The 4th 'Polymer Colloids' Gordon Research Conference seems to have been as successful as the previous three. The minutes of the Annual Business Meeting appear on a following page. As explained there, it was not possible to decide whether to hold the 1984 Annual Meeting in Montreal or Pittsburgh but a final decision should be taken in time to be notified in the Spring Newsletter.

The deadline for copy for the Spring Newsletter will be Monday 26th March 1984. It is important to ensure that reproduction costs (@ 4 p per sheet) are no higher than they need be. Contributions should not normally exceed 3 pages, single-spaced typing should be used if at all possible, and the carrying over of a few lines to a new page avoided.

The Plastics and Rubber Institute is planning a 2nd International Conference on Polymer Latex to be held in London in June or November 1983. Although 400 word summaries of proposed contributions are requested by 10 October 1983, it might be possible to accept later offers. The Institute's Telex is 912881. The address is Mr M.D.Shuttleworth, P.R.I., 11 Hobart Place, London, SW1W OHL.

Other forthcoming international conferences of possible interest are the 5th International Symposium on Surfactants in Solution (K.L.Mittal) to be held near Bordeaux, France, 9-13 July 1984 (Information from P. Lalanne, Centre de Recherche Paul Pascal, Domaine Universitaire, 33405 Talence CEDEX, France) and the International Rubber Conference in Moscow, 4-8 September 1984 (Information from Prof. V.A.Berestnev, Krasnobogatyrskaya St. 42, Moscow 107258, U.S.S.R.)

David Blackley has had a new book published by Applied Science, London at £ 36 entitled 'Synthetic Rubbers: their chemistry and technology' ISBN 0 85334 152 4.

The price of the two-volume set 'Science and Technology of Polymer Colloids' containing the papers given at the N.A.T.O. Advanced Study Institute in Bristol in 1982 is approximately £55. Distributers are Kluwer Academic Publishers, Dordrecht. ISBN 90-247-2334-7.

David Blackley apologies for failing to provide a contribution for this issue - the first he has missed - a three-week trip to Malaysia and Thailand at the critical time is the reason.

The technical departments of I.C.I. Petrochemicals and Plastics Division have removed from Welwyn Garden City to modern laboratories on Teeside: Derek Rance's address is now I.C.I. plc Petrochemicals and Plastics Division, P.O. Box 90, Wilton, Middlesbrough, Cleveland, TS6 8JE, England.

The programme for the International Symposium on Emulsion Copolymerisation and Copolymers to be held at Lyons, France, 7-9 March 1984 should be available by the time this issue of the Newsletter reaches members. Inquiries to Christian Pichot, C.N.R.S. Laboratoire des Materiaux Organiques, B.P. 24, 69390 Vernaison, France. Telephone (7) 802.13.44. Telex 900225 CNRS VILRB-F.

Vivian Stannett is on secondment to the Office of Naval Research London Branch Office (223 Old Marylebone Road: Telephone 01-409 4340) until the end of December 1983: his duties there have prevented him providing a contribution for this issue.

A.S.D.

Lehigh University

Bethlehem, Pennsylvania 18015

EMULSION POLYMERS
INSTITUTE

CO-DIRECTORS

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July 18, 1983

TO: A. S. Dunn
        F. L. Saunders

FROM: J. W. Vanderhoff

SUBJECT: Meeting of the Polymer Colloid Group

The Polymer Colloid Group met July 14, during the Gordon Research Conference "Polymer Colloids" held July 11-15, 1983, at Tilton, New Hampshire. Present were D. R. Bassett, D. C. Blackley, J. S. Dodge, M. S. El-Aasser, R. M. Fitch, R. G. Gilbert, J. W. Goodwin, F. K. Hansen, A. Klein, I. M. Krieger, B. Kronberg, R. H. Ottewill, C. Pichot, I. Piirma, R. L. Rowell, T. G. M. van den Ven, J. W. Vanderhoff, and R. A. Wessling.

It was resolved that A. S. Dunn be given a vote of thanks for his sterling services as Secretary.

The members were reminded that the next contribution for the Newsletter would soon be due and that there were some notable defaulters the last time. Those defaulters present promised to meet the next deadline.

The two main subjects discussed were future meetings and membership.

The next Gordon Research Conference will be held in summer 1985 with R. A. Wessling as Chairman. It was decided to continue the present biennial schedule. R. H. Ottewill was elected Vice-Chairman for this 1985 meeting and thus will be Chairman for the summer 1987 Conference.

The next meeting of the Group will be a symposium organized by T. G. M. van de Ven for the 1984 Canadian CIC meeting to be held in Montreal June 3-6, 1984. These dates conflict with the year-end examinations in the U. K. and Norway, the Lund microemulsion symposium in Sweden, and the Lehigh Emulsion Polymers Short Course.

Also, I. M. Krieger is organizing a session on rheology of dispersions for the Colloid and Surface Science Symposium to be held in Pittsburgh June 11-13, 1984. A show of hands indicated that eight of those present would attend the Montreal meeting; moreover, one or two papers would be contributed by Lehigh, although J. W. Vanderhoff and M. S. El-Aasser would not be able to attend. Therefore, it was decided that T. G. M. van de Ven should proceed with the organization of the program.

Another show of hands indicated that ten of those present would attend the Pittsburgh meeting. Therefore, the question as to the locaton and time of the next business and discussion meetings of the Group was left to T. G. M. van de Ven and I. M. Krieger. Possible times discussed were Sunday June 3 or Thursday June 7 in Montreal, or Sunday June 10 or Thursday June 14 in Pittsburgh. Accommodations could be easily arranged in Montreal, but there might be some difficulty with accommodations in Pittsburgh, as there is no member of the Group in that city. It was left to T. G. M. van de Ven and I. M. Krieger to work out the best compromise for the busines and discussion meetings.

Travel funds for foreign speakers might be available for both meetings.

Also announced was the CNRS meeting on emulsion copolymerization to be held in Lyon in March 1984 (contact C. Pichot, CNRS, Laboratoire des Materiaux Organique BF 74, Vernaison 69390, France) and the AIChE meeting on various aspects of emulsion polymers to be held in Philadelphia in August 1984 (contact S. M. Ahmed, Hercules, Inc., Research Center, Wilmington, Delaware 19808, U.S.A.).

Several possibilities were discussed for the 1986 meeting. R. M. Fitch proposed the Wingspread Conference Center, Racine, Wisconsin, which holds conferences supported by the Johnson Foundation. He will investigate this possibility. The possibility of holding another conference under NATO sponsorship will be investigated by R. H. Ottewill. The possibility of securing support from the Engineering Research Foundation (which sponsors conferences similar to the Gordon Research Conferences) will be investigated by M. S. El-Aasser and R. M. Fitch. And, of course, the Group is always welcome to meet at Lehigh, where summer housing is available and the auditorium facilities are good; the meeting could be held in conjunction with the Emulsion Polymers Short Course, which would help defray the travel expenses of members who could speak at the Short Course.

Elected to membership was Donald C. Sundberg, Department of Chemical Engineering, Kingsbury Hall, University of New Hampshire, Durham, New Hampshire 03824, U.S.A.

The meeting was adjourned, with the intention of meeting next in summer 1984, either in Montreal or Pittsburgh.

PRELIMINARY CALL FOR PAPERS

International Symposium on Polymer Colloids.

Sponsored by the Macromolecular Science Division of the Canadian Institute of Chemistry.

The symposium is part of the 67th annual CIC meeting to be held June 3—6, 1984 in Montreal, Canada.

The topics will include: Preparation and Reaction Engineering, Characterization, Stability, Applications and Rheological Properties.

Details regarding registration can be found in the September issue of "Chemistry in Canada" and will be sent to all interested in attending.

If you are interested in attending the meeting and/or presenting a paper, please return the enclosed form. Abstracts of papers should reach us by the end of January, 1984.

Please circulate this announcement to your colleagues.

