

POLYMER COLLOID GROUP NEWSLETTER

Vol. 13 No. 1

20 May 1983

The 4th Gordon Research Conference on 'Polymer Colloids' at Tilton School, is the next major event in the Group's calendar. Details of the programme appear on page 3 and also (along with similar information on all the other Gordon Conferences) in the March 3rd issue of 'Science'!

There are also details of the R.S.C. Faraday Division Autumn General Discussion on 'Concentrated Colloidal Dispersions' to be held in Loughborough, England. Ron Ottewill and Jim Goodwin are on the Organising Committee for this. Papers for presentation at General Discussions are preprinted and sent to registered participants about 3 weeks in advance in the hope that they will be able to make considered comments at the meeting which they will later submit in writing for publication with the papers in the Discussion volume; authors are allowed only five minutes to highlight the main points of their papers to permit adequate time for discussion which is usually fast and furious. Details on page 4.

The dates for the Symposium on 'Emulsion Copolymerization and Copolymers' sponsored by the C.N.R.S. at Lyon, France have now been fixed as March 7 - 9, 1984. The intention is to cover kinetic studies, thermodynamic aspects, emulsifier-polymer interactions, colloidal properties, control of surface groups, and structure-property relations. Further details on page 5.

Bob Fitch has been appointed Vice-President for Corporate Research of Johnson Wax and his address is now S.C. Johnson & Son, Inc., Racine, Wisconsin 53403, U.S.A.. Vivian Stannett has been seconded to the London Branch of the U.S. Office of Naval Research for 18 months: his address (until the end of December 1983) is U.S. Office of Naval Research, 223 Old Marylebone Road, London NW1 5TH: telephone 01-409 4340. His remit is to maintain contact with polymer research groups in Britain and Europe.

Members who are keen on kinetics may wish to note that the definitive paper by M Morbidelli, G Storti, and S. Carra on 'Role of Micellar Equilibrium on Modelling Batch Emulsion Polymerization Reactors' has now been published in J. Appl. Polym. Sci. 29 (1983), 901-19 [3].

Alan Robertson is now Director of the Applied Chemistry Division of the Pulp and Paper Research Institute of Canada and offers his resignation since this means he is no longer active in polymer colloid research although he is still interested in the Group's activities. Theo van de Ven will be organising a Polymer Colloid Symposium for the Macromolecular Science Division of the Chemical Institute of Canada at their 1984 annual meeting which is to be in Montreal, June 3 - 6: Bob Pelton of the Pulp and Paper Research Institute will be co-organiser. This will probably constitute the Group's 1984 meeting. Members who would like to present papers at this meeting should write to Dr T. van de Ven, Dept of Chemistry, Pulp and Paper Building, McGill University, 3420 University St., Montreal, PQ, Canada, H3A 2A7. The 58th A.C.S. Colloid and Surface Science Symposium at Carnegie Mellon University Pittsburg is scheduled for the following week June 10-13, 1984.

The papers presented at last year's N.A.T.O. Advanced Study Institute at Bristol have now been published by Martinus Nijhoff Publishers BV, Lange Voorhout 9-11, P.O. Box 566, 2501 CN, The Hague, Holland in two volumes edited by Poehlein, Ottewill, and Goodwin entitled 'Science and Technology of Polymer Colloids'. No information on the price is to hand, however.

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Group member S. Muroi has published a book (in Japanese) entitled 'Introduction to Macromolecular Latexes' Publishers are Kobunsha of Tokyo. Price 2500 yen.

The 14th Annual Short Course on 'Advances in Emulsion Polymerization and Latex Technology' at Lehigh University is scheduled for 6 - 10 June 1982 with Wiley Daniels, Alan Rembaum, Ron Ottewill, and John Ugelstad as guest speakers. The 6th Annual European Short Course at Davos, Switzerland will be held from 15-19 August 1983.

Members are reminded that to minimise reproduction and distribution costs Newsletter contributions should be typed single spaced. So far as possible, partially filled pages should be avoided and length limited to three pages per Group member (including any diagrams). Academic members are expected to send a contribution (however brief) to each issue and industrial members to contribute whenever they can. Because the number of members now exceeds the number of reprints of publications most members are likely to have available, it is useful to include references to, and abstracts of, papers which have been published or are in the course of publication.

