.

EXPERIMENTAL

Materials

The polymeric surfactants were synthesized by transesterification of a PMMA chain with a monohydroxy polyethylene oxide of varying chain lengths. The composition of the grafted polymers was preliminarily analyzed using the C-H stretch bands in the IR spectra. The molecular weights of the starting materials and the degrees of transesterification are given in Table I.

The nonionic surfactants were nonylphenol polyethylene oxide ethers with 10, 20 or 50 EO units in the PEO chain. They were supplied by Berol Kem AB, Stenungsund, Sweden.

The polyvinyl chloride (PVC) and polystyrene (PS) latexes were prepared without the use of any emulsifier. Potassium persulfate was used as initiator and thus the surface charge that stabilizes the latexes originates from sulfate radicals. The synthesis of the PVC latex was carried out at the Department of Polymer Technology at Åbo Akademi, Finland. The PS latex was synthesized in this laboratory.

Methods

The surfactant was added to the PVC latex and the mixture was allowed to equilibrate for 24 h at room temperature. The final solids contents of the latex was always 4%. The sample was then sheared (shear rate = 14000 s⁻¹) for 10 min. in an apparatus consisting of two concentric cylinders. After the shearing the sample was diluted 100 times and filtered. The ratio of the absorbance of the filtrate at 500 nm, a_1 to that of a similarly diluted but unsheared sample, a_0 is taken as a measure of the stability, i.e. a_1/a_0 varies from 0 (unstable latex) to 1 (completely stable).

Freeze-thaw stability. Samples were prepared as for the mechanical stability tests. They were kept at -18°C for four days and then thawed. The stability was then determined as for the tests of mechanical stability. Only one freeze-thaw cycle per sample was performed.

The adsorption of the surfactants was measured on a monodisperse, emulsifier-free PS latex. The surfactant-latex mixture was allowed to equilibrate for 24 h after which concentration of surfactant in the aqueous phase was determined by measuring its refractive index increment.

RESULTS AND DISCUSSION

Mechanical Stability of a PVC Latex

Figure 1 shows the effect of added polymeric surfactant on the mechanical stability of a PVC latex. In all cases, except one, the stability rapidly raises to one, i.e. complete stability, at a polymeric surfactant level just below 1 mg/m². This compares very well with the effect on the mechanical stability of the NP-EO_n nonionic surfactants shown in Fig. 2a-c. Here the stabilization sets in at surfactant levels of 0.6-0.7 mg/m². Using molecular dimensions from X-ray data on solid surfactants (5) one finds that this level corresponds to a calculated close packed monolayer of the surfactants lying down on the surface.

A straightforward interpretation is that both the polymeric surfactants and the nonionics at low concentrations probably adsorb flat on the latex surface. When the latex surface is fully covered, the surfactants begin to extend their ethylene oxide chains into the aqueous solution and steric stabilization sets in.

These effects may be compared to the results of increasing the surface charge density by adsorbing sodium dodecyl sulfate, SDS, on the latex. Fig. 2d shows that the mechanical stability raises continuously until a monolayer of SDS is formed at ~ 1 mg SDS/g latex. Salt stability tests clearly demonstrated that SDS and NP-EO_n stabilize latex dispersions by electrostatic and steric stabilization mechanisms, respectively. Thus, mechanical stability can be achieved by both electrostatic and steric stabilization as shown in Fig. 2.

Freeze-Thaw Stability of a PVC Latex

Figure 3 shows the effect of polymeric surfactants on the freeze-thaw stability of a PVC latex. All the polymeric surfactants are able to stabilize the latex. However, freeze-thaw stability sets in at a higher surfactant level than mechanical stability. This is also found for the nonionic surfactants shown in Fig. 4a-c. For both types of surfactants this level corresponds to the maximum adsorption of the surfactants on PS latex (see below). Previous work (6) has shown that in the adsorption of NP-EO_n on PVC or PS latexes the plateau value of the adsorption isotherm is reached when the surfactants are close-packed with the hydrophobic nonylphenol part in contact with the surface and the ethylene oxide chain directed towards the aqueous solution.

Thus, in order to achieve freeze-thaw stability a close-packed layer of surfactants standing upright on the latex surface is required. SDS does not stabilize the latex (Fig. 4d). Hence, freezer-thaw stability apparently requires steric stabilization.

While stabilization against shear just requires that some EO chains extend into solution, freeze-thaw stability thus requires higher surfactant concentration, corresponding to a close-packed monolayer of extending EO chains.

Adsorption on a PS Latex

The adsorption isotherms for the polymeric surfactants on the PS latex are shown in Fig. 5. In all cases the adsorbed amount reaches a limiting value. All isotherms approximately obey a Langmuir-type equation, i.e.

$$\Gamma = \Gamma_{\infty} \frac{bc}{1+bc} \quad (1)$$

where Γ_M is the limiting, or maximum, adsorbed amount, c is the concentration in the equilibrium solution and b is the equilibrium constant governing the partitioning of the surfactant between the equilibrium solution and the surface.