Please return forms to:

Dr. T.G.M. van de Ven, Department of Chemistry, McGill University, 3420 University Street, Montreal, Quebec, Canada. H3A 2A7

or

Dr. R. Pelton, Pulp and Paper Research Institute of Canada, 570 St. John's Boulevard, Pointe Claire, Quebec, Canada. H9R 3J9

NAME:_____

AFFILIATION:_____

MAILING ADDRESS:_____

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☐ I am interested in attending the International Symposium on Polymer Colloids

☐ I would like to present a paper
Proposed title:_____

☐ I would like to present a short communication (20 mins).
Proposed title:_____

☐ I will need financial assistance in attending symposium

☐ I would like to make use of the McGill dormitories

☐ I will make my own hotel reservations

Comments:_____

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A SYMPOSIUM ON EMULSION POLYMERS AND EMULSION POLYMERIZATION

Sponsored by the American Institute of Chemical Engineers at their 1984 National Summer Meeting.

AUGUST 19-22, 1984
PHILADELPHIA, PA, U.S.A.

Topics:
New Concepts in Emulsion & Dispe Polymerization, Computer Modelir in Emulsion & Dispersion Polymerization, Rheology of Virgin and Compounded Latices, Applications of Polymer Colloids in Biological Systems.

CALL FOR PAPERS

Please send title and a short abstract (60 words) of your paper be December 31, 1983. Complete manuscript of accepted papers will be due on May 1, 1984.

Submit Abstract to
Dr. Syed M. Ahmed
(Symposium Chairman)
Research Center
Hercules Incorporated
Wilmington, DE 19894

UMIST

The University of Manchester Institute of Science and Technology

PO Box 88, Manchester M60 1QD
Telephone 061-236 3311
Dr A. S. Dunn

Department of Chemistry

Are Latex Particles Nucleated from Micelles at All?

There is a sharp increase in the number of latex particles formed and, consequently, in the Interval II polymerisation rate at the c m.c. of the emulsifier in the case of monomers of low water solubility (e.g. styrene) which is not observed for monomers with a higher water solubility (e.g. vinyl acetate, methyl methacrylate). For these latter monomers, the Fitch-Roe homogeneous nucleation mechanism is now generally accepted: this must also apply to styrene etc. below the c.m.c. when there is no possibility of micellar nucleation in the absence of micelles. We argued in a paper presented in the Emulsion Polymerisation Symposium at the 54th A.C.S. Colloid and Surface Science Symposium held at Lehigh University in June 1980 (subsequently published in J.Dispers. Sci. Tech. 2 (1981) 175 [2-3])that this inflexion in the particle number - emulsifier

concentration or rate - emulsifier concentration curve could be used to determine the c.m.c. of emulsifiers under polymerisation
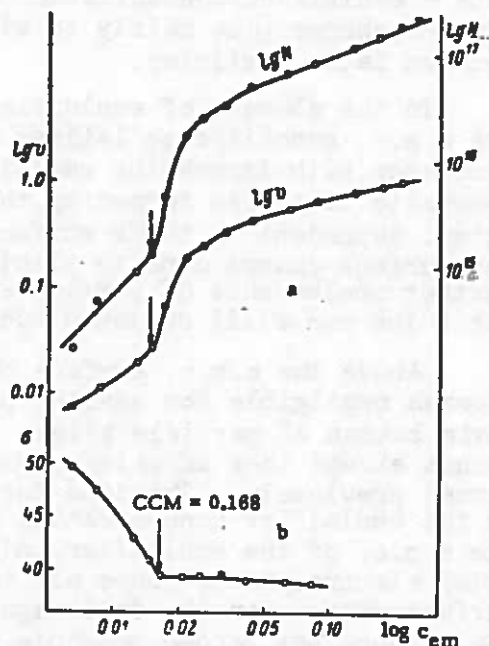

Fig. 1. Dependence of number of particles N (1/100 g of aqueous phase), rate of polymerization v (g/min·100 g of aqueous phase) (a) and surface tension σ (dyn/cm) of initial aqueous phase of emulsion (b) on potassium laurate concentration c_{em} (mole/liter). pH of initial aqueous phase was 11.2 (40°):

F rom M.S.Ryabova, N.I.Smirnov, & S.N Sautin, Zh Prikl. Khim. 49 (1976) 920 [4]: English translation: J. Appl. Chem. USSR 49 (1976) 850.

conditions in cases in which other methods might be difficult to apply. It was not clear, however, precisely which point on the curve should be taken as characteristic of the c.m.c. It now appears from the careful work of the Leningrad group (Fig. 1) that it is the first inflexion which characterises the c.m.c.

But it is only beyond the second inflexion that the order in emulsifier attains something like the value of 3/5 required by the Smith-Ewart theory. It should be noted that the 3/5 order is a necessary consequence of the Smith-Ewart assumption that particle nucleation ceases when the area of the latex particles has increased sufficiently to adsorb all the emulsifier in a saturated monolayer (with the consequence that the micelles disappear) and that it cannot account for emulsifiers exponents above or below 0.6 which are observed with some emulsifiers, e g. Piirma and ang (A.C.S. Symposium Series 24 (1976)34) using mixtures of sodium dodecyl sulphate with a non-ionic emulsifier found that the emulsifier exponent rose to 0.76 for a mixture containing only 4.84 mole % of the anionic emulsifier.

An alternative explanation of the shape of the S-shaped particle number/ rate - emulsifier concentration curve may be the effect of increasing surface charge (due mainly to adsorbed emulsifier) on the rate of coalescence between latex particles.

In the absence of emulsifier and at emulsifier concentrations below the c.m.c. monodisperse latices are obtained with a particle size which decreases with increasing emulsifier concentration. These particles are composite particles formed by the coalescence of primary particles to an extent dependent on their surface charge i.e. coalescence proceeds until the surface charge density attains a sufficiently high value to prevent further coalescence of particles of similar size although primary particles can still coalesce with the composite particles.

Above the c.m.c. surface charge increases and the rate of coalescence becomes negligible for smaller particle sizes progressively resulting in a distribution of particle sizes. Beyond the upper inflexion no coalescence occurs except that of primary particles with larger particles which have formed previously. The time for which coalescence can be prevented depends on the emulsifier concentration and the ionic strength (which depends on the c.m.c. of the emulsifier and the initiator concentration in absence of added electrolytes). Once all the available emulsifier has been adsorbed, surface charge density falls again as the particles grow and limited coalescence may become possible again changing the shape of the particle size distribution.

Monomers which are less water soluble than styrene are not polymerised in emulsion by water soluble initiators unless the concentration in the aqueous phase is increased e g. by addition of a little alcohol (cf. D...J.Osmond, ICI Paints Division, in the Polymer Colloid Newsletter, 7 (1977) [1 - April]). Consequently it seems possible that micelles do not actually play any part in the mechanism of emulsion polymerisation and the fact that the critical surface charge density is attained for hydrocarbon monomers at about the same concentration as the c.m.c. is more or less coincidental (i.e. both phenomena are a consequence of the hydrophobic effect). The more polar polymers (acrylic esters, vinyl acetate etc.) adsorb ionic surfactant much less strongly than hydrocarbon polymers. Consequently the concentration at which the critical surface charge density is attained will be much higher than the c.m.c. under polymerisation conditions (although it might coincide confusingly with the c.m.c. determined in absence of additives taken from the literature). Sutterlin does find S-shaped rate-emulsifier concentration curves in his experiments with acrylic ester using a semi-continuous polymerisation technique (cf. Fitch ed. 'Polymer Colloids II' (1980) p. 583).

Polymer Colloid Newsletter

R. M. Fitch
Corporate Research
Johnson Wax

Appended are pages from recent publications which may be of
interest to members. The one with Tarcha, Dumais, and Jelinski
is in press with J. Polym. Sci., Polymer Physics Ed. The
abstract is for a main lecture that I am to give at the
conference on "Polymers and Water" to be held at Bad Nauheim, W.
Germany, April 2-3, 1984 and spo nsored by the Polymer Division
of the Gesellschaft Deutscher Chemiker. I have not seen a final
program, so that I don't know how many other papers there will be
on emulsion polymerization. Interested persons could contact
Prof. Dr. Hans Rudolf, Bayer AG, FE Chemische Forschung, 5090
Leverkusen, W. Germany. The paper by Liang and me on dynamic
mechanical behavior of polymer monolayers may have some interest
to those involved in steric stabilization. It will be published
in the ACS Symposium Series (August, 1983 ACS Meeting in
Washington, D.C.) under the editorship of Des Goddard of Union
Carbide. I'd be happy to send manuscripts of any of these to
interested persons.