Contributions for the Autumn issue of the Newsletter should reach me at the Chemistry Department, UMIST, P.O. Box 93, Manchester M60 1QD, England by Monday 26th September 1983.

A. S. Dunn

4th Gordon Research Conference on 'Polymer Colloids'Tilton School, New Hampshire

10 - 15 July, 1983

Chairman: John W. VanderhoffVice-chairman: Ritchie WesslingMonday 11 July

I.M.Krieger 'Rheology of sterically stabilized polymer colloids in non-aqueous media.'  
 J.E.Glass 'Rheology of pigmented latex systems containing polymeric surfactants'  
 C.A.Silebi 'Structure formation in thickened latex systems'  
 Y.J.Shih 'Latex particle surface reactions'

Tuesday 12 July

R.H.Ottewill 'Swelling of latex particles by monomer'  
 J.Ugelstad 'Swelling of latex particles and large particle size monodisperse latex particles'  
 G.Reinisch 'Mechanism of emulsion polymerization of vinyl chloride'

Wednesday 13 July

D.C.Blackley 'Mechanical destabilization of natural rubber latex particles'  
 A. Klein 'Formation of coagulum in emulsion polymerization'  
 R.M.Fitch 'Interactions among particles: surface charge effects'

Thursday 14 July

B.W.Greene 'Surface characterization of styrene-butadiene latexes'  
 H.J.Yue 'NMR characterization of latex polymers'  
 B.Kronberg 'Adsorption of ionic and non-ionic emulsifiers on the surfaces of colloidal particles'

Friday 15 July

F.Candau 'Polymerization in inverse microemulsions'  
 M.S.El-Aasser 'Inverse emulsion polymerization of acrylamide'

Attendance is limited to about 100 participants. Applications to attend should be sent to Dr Cruickshank as soon as possible: he will return a Registration Card to accepted applicants which must be returned with the Registration Fee 3 weeks prior to the Conference.

Registration Fee (which includes accommodation and meals) is U.S. \$ 230 for active participants. Participants families can also be accommodated provided children are over 12. There is also a limited amount of alternative accommodation in the vicinity.

Apply to: Dr Alexander M Cruickshank,  
 Director, Gordon Research Conferences,  
Before 11 June: Pastore Chemical Laboratory, After 11 June: Colby-Sawyer College,  
 University of Rhode Island, New London,  
 Kingston, New Hampshire 03257,  
 Rhode Island 02881, U.S.A.  
 U.S.A.

Telephone: (401) 783 4011

Telephone: (603) 526 2970

The Annual Business Meeting of the Polymer Colloid Group will be held during the Conference.

A Chartered bus service is available for booked participants leaving Logan International Airport, Boston, Massachusetts on Sundays at 4.00 p.m. returning after lunch on Fridays to reach the Airport about 3.30 p.m. Concord Trailways provide alternative daily services which, however, now bypass Tilton village, leaving the Airport at 8, 9.30, 11 15 a.m. and 1.15, 3.30, and 7.30 p.m. to Tilton Junction, 2 miles from Tilton School.

Further information. The Final Programme with details of Fees and Application Form for Attendance, Preprints, Accommodation etc. will be issued in May 1983. Request this from: Mrs Y A. Fish, The Royal Society of Chemistry, Burlington House, London W1V 0BN, England.

The Chairman of the Organising Committee is Professor R.H. Ottewill (Bristol)

Phase separations induced in colloidal suspensions by dissolved polymer

A P Gast, C K Hall and W B Russel Princeton University, USA

Rheological investigations of the effect of addition of free polymer to concentrated sterically stabilised polystyrene latex dispersions

D Heath and Th F Tadros ICI Plant Protection Division, Bracknell

Effect of temperature on the viscous behaviour of sterically stabilised latexes

M D Croucher and T H Milkie Xerox Research Centre of Canada, Ontario

Centrifugal sedimentation and viscous flow of weakly-flocculated concentrated dispersions - a comparative study

R Buscall and I J McGowan ICI Corporate Colloid Science Group, Runcorn

Percolation and critical points in microemulsions

D Langevin L'École Normale Supérieure, Paris, France

Phase transitions in liquid-liquid thermodynamically stable dispersions: concentrated aqueous microphases in hydrocarbons

H-F Eicke University of Basel, Switzerland

Electric birefringence studies on concentrated aqueous polyoxyethylene surfactant systems

P G Neeson and B R Jennings Brunel University and G J T Tiddy Unilever, Port Sunlight

Viscoelastic detergent solutions

H Hoffmann, H Rehage, W Schorr and H Thurn University of Bayreuth, West Germany

An informal Poster Session will be included if demand warrants it: preliminary abstracts (300 words) should be sent as soon as possible (and in any event, no later than 29 April 1983) to the Chairman of the Organising Committee, Professor R H Ottewill, Department of Physical Chemistry, The University, Cantock's Close, Bristol BS8 1TS.