Table II shows Γ_M and b obtained from fitting eq. (1) to the experimental results. In the table previous results of the adsorption of NP-EO on PS latex (6) have been included. The table reveals that the limiting adsorbed amount, Γ_M , expressed in mass per unit latex surface is approximately the same for all the surfactants. If we assume that the IR determination of the composition of the polymeric surfactant is accurate enough, we can calculate the molecular cross sectional surface area, also shown in Table II. These values are approximately 20-30% of the area the molecules would occupy if the whole PMMA backbone were in touch with the surface, as shown in Fig. 6a. We thus conclude that the configuration shown in Fig. 6b is more probable. Such a configuration could be more favorable (a) because it is entropically more favorable than the configuration in Fig. 6a and (b) because it would imply a lower number of contacts between the PMMA backbone and the water molecules.

In Table II the partition coefficients, b , differ very much when comparing the polymeric surfactants with the NP-EO. The reason for this fact could be that while the NP-EO molecules are singly dispersed in water (at concentrations below the plateau value, which occurs around the cmc) the polymeric surfactants form monomolecular associates, where the PMMA backbone is folded up to form a core, and the PEO side chains are in contact with the water. Assuming such a configuration the polymeric surfactants would not gain much energy upon adsorption on the latex surface.

The adsorption of NP-EO, however, is associated with a loss of unfavorable nonylphenol-water contacts. It has been shown that ca 80% of the adsorption free energy is due to the exchange of nonylphenol-water contacts to nonylphenol-nonylphenol and water-water contacts. The remaining 20% of the adsorption free energy is due to the replacement of surface-water contacts to surface-nonylphenol contacts (7).

Thus, if the polymeric surfactants in the aqueous solution have a configuration that minimizes contacts between the hydrophobic moiety and water molecules, the largest contribution to the adsorption free energy will vanish. This would explain the relatively low values of the equilibrium constant b , in Table II.

We thus conclude that the polymeric surfactants give the same stabilization behaviour as the nonionic surfactants. The greatest difference between the two types is in their driving force of adsorption, i.e the equilibrium constant, b . A possible explanation for this difference would be that the conformation of the polymeric molecules in aqueous solution is always such that the contacts between hydrophobic moiety and water are minimized. This effect, in the case of NP-EO, would become important only above the cmc. Thus, at least for this type of surfactant, adsorption of the polymers is actually much weaker than for the simple surfactants.

TABLE I
Characterization of the Polymeric Surfactants

	M_{PMMA}	M_{PEO}	Degree of substitution x a)
A	83 000	350	12
B	83 000	550	10
C	83 000	550	9
D	83 000	750	6
E	83 000	750	9
F	20 000	750	8

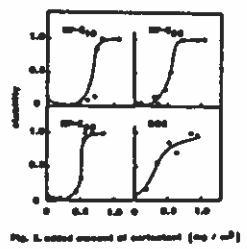
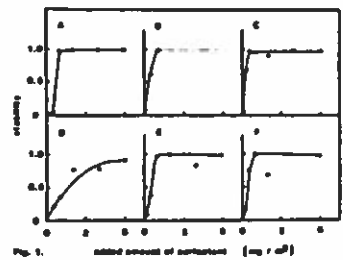
a) from IR spectroscopy

TABLE II
Adsorption Data of Polymeric Surfactants and Nonionic Surfactants on PS Latex

Surfactant	Γ_M mg/m ²	A_2 Å ² /molecule	b ml/mg
B	2.2	$9.4 \cdot 10^3$	1.7
C	1.7	$12 \cdot 10^3$	0.7
D	2.0	$10 \cdot 10^3$	1.4
E	2.0	$11 \cdot 10^3$	1.1
F	1.8	$2.4 \cdot 10^3$	1.9
NP-EO ₁₀	2.0	54	136
NP-EO ₂₀	1.7	106	49
NP-EO ₅₀	2.0	200	9

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Figs. 1 and 2. Mechanical stability, a_1/a_0 , of a PVC latex as a function of added amount of polymeric surfactant (Fig. 1), and nonionic surfactant (Fig. 2); per unit latex surface area.

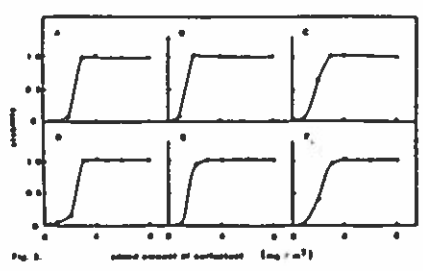


Fig. 3.

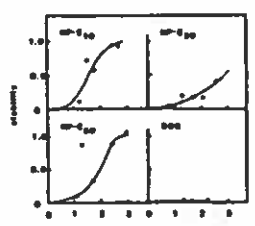


Fig. 4.

Figs. 3 and 4. Freeze-thaw stability, a_1/a_0 , of a PVC latex as a function of added amount of polymeric surfactant (Fig.3), and nonionic surfactants (Fig. 4), per unit latex surface area.

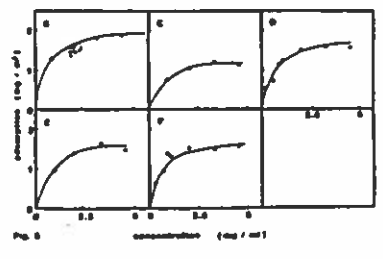


Fig. 5.

Fig. 5. The adsorption isotherms of polymeric surfactants on PS latex.

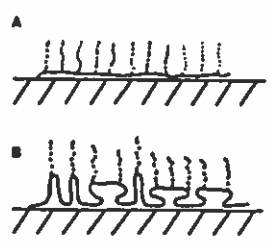


Fig. 6.

Fig. 6. Possible configurations of the polymeric surfactants on a hydrophobic surface.

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