Work here at Johnson Wax will involve the use of dielectric
spectroscopy (frequency response analysis) to measure
conductivity, double layer capacity and surface electrical
potentials of polystyrene model colloids. These will be compared
to results obtained by titration, coagulation kinetics,
electrophoresis, and QELS.

R. M. Fitch:bhs
September 26, 1983

Particle Morphology of Self-Hydrolyzed Acrylate Polymer Colloids.
A ^{13}C NMR and DSC Study.

P. J. Tarcha[1], R. M. Fitch[2]

Department of Chemistry and Institute of Materials Science
University of Connecticut, Storrs, CT 06268

J. J. Dumais, L. W. Jelinski

Bell Laboratories, Murray Hill, New Jersey 07974

Introduction

Acrylate polymer colloids which have initiator-derived acidic surface groups undergo self-catalyzed hydrolysis in aqueous media. These systems have potential as controlled release agents for biologically active alcohols and amines, and it is thus of interest to understand the kinetics and mechanism of hydrolysis of these systems. The kinetics of self-hydrolysis in a series of alkyl polyacrylate latexes, in which the alkyl groups are methyl, cyclohexyl, benzyl, and β-napthyl and of poly(methyl methacrylate) latexes have been found to follow similar patterns (1). Two constant-rate intervals are generally observed, the first rate being faster but of shorter duration (6-10 hours at 90°C). The second rate has been observed to remain constant for as long as 1200 hours at 90°C. Typical hydrolysis results are shown in Fig. 1.

The rate behavior has been interpreted in terms of a reaction zone in the outer regions of the particle, within which the concentrations of reactants do not change significantly. This model leads to the expectation that the latex particles will obtain a core-shell morphology, in which the core is pure acrylate polymer, and the shell is mainly the product poly(acrylic acid) (PAA).

If the particle interior is sufficiently hydrated, random hydrolysis might occur, catalyzed by both surface strong acid groups migrating into the particle and by those buried inside. If the microsphere

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Methyl acrylate polymer colloids which have been self-catalytically hydrolyzed by bound strong acid surface groups derived from the initiator, have been studied by ^{13}C NMR and thermal measurements. NMR is sensitive both to chemical structure and to the molecular dynamics of the polymer chains observed. The temperature-dependence of the NMR integrated intensity at various levels of hydrolysis supports a model of a reaction zone of constant composition up to at least 30% hydrolysis. It appears that as a result of this kind of reaction, the particle obtains a core-shell morphology, in which the shell is composed of a PAA/PMA copolymer. This shell is swollen and plasticized by water, resulting in greatly enhanced segmental mobility of the polymer chains as evidenced by marked narrowing of the NMR lines.

Thermal analysis indicates that PMA is compatible to a considerable extent with its partially hydrolyzed analog.

New Scientific Aspects of Emulsion Polymerization

by
Robert M. Fitch
Vice President, Corporate Research
The Louis Laboratory, S. C. Johnson & Son, Inc.
Racine, Wisconsin 53403, U.S.A.

Abstract

Recent developments in the theory of particle formation in
emulsion polymerization will be discussed.   Primary emphasis
will be placed on the homogeneous nucleation mechanism.   A review
will be given of the Hansen-Ugelstad/Fitch-Tsai (HUFT) theory.
It will be applied, with extensions, to recent experimental
results on the polymerization of an homologous series of acrylate
esters and methyl methacrylate.   Light scattering intensity was
employed to follow the kinetics of nucleation and growth of the
latex particles during the first few tens of seconds of
reaction.   Other variables included were monomer and surfactant
concentrations.   Factors which were found to be particularly
important are the critical chainlength at which nucleation
occurs, particle swelling by monomer, and surfactant
concentration as it affects coagulation kinetics, and the rate
constant for the capture of oligomeric radicals by particles.
Values for these parameters have been obtained by means of
computer modeling of the experimental data.   Experiments on
heterogeneous nucleation also have been carried out, including
micellar nucleation.   These include polymerizations "seeded" by
latex particles, fine monomer emulsions, or monomer-swollen
surfactant micelles.

RMF:bhs
September 26, 1983

Do Not Type on This Line

Dynamic Behavior of Hydrophobically Modified Hydroxyethyl Celluloses at Liquid/Air and Liquid/Liquid Interfaces

Do not type past this

Shu-Jan Liang and Robert M. Fitch[1]

Institute of·Materials Science and
Department of Chemistry

The University of Connecticut
Storrs, Connecticut 06268

A new class of amphiphilic, surface-active graft co-polymers, hydrophobically modified hydroxyethyl celluloses (HM-HEC's) are comprised of a cellulose backbone with short polyethylene oxide (PEO) and grafted alkyl side chains. They are excellent steric stabilizers of O/W emulsions.

Polymer monolayers, formed by adsorption from solution at various liquid interfaces, were compressed and expanded in a modified Langmuir trough with a Wilhelmy plate. Variables included polymer molecular weight, alkyl chain length and degree of grafting. The mono-layers generally exhibited large hystereses in dynamic pressure/area curves.

A quantitative model is proposed for the dynamic response, which is based on the hypothesis that the elastic part is due to thermal motions, while the viscous part is due to adsorption and desorption of chain segments and molecules.

The rheological properties of a fluid interface may be charac-terized by four parameters: surface shear viscosity and elas-ticity, and surface dilational viscosity and elasticity. When polymer monolayers are present at such interfaces, viscoelastic behavior has been observed (1,2), but theoretical progress has been slow. The adsorption of amphiphilic polymers at the inter-face in liquid emulsions stabilizes the particles mainly through osmotic pressure developed upon close approach. This has become known as steric stabilization (3,4,5). In this paper, the dynamic behavior of amphiphilic, hydrophobically modified hydroxy-ethyl celluloses (HM-HEC), was studied. In previous studies HM-HEC's were found to greatly reduce liquid/liquid interfacial tensions even at very low polymer concentrations, and were extremely effective emulsifiers for organic liquids in water (6).

[1]Current Address: S. C. Johnson & Son, Inc., 1525 Howe Street, Racine, Wisconsin 53403

Kinetics of the Diffusion of Small Molecules across Polymer Monolayers

SHU-JAN LIANG AND ROBERT M. FITCH[1]

*Department of Chemistry and Institute of Materials Science, The University of Connecticut,
Storrs, Connecticut 06268*

DEDICATED TO THE MEMORY OF HERBERT FREUNDLICH

A new method for following the diffusion kinetics of small molecules into polymers and liquids involves measurement of the time dependence of the angular light-scattering intensity exhibited by a monodisperse colloid during swelling by the diffusant. The colloidal particles may be comprised of glassy or rubbery polymer or of a liquid. The experiments are conducted at constant external diffusant activity. Characteristically, after the first few minutes the diffusion rate becomes dependent upon the "surface barrier," i.e., the concentration gradient at the interface. When polymers are adsorbed at the interface the diffusion is retarded to an extent which apparently depends upon the chain conformations and the magnitude of polymer–diffusant interactions. Furthermore, slow changes in the kinetics over a period of several days are observed which are also attributable to conformational changes. Confirmation of these results was obtained by measurement of sedimentation velocities during ultracentrifugation of the corresponding polymer-coated latex particles at various times over a period of 7 days.