FARADAY DISCUSSION NO. 76

16 September 1983

CONCENTRATED COLLOIDAL DISPERSIONS

at Loughborough University of Technology, Loughborough, UK.  
PRELIMINARY PROGRAMME

Concentrated colloidal dispersions viewed as one-component macrofluids

J B Hayter Institut Laue-Langevin, Grenoble, France

Concentrated colloidal dispersions in non-polar solvents. Model dispersions for hard-sphere interactions: silica and micro-emulsion particles in hydrocarbons

A Vrij University of Utrecht, The Netherlands

The properties of concentrated polystyrene latex dispersions

J W Goodwin, R H Ottewill, A Parentlich and R A Richardson University of Bristol

Neutron scattering studies of concentrated oxide sols

J D F Ramsay, R G Avery and B O Booth AERE, Harwell

Electrical double layer interactions in concentrated colloidal systems

B Beresford-Smith and D Y C Chan Australian National University, Canberra

Hydrodynamic interactions and diffusion in concentrated particle suspensions

P N Pusey and R J A Tough Royal Signals and Radar Establishment, Malvern

Dynamical properties of colloidal dispersions

R Klein and W Hess University of Konstanz, West Germany

Diffusion in concentrated monodisperse colloidal solutions

W van Meegen Royal Melbourne Institute of Technology, Australia

Simulation of particle motion and stability in concentrated dispersions

J Bacon, E Dickinson and R Parker University of Leeds  
M Lal Unilever, Port Sunlight

Cluster expansion for diffusion in a concentrated suspension

B U Felderhof Technische Hochschule Aachen, West Germany

Microstructure of sheared suspensions

B J Ackerson Oklahoma State University, USA  
and N A Clark University of Colorado, USA

Small angle neutron scattering investigations of ferrofluids

D J Cebula Rutherford Appleton Laboratory, SERC, Didcot

and S W Charles and J Poplewell University College of North Wales, Bangor

Light scattering and neutron scattering from concentrated dispersions of charged unilamellar vesicles

A Muddle, J S Higgins, P G Cummins and I G Lyle Imperial College, London

FIRST ANNOUNCEMENT

INTERNATIONAL SYMPOSIUM ON EMULSION COPOLYMERIZATION AND COPOLYMERS  
LYON (France)                    march 7 - 9, 1984

Sponsored by : Centre National de la Recherche Scientifique (CNRS)  
Organised by : J. GUILLOT - C. PICHOT  
                  Laboratoire des Matériaux Organiques - BP 24 - 69390 VERNAISON (France)  
                  Tel : (7) 802.13.44

*This Symposium is concerned by kinetics of the many Emulsion copolymerization processes and by the structure - properties relationship in latex and copolymers.*

*This three-day Symposium will be restricted to a limited number of participants.*

*About 15 plenary lectures will be given by invited speakers and a limited number of communications or posters will be accepted from participants.*

- TOPICS : 1 - Kinetic studies and Emulsion copolymerization processes
- 2 - Thermodynamic aspects - Polymer-Emulsifier interactions
- 3 - Colloidal properties - Surface structure control - Functionalization
- 4 - Structured latexes ("core-shell" morphology)
- 5 - Structure-properties relationship in latexes and emulsion copolymers
- (Several panel discussions are also intended to be organized.)

*People interested in receiving the First Circular are kindly requested to fill the attached form below and send it as soon as possible to Drs J. Guillot and C. Pichot*

*Members of the Scientific Committee and Invited Speakers are listed overleaf.*

INTERNATIONAL SYMPOSIUM ON EMULSION COPOLYMERIZATION AND COPOLYMERS

LYON (FRANCE)  
march 7-9, 1984

*I am interested in receiving more information about this Symposium. Please send me the First circular and