INTRODUCTION

The diffusion kinetics of small molecules into colloidal particles comprised of polymers or liquids, may be controlled by (a) the activity of the diffusant in the external phase, (b) the migration rate of the diffusant through the interface, (c) the solubility of the diffusant, and (d) the mobility of the diffusant within the particles. Investigation of swelling kinetics has been carried out using various techniques, such as centrifugation (1), size determination with a Coulter counter (2), vapor pressure measurement (3), and small angle neutron scattering (4). However, the results reported showed great dissimilarities, most of which may be attributable to variations of the activity of the diffusant in the external (aqueous) solution during the swelling. In this paper, the swelling kinetics by tetrahydrofuran (THF) of monodisperse polystyrene latexes are studied by means of

the time dependence of angular light-scattering intensities. The experiments are conducted at constant external diffusant activity. In some experiments, a copolymer of poly(acrylic acid) and cetyl–eicosyl (50–50) acrylate and in others, a hydrophobically modified hydroxyethyl cellulose are employed to coat the polystyrene particles. The effects of the adsorption of polymer on the swelling kinetics are investigated. Previous studies in suspension polymerization suggested the possibility of retardation of diffusion of monomer molecules across the layer of protective colloid (5).

EXPERIMENTAL

1. Materials

Monodisperse polystyrene latex (PS-B2). The latex (PS-B2) was prepared by seed polymerization using potassium persulfate initiator. Steam distillation was employed to remove unreacted monomer from the poly-

[1] To whom correspondence should be addressed.

COLLOID RESEARCH AT MCMASTER UNIVERSITY - RECENT DEVELOPMENTS

by

Archie Hamielec

1. McMaster Institute for Polymer Production Technology

Search for sponsor companies for the Institute ($15,000 US/yr. for a 3-year period) has begun in earnest. To date 7 companies have joined and the target number by year end is 12. The target number at steady-state is 30.

2. Semi-batch and continuous emulsion polymerization - adhesives

No further progress to report.

3. Semi-batch and continuous emulsion polymerization of styrene/butadiene

No further progress to report.

4. Semi-batch emulsion polymerization of styrene/acrylonitrile

No further progress to report.

5. Bulk and solution polymerization of p-methyl styrene

Extensive experimentation on the kinetics of synthesis of the new Mobil Chemical Co. monomer, p-methyl strene (>98% para isomer) has permitted the development of effective process models of batch and continuous reactors for the production of crystal poly(p-methyl styrene).

6. Thermal degradation of poly(p-methyl strene)

This work is being done in the Institute of Physical Chemistry, University of Heidelberg in collaboration with Professor K.H. Ebert.
No progress to report at this time.

7. Aqueous free radical polymerization of acrylamide at high polymer concentrations

Extensive experimentation on the kinetics of synthesis of polyacrylamide at high polymer concentrations has lead to the development of a polymer reactor model which accounts for diffusion-controlled termination.

The work reported herein is being done in collaboration with Dr. J.F. MacGregor, McMaster University.

For publication in 'Journal of Polymer Science'

Morphology of Core-Shell Latex Particles

S. MUROI, Coating Materials Laboratory, Asahi Chemical Industry,
Co., Ltd., Shizuoka, Japan

INTRODUCTION

Many studies [1-5] have shown that with stage feed polymerization of monomer or monomer mixture II in the presence of seeds of homopolymer or copolymer I from a second monomer or monomer mixture, the structure of the resulting latex particles ranges from the homogeneous through the simple-domain to the core-shell depending on the solubility of monomer II in polymer I, the miscibility between polymers I and II, and the hydrophilicity, interfacial tension and molecular weight of polymer I.

Practical study has been most extensive for the core-shell morphology, as films produced from this type display a higher gas barrier [6] and a higher modulus [7, 8] than those produced under similar conditions from homogeneous latex particles formed from the same basic components.

Lee [5] has demonstrated that the determining factor in forming core-shell morphology is the hydrophilicity of polymer and that in two-stage polymerization the shell is always composed of the more hydrophilic polymer, by electron microscope observation, surface acid titration, alkali swelling, and surface reactivity.

In the present study the internal structure of latex particles was observed more directly by utilization of the progressive dissolution of the carboxylated latex particle from the surface, which has been reported in various studies [8-11] to occur with increasing pH. The starting materials were methylacrylate monomer (MA) for the more hydrophilic polymer, ethyl acrylate monomer (EA) for the less hydrophilic polymer, and methacrylic acid monomer (MAA) for carboxylation.

EXPERIMENTAL

Preparation of Latex Samples

All latex samples were prepared by two-stage-feed emulsion polymerization in 1l flasks, with the ingredients shown in Table 1 and the monomer mixtures shown in Table 2.

Table 1. Emulsion polymerization recipe

Stage	Ingredients	Weight, grams	
1st Stage	Monomers	50.00	premix
	n-Dodecyl mercaptan	0.10	
	Levenol WZ	0.40	
	Potassium persulfate	0.15	
	Emulgen 913	1.60	
	Distilled water	470.25	
2nd Stage	Monomers	50.00	premix
	n-Dodencyl mercaptan	0.10	
	Potassium persulfate	0.15	premix
	Distilled water	14.85	

Table 2. Monomeric composition of latex samples

Sample	Feed Composition mol-%		Theoretical Composition mol-%		
No.	First Stage	Second Stage	MA	EA	MAA
I	EA/MAA(90/10)	MA/MAA(90/10)	0.481	0.419	0.100
II	MA/MAA(90/10)	EA/MAA(90/10)	0.481	0.419	0.100
III	EA/MAA(90/10)	EA/MAA(90/10)	--	0.900	0.100
IV	MA/MAA(90/10)	MA/MAA(90/10)	0.900	--	0.100
V	EA/MA/MAA (45/45/10)	EA/MA/MAA (45/45/10)	0.450	0.450	0.100

Ratio of first-stage feed to second-stage feed: 1/1 by weight

For each sample, the first-stage mixture was fed into the flask, which was then purged with nitrogen gas and heated to 75°C. After polymerization at 75°C for 1 hr. to obtain conversion of 95% or more, the second-stage feed mixture was added at constant rate over 1.5 hrs. and the flask was then maintained at 75°C for an additional 5 hrs. It was confirmed by light scattering measurement and electron microscope observation that the first-stage feed monomers formed polymer seeds and that the second-stage feed monomers were polymerized without forming other new particles.

The sample latex thus prepared was purified primarily by dialysis in cellophane tube and secondarily by ultra-centrifugation at 30,000 rpm for 5 mins. The purified latex sample was diluted with distilled water to a polymer concentration of 7%, and the sample was stabilized by addition of a surfactant mixture of the same content as that used in the polymerization, to achieve a saturated coating of the latex particles.

Determination of Optical Density with Increasing pH

The latex was diluted with water to a polymer concentration of 0.1%, and the pH was then gradually increased by addition of 0.1N aqueous NaOH at 1 mℓ/min. to 1,000 mℓ of the polymer solution while stirring. Samples were taken at appropriate intervals in 10 mm-square quartz cells, and their optical density measured by a photometer under incident light of 610 μ m. Lambert-Beer's law was applied to obtain readings corrected for polymer dilution by the NaOH solution. A temperature of 20°C was maintained throughout.

Separation of Dissolved Polymers from Latex Particles

500g of latex was placed in a 1ℓ flask equipped with a stirrer. 0.1N aqueous NaOH solution was added gradually by burette while stirring. During this addition, 20 mℓ samples of the latex were taken at appropriate intervals. Each of these samples was subjected to ultra-centrifugation at 30,000 rpm for 30 mins. to separate the dissolved polymer from the undissolved latex particles, in the manner described in a previous paper[11]).

Determination of Dissolved Polymer

Separated fraction containing dissolved polymer was subjected to analysis by NMR absorption and titration. For the non-carboxyl component the ratio of MA content to the sum of MA and EA content, and thus the MA content, was determined by ordinary NMR absorption spectroscopy, with correction for the presence of surfactant. Preliminary trials demonstrated extremely close correlation between known and measured composition. MAA content was determined by acid titration.

RESULTS

Effect of Elevated pH on Optical Density

The relation between the pH and the optical density for each of the six latex samples is shown in Fig. 1. The samples can be
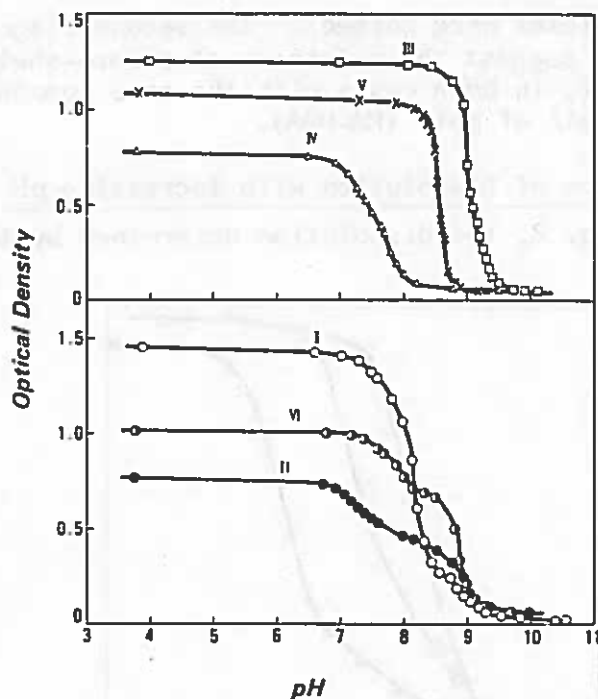

Fig. 1. Change in optical density of latex samples with rising pH

O : Sample I (EA-MAA/MA-MAA),   ● : Sample II (MA-MAA/EA-MAA),
□ : Sample III (EA-MAA/EA-MAA),   △ : Sample IV (MA-MAA/MA-MAA),
X : Sample V (EA-MA-MAA/EA-MA-MAA),   ◑ : Sample VI (Blend of
Sample III and IV in equal in weight ratio)

divided into two categories according to the number of inflections on the optical density curve. Samples III, IV and V of Category I each display one inflection. In Category 2, Samples I, II, and VI each display two inflections.

Category 1 is characterized by an S-shaped curve with one
inflection, in which the optical density is largely unaffected by
the initial increases in pH, next falls rapidly through the point
of inflection over a relatively narrow range of rising pH, and then
again becomes largely unaffected by any further increase in pH.
The pH at the point of inflection, or "transition pH ",was lowest
for the most hydrophilic polymer (pH 7.5, Sample IV), highest for
the least hydrophilic polymer (pH 9.0, Sample III), and intermediate
for the third polymer (pH 8.6, Sample V).

In contrast, two transition pHs occurred with the Category 2
samples. This is most clearly evident in the curve for Sample VI,
a blend of Samples III and IV, in which the first transition pH
of 7.7 corresponds to that of Sample III and the second of 8.9 to
that of Sample IV. Although the transition pHs for the other samples
are less evident, they can be detected at pH 8.2 and 9.0 for
Sample I and pH 7.2 and 9.0 for Sample II.

As no new particles were formed in the second-stage polymeriza-
tion, these results suggest the existence of a core-shell morphology
for Samples I and II, in both cases with the core composed of poly
(EA-MAA) and the shell of poly (MA-MAA).

Advance of Dissolution with Increasing pH

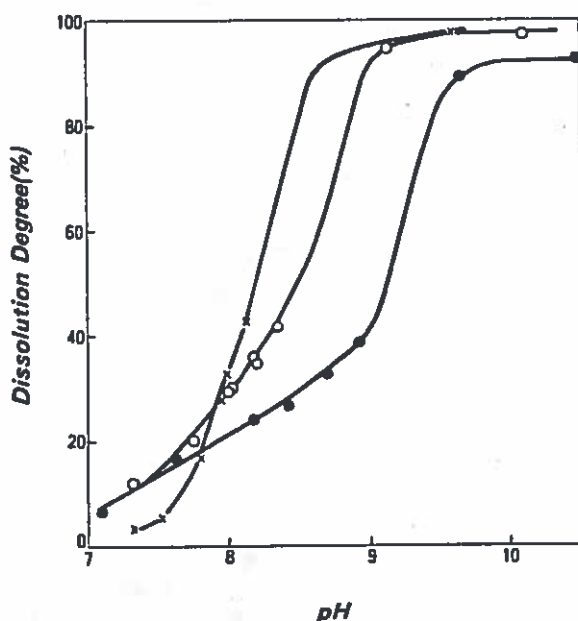As shown in Fig. 2, the dissolution determined by the ultra-

Fig. 2. Dissolution of latex samples with rising pH

O : Sample I, ● : Sample II, X : Sample V

centrifugation progressed with increasing pH. The curves show
that the dissolution progressed rapidly in the range of pH 7.5
to 9.0, which coincides fairly well with the range of rapid decline
in optical density and thus suggests that the change in optical
density was due primarily to the latex particle dissolution.

The absence of a second transition pH corresponding to that shown by the optical density curves may be attributable to the comparatively small number of observations.

Composition of Dissolved Polymers

As shown in Fig. 3, the MA content as a proportion of the
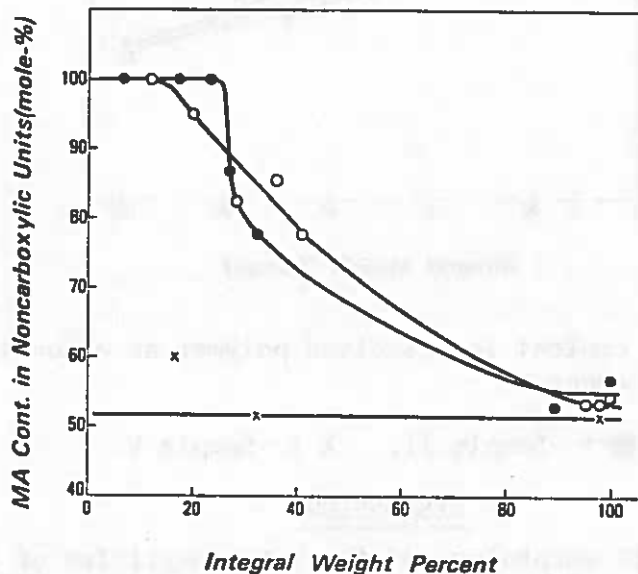

Integral Weight Percent

Fig. 3. MA content in noncarboxylic units of dissolved polymer as a function of integral weight percent

O : Sample I, ● : Sample II, X : Sample V

dissolved noncarboxylic units decreased with the progressing dis-solution of the latex particles for Samples I and II, but remained approximately constant for Sample V. With Samples I and II, the EA units were absent from the dissolved polymer samples taken initially, but their concentration increased in subsequent samples as the latex particle dissolution progressed, until it approached the theoretical limiting value of 46.6 mol-%.

The marked similarity between Samples I and II in respect to decreasing MA content with advancing particle dissolution despite the reversed order of the polymerization stages corresponds closely to the changes which were observed in their optical density.

For all three of these samples, as shown in Fig. 4, the MAA content was high in the initial dissolved polymer samples and decreased in subsequent samples taken as the particle dissolution progressed, until it approached the theoretical limiting value of 10 mol-%.
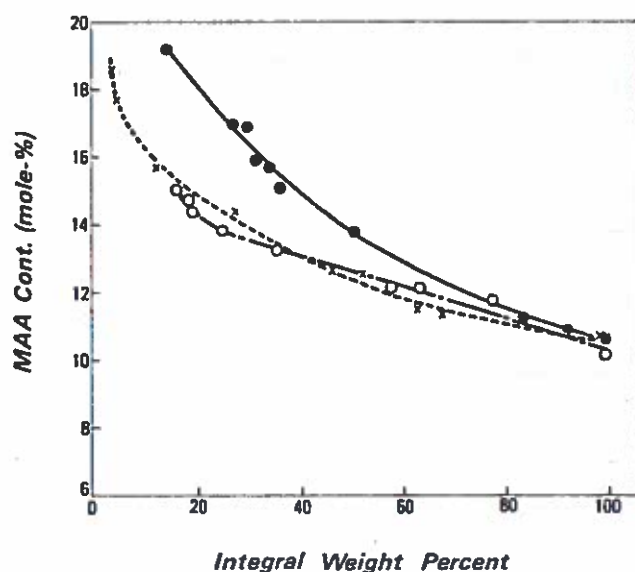
Integral Weight Percent

Fig. 4. MAA content in dissolved polymer as a function of integral weight percent

○ : Sample I,   ● : Sample II,   X : Sample V

DISCUSSION

The core-shell morphology of the latex particles of Samples I and II is clearly evidenced by the optical density measurements and the analysis of the alkali-dissolved polymers. To more clearly illustrate this morphology, Fig. 5 shows the distribution of each monomer unit in the particle as a function of the distance from the particle center, as determined by differentiation of their respective integral distribution curves by the method described in our above-cited previous paper[11]

The shells of the latex particles in both Sample I and Sample II, which were prepared under conditions tending to produce core-shell morphology, were found to be composed of poly(MA-MAA), which decreased gradually in concentration with increasing proximity to the center of the particles. On the other hand, poly(EA-MAA) was not present in the outer shell but was found in increasing concentrations, together with poly(MA-MAA), with increasing proximity to the center.

This morphology was shared by both Sample I and Sample II, even though Sample II had been prepared by polymerizing EA-MAA mixture in the presence of poly(MA-MAA) seeds and Sample I by polymerizing MA-MAA mixture in the presence of poly(EA-MAA) seeds, thus clearly showing the inversion morphology of the Sample II latex particles. This conclusion is in accord with the results of the above-cited study by Lee[5]

In contrast the latex particles of Sample V, which was prepared under copolymerization conditions, were shown to contain MA in concentrations which were virtually uniform from the surface to the center.
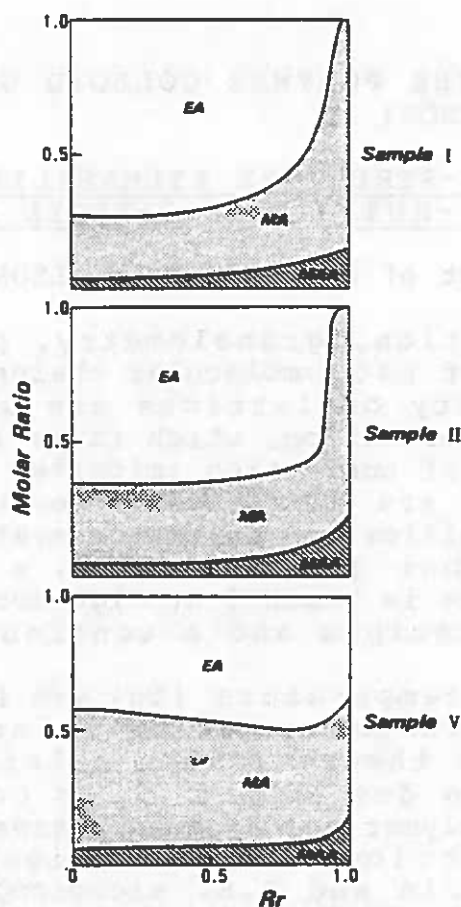
Fig. 5. Distribution of each monomer unit as a function of
particle radius (Rr)

In all of the sample latexes, the MAA concentration was high
at the particle surface and decreased toward the center, in conform-
ance with the tendency described in the literature[11, 12)

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CONTRIBUTION TO THE POLYMER COLLOID GROUP NEWSLETTER
(submitted by C. PICHOT)

SYNTHESIS PROCESS-STRUCTURE FILMABILITY RELATIONSHIP OF
ACRYLONITRILE/n-BUTYL AND 2-HEXYL ETHYL ACRYLATES
COPOLYMERS.
B. ROCCHETTI-Abstract of a thesis-Univ. LYON I-Sept.29,1983.

Copolymer composition, granulometry, particle structure
(microstructure of macromolecular chains and morphology),
thence filmability of lattices are sensitive to the
mechanism of polymerization, which takes into account above
all of two types of nucleation (micellar and homogeneous).
Experimental data are discussed in terms of acrylonitrile
concentration, emulsifier and initiator systems.
When semi-continuous process is used, a kinetical control
by the addition rate is reached at high conversion with high
initial monomer recipes and a continuous addition of
initiator.
Glass transition temperature (Tg) are found to be higher
than theoretical values, what is related to copolymer
heterogeneity. A theoretical simulation approach of
syntheses has been developped which considers monomer
partition between polymer and aqueous phases.
Filmability behaviour was investigated on basis of
qualitative criteria and S.E. microscopy of the particle
coalescence. Results are related to instantaneous copolymer
composition, Tg, morphology and size of latex particles.

RATE OF POLYMERIZATION AND PARTICLE SIZE IN
COPOLYMERIZATION OF MONOMERS OF DIFFERENT POLARITIES :
STYRENE (S) ACRYLONITRILE (AN) SYSTEM - J. RODRIGUEZ
PALENCIA - J. GUILLOT.

The study deals with the influence of composition and
concentration of persulfate-metabisulfite initiator system
and the influence of emulsifier (SDS) concentration, on
polymerization rate, particle size, conversion limit and
S-AN copolymer composition prepared in batch polymerization
with various initial monomer feeds.
From this investigation it seems possible to derive a quite
accurate and general relationship between these
characteristics through a mechanism which takes into
consideration monomer solubility in water and polymer phases
and two types of nucleation...

FEATURES OF EMULSION COPOLYMERIZATION OF ACRYLONITRILE -
A. GUYOT - Abstract of paper to be presented at the
International Berlin Workshop on Polymer Reaction
Engineering (October 5-7, 1983).

Emulsion copolymerization of acrylonitrile was studied in
batch, corrected batch and semi-continuous processes ;
comonomers are butadiene, styrene or alkylacrylates.

Although acrylonitrile is highly water soluble, the copolymerization process was shown to take place mostly inside the particles. Depending on the saturation of the water phase in comonomer or in emulsifier, the nucleation process may be micellar or homogeneous. A special features is the limitation of the particle size and the continuous formation and deactivation of the particles, as well as the relationship between polymerization process, composition, structure and some properties of the copolymers.

CONTROL OF SURFACE AND STRUCTURAL PROPERTIES IN EMULSION COPOLYMERS - B. EMELIE.

Methyl methacrylate (MMA) - n. Butyl acrylate (BuA) batch emulsion copolymerization was investigated using $S_2O_8K_2$ as initiator and a polyoxyethylated nonyl phenol ether (25 moles of ethylene oxide) as nonionic surfactant. A kinetic study showed that, due to the high solubility of the emulsifier in the water-soluble monomer (MMA), the copolymer composition was affected with comparison to the SDS emulsified copolymerizations.

In the case of mixtures with SDS, the CMC was found to be very close to the CMC of the nonionic surfactant, over a wide range of compositions. That allows to control the particle size of the latexes using different ratios [anionic surfactant]/[nonionic surfactant].

Batch copolymerizations carried out in presence of a carboxylic acid monomer (acrylic or methacrylic acid) seem to point out the presence of molecular associations between the ethylene oxide groups of the emulsifier and the carboxyl groups of ionic comonomers. It appears that a more stable complex is obtained with methacrylic acid, under the polymerization conditions used in this study.

PREPARATION AND CHARACTERIZATION OF STYRENE-nBUTYL ACRYLATE EMULSION COPOLYMERS - J.L. GUILLAUME.

Batch emulsion copolymerizations of styrene (S) with n. butyl acrylate (BuA) were carried out with or without emulsifier. In presence of sodium dodecyl sulfate (SDS), monomer reactivity ratios were derived ($r_S = 0.59$; $r_{BuA} = 0.23$) ; it was found a continuous decrease of the particle number during the polymerization ([SDS] > CMC), contrary to what was expected by the classical theory. This phenomenom appeared to be not dependent on the comonomer mixture composition as well as on the type and amount of initiator. Experiments are beeing carried out to investigate the following parameters : nature and concentration of surfactant - monomer/aqueous phase ratio.

Emulsifier-free copolymerizations were also studied ; it was found that, under identical conditions, the final particle size was the same, regarding of the comonomer mixture composition. However, as the butyl acrylate content increased, results in a lower surface change density (strong acid group) and higher molecular weight of the final copolymer. One of the reasons to explain this result could be the high polymerization rate of n. butyl acrylate : monomer sequence distribution analysis of the copolymers by ^{13}C.NMR would corroborate this assumption.

INVERSE EMULSION COPOLYMERIZATION STUDIES - V.GLUKHIKHE - C. GRAILLAT - C. PICHOT.

Copolymerizations of acrylamide (Am) with methacrylic acid (MA) were investigated using AIBN as initiator. Selection of the emulsifier system was based on stabilization and interfacial tension studies of the initial monomer emulsions. Mixture of surfactants such as Sorbitan Sesquioleate - C_{18} mercapto terminated acrylamid oligomers was found to impart good stability. Due to its partition between organic and aqueous phases, MA comonomer was assumed to act as a cosurfactant.

Kinetics of copolymerizations was determined as a function of MA content and aqueous phase pH. A higher rate of polymerization than that for both monomers was found at pH = 10 ; the reverse is true at pH = 4. Quantitative data on the partition of MA in organic and aqueous phase were also determined. It was detected that under acidic conditions a high amount of MA prevails in toluene, depending on the acrylamide concentration.

From these experimental results monomer reactivity ratios were derived. As expected, a strong effect of pH on these parameters (mainly r_{MA}) was confirmed :

$$r_{Am} = 0.55 \; ; \; r_{MA} = 0.15 \text{ at pH} = 10$$
$$r_{Am} = 0.58 \; ; \; r_{MA} = 4.15 \text{ at pH} = 4$$

These differences were found to also have an effect on the molecular characteristics of the copolymer (molecular weight and monomer sequence distributions).

From this study, it appears that under basic conditions, the main polymerization loci are the initial monomer droplets whereas under acidic conditions a more complicated polymerization mechanism probably occurs. It is assumed that not only polymerization takes place in both phases, but a diffusion process of methacrylic acid (or MA rich oligomers) through the organic phase could control the kinetic.

Contribution to Polymer Colloid Group Newsletter

from

The University of Akron

Submitted by Irja Piirma

1. Ever since the observation of phase inversion during emulsion
polymerization of styrene with the nonionic surfactant Emulphogene
BC-840 the study has been expanded to include a large number of
important monomers and commercially available nonionic surfactants.
Preliminary results indicate that all the monomers studied show the
formation of normal o/w emulsions at lower polymerization temperatures,
and a w/o emulsion at higher temperatures. The PIT value varies from
system to system. When w/o emulsion is the starting phase for polymer-
ization, an inversion to o/w occurs at some stage of conversion due to
the decrease in the concentration of the hydrocarbon phase. It was
found that the best procedure to judge a system for its feasibility
as to the formation of o/w emulsion exclusively was to construct a
phase diagram for volume fraction vs. temperature and volume fraction
vs. HLB value of surfactant.

2. There is a study going on with p-methyl styrene to investigate
the kinetics of this monomer in emulsion polymerization. As had
been found previously by Gerrens, this monomer does not follow the
so-called ideal Smith-Ewart kinetic scheme. The study with this
monomer is also going to be expanded to include nonionic and mixed
ionic-nonionic emulsifier systems.

3. Synthesis of some graft and block copolymers is under way. For
example polyvinyltoluene-g-N-vinyl pyrrolidone and lauryl meth-
acrylate-co-N,N-dimethyl acrylamide have been synthesized so far
and are being tested as surfactants in polymerization.

CONTRIBUTION TO THE POLYMER COLLOID GROUP NEWSLETTER

Submitted by F. L. Saunders, Dow Chemical Co., Midland, MI - U.S.A.

SURFACE CHARACTERIZATION OF EMULSIFIER-FREE STYRENE/ BUTADIENE LATEXES

B. W. Greene

Several styrene/butadiene latexes were prepared by conventional emulsion polymerization in the absence of emulsifier using various concentrations of ammonium persulfate as the initiator. These were subsequently cleaned up by dialysis or serum replacement and characterized by conductometric titration, surface tension, stability, and electrophoretic mobility measurements. The conductometric titration results indicated the presence of only strong acid groups on the surface of the latexes and showed that the surface charge densities were low (approximately 1 - 3 charged groups/500 A^2). The surface tension data were in agreement with the latter, showing that most of the latex surface was "free" to adsorb surfactant. The mobility of the latexes in water and in the presence of divalent (2:1) electrolyte was as expected for colloids with strong acid surface groups. However, the mobility of the latexes in the presence of monovalent (1:1) electrolyte was anomalous, showing the behavior expected for colloids with weak acid surface groups. The latter results were interpreted in terms of structural effects.

KINETICS OF EMULSION POLYMERIZATION OF STYRENE-SIMULATION MODEL WITH VARYING FREE RADICAL CAPTURE EFFICIENCY

C. I. KAO, D. P. GUNDLACH, R. T. NELSEN

A kinetic model has been developed and successfully applied to describe the reaction profiles of the seeded emulsion polymerization of styrene. The model incorporated a mechanism for the capture of aqueous phase oligomeric free radicals by latex particles. Both the collision and diffusion mechanism were considered. The experimental data agreed well with the collision mechanism. The rate of the free radical capture by latex particles is proportional to latex particle surface area (Dp^2), and also is a strong function of the rate of free radical generation per latex particle. The model predicts that the rate of polymerization is dependent on the latex particle diameter to the 2.5 power in the gel region. This was demonstrated experimentally by Vanderhoff, et.al. Propagation and termination rate constants for styrene in the 70-90°C temperature range were also determined.

POLYMER COLLOID GROUP - NEWSLETTERS.

Activity in Trondheim.

Our work have been very much centered on use of monosized polymer particles in medical applications. We have for this purpose been making monosized polymer particles with different functional groups and measured bound antibody and activity of bound antibody to bind antigen Our work with magnetic particles are very challenging. We have as reported bound antibody to porous magnetic particles which have been used for treatment of patients with neuroblastoma by a removal of cancer cells from the bone marrow, at the Institute of Child Health in London.

The method has been used on several patients and even if it is still too soon to draw any conclusion, the medical doctors are very encouraged as the patients have yet not shown any reformation of cancer cells and are in good condition.

These particles have been porous magnetic particles. For some other cancer cells than neuroblastoma cells, they did not bind to the cells satisfactorily. An example is liver cancer cells.

We have investigated other types of particles, especially compact ones with hydroxyl groups at the surface and with covalent coupling of the antibody.
These particles have proven to be much more effective and we are investigating the preparation and use of new magnetic particles, all characterized by being monodisperse but with different surface and different ways of antibody binding.

In the figure below we show an example of new magnetic particles, i.e. hydrophilic,biotolerable and possibly biodegradable particles. The shape is due to that we in this case have prepared the particles in a way which leads to expelling of the original polystyrene seed particle.
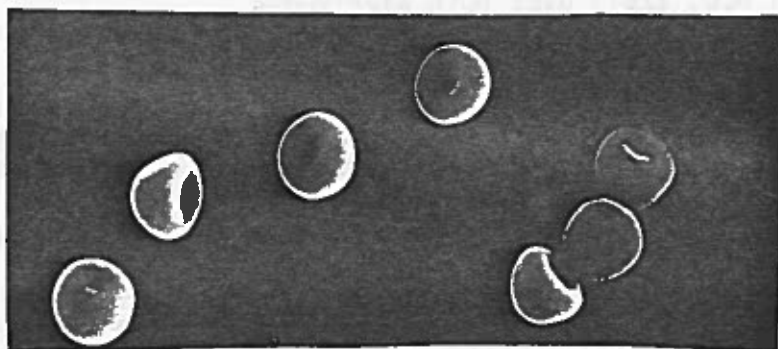
Our work with non-magnetic particles for marking of cancer cells and magnetic particles for removal of cancer cells will soon appear in several papers. Especially a common paper by J. Ugelstad, A. Rembaum, J. Kemshead, K. Nustad andr R. Schmid will be published in a book given out in connection with a meeting in Amsterdam in the end of October on use of microspheres in connection with cancer, where both Rembaum and I are invited to present papers.

Trondheim, 25. September 1983

John Ugelstad

Contribution to the Polymer Colloid Group

T.G.M. van de Ven
Pulp and Paper Research Institute of Canada
and
Department of Chemistry, McGill University,
Montreal, Canada, H3A 2A7

The following are summaries of a letter submitted to the Journal of the Optical Society of America, a paper submitted to JCIS and a note to be submitted (probably JCIS).

Creating color patterns with ordered latices (M. Tomita and T.G.M. van de Ven)

Color patterns can be created by applying different electrical voltages over various regions of an ordered latex dispersion. From electrically induced changes in diffraction patterns, consisting of a bright halo containing a dark ring, obtained by illuminating and observing the latex dispersion normally, the structure of the latex dispersion responsible for the color changes can be deduced.

A sample of ordered latex is placed between two electrodes E_1 and E_2, E_1 consisting of a gold coated glass plate and E_2 being a stainless steel electrode. The electrodes are separated by a rubber spacer (of thickness 1 mm). In order to observe variations in color, in some experiments E_2 was partly coated by insulating paint, leaving a cross-shaped stainless steel electrode. To observe the dark ring, the sample was illuminated normally through the gold-coated glass plate using a He-Ne laser. The back scattered light was reflected onto a mirror and photographed with a 35 mm camera. The mirror had a hole at its center to allow passage of the laser beam. The angle between the laser beam and mirror was 45°. We applied either an A.C. field (frequency range 0.1 - 1000 Hz) or a D.C. field over both electrodes.

Without the electric field the latex appeared green. With the field, depending on its polarity, a reddish pink or a dark blue cross appeared in a green background. Because the color is due to Bragg diffraction, the colors of both background and cross changed with illumination and observation angle. The contour of the cross was less sharp than that of the electrode and showed more or less rounded corners. The pink cross was more distinct than the dark blue one, probably because of a larger color contrast.

Changes in dark ring radius can best be seen by applying an A.C. field, in which case the dark ring radius oscillates periodically. Oscillations were observed for peak to peak voltages in the range 1 - 2 V and for frequencies up to 10 - 20 Hz. At higher frequencies the dark ring appeared immobile. It was observed that not only the dark ring, but also the halo was oscillating. However, their phases were opposite, i.e. when the dark ring expanded, the halo shrank. Changes in the outer radius of the halo were smaller than changes in dark ring radius. At higher voltages the dark ring disappeared as in the case of a D.C. field, but the halo oscillation became more pronounced.

From these experiments it can be concluded that the spacing between layers is smallest near the positive electrode and largest near the negative one. For each particle the force exerted on it by the external electric field is balanced by double layer forces arising from an asymmetrical distribution of particles. As a result the spacing between layers varies gradually from one electrode to the other. Due to incoherent scattering and absorption of light in the dispersion, not all particles contribute equally to the intensity of the diffracted light, but the contribution of particles near the glass plate dominates and determines the color of the diffracted light and the dark ring radius. When the gold coated glass plate is negative, the spacing between layers near the plate increases, resulting in a pink color, while when the plate is positive the spacing decreases, resulting in a blue color. We have shown before that the radius of the dark ring decreases with increasing volume fraction, while the outer radius of the halo increases with increasing volume fraction. When the ordered latex is subjected to an oscillating electric field, the local volume fraction near the glass plate increases and decreases periodically. As a result the dark ring and the halo oscillate periodically as well. Because of the different dependence on volume fraction the phases of the oscillation of dark ring and halo are opposite, i.e. when the dark ring contracts, the halo expands and vice versa.

The structure of sheared ordered latices (M. Tomita and T.G.M. van de Ven)

Shear-induced changes in the structure of ordered latices have been observed by grating diffraction and right angle Bragg diffraction. The former method provides information about the two-dimensional structure of the layer of latex particles parallel to the wall, while the latter provides information about the packing of the two-dimensional layers. Both methods showed that order is maintained when ordered latices are subjected to shear. Grating diffraction experiments revealed that at moderate shear rates the hexagonal packing of latex particles was compressed in the flow direction and expanded in the direction normal to the flow, and that at high shear rates the hexagonal packing was compressed in all directions. The right angle Bragg diffraction experiments revealed that at high shear rates the spacing between the sliding layers increased by 1.5 to 10%. These observations are qualitatively explained by a proposed sliding layer model.

Calculation of diffraction angles in ordered latices (M. Tomita and T.G.M. van de Ven)

The meaning and validity of a widely used equation for light diffraction in ordered latices has been reconsidered. A new method to calculate diffraction angles has been proposed by applying a theory describing the deviation from Bragg's law in X-ray diffraction. It has been shown that the equation, originally derived intuitively, is a good approximation when the angle of the incident light and the diffraction angle are close to 90° and when the volume fraction of latex particles is low.

The equation usually assumed is

$$\lambda_A = 2n_\ell \, d \, \sin\theta$$

λ_A = wavelength of light in air, n_ℓ is defractive index of dispersion, d = spacing between layers and θ is diffraction angle.

Instead we propose

$$2d\ n_w\ \sin\theta = \lambda_A \left(1 + \frac{\delta}{\sin^2\theta} \right)$$

with

$$\delta = -\frac{3}{2} \frac{m^2 - 1}{m^2 + 1} \phi$$

m being the refractive index ratio and ϕ the volume fraction.

POLYMER COLLOID GROUP LETTER

autumn 1983

Dispersions of Model Colloids

Current Research at the Van 't Hoff Laboratory in Utrecht

by A. Vrij, Padualaan 8, 3584 CH Utrecht, The Netherlands.

Self diffusion coefficient of silica particles in colloidal dispersion.

When colloidal particles are dispersed in a fluid medium with nearly
the same refractive index, they will look transparant and are amenable to
light scattering studies, even at high volume fractions. Mrs. Kops-Werkhoven
of our group has studied <u>dynamic</u> light scattering on such systems as a
function of particle concentration. Silica particles were synthesized as
follows. Ethoxy silane was hydrolized in an alcohol medium (with NH_3 and water)
according to the method of Stöber.

The spherical, fairly monodisperse particles were made lyophilic by a
terminal bonding of octadecyl alcohol chains to the surface OH-groups. The
particles were dissolved in cyclohexane or cycloheptane. The refractive index
difference between particles and solvent could be monitored by changing the
temperature. The particle radius was $\sim$ 70 nm. At low concentrations the
dispersions showed a single exponent in the *field auto correlation function*

$$g^{(1)}(K = 0,\tau) \sim A \exp(-DK^2\tau)$$

from which the diffusion coefficient D could be determined.
This was described in the previous letter.

Further the following experiment was performed.
A solvent and temperature were chosen in which the particles were nearly
invisible. To these colloidal silica particles in suspension were added a
small percentage of other silica particles with about the <u>same size</u>, but a
<u>different</u> refractive index and thus scattering power.
The two preparations of silica particles were synthesized in <u>different solvents</u>
i.e. ethanol and propanol. This results in particles having a slightly different
refractive index. The difference is, however, large enough to give widely
different scattering power (60x) when one of the particles is nearly matched
in refractive index with the solvent and temperature.

In this way the scattering and the diffusion coefficient of the <u>tracer</u>
particles can be measured as a function of   particle concentration.
This gives the so-called <u>self</u>-diffusion coefficient, which is rather different

from the <u>collective</u> diffusion coefficient (measured by the relaxation of a
concentration gradient) and has a different value in non-dilute solutions
of particles.

Mrs. Kops-Werkhoven in our laboratory measured both diffusion coefficients
with silica particles and found that the collective diffusion coefficient
slightly increases with concentration, whereas the self-diffusion coefficient
to the contrary decreases with concentration. This is typical for particles
that mimic so-called "hard-sphere" interactions.

Reference: M.M. Kops-Werkhoven, C. Pathmamanoharan, A. Vrij and H.M. Fijnaut.
"Concentration dependence of the self-diffusion coefficient of hard,
spherical particles measured with photon correlation spectroscopy."
J. Chem. Phys. 77 (1982) 5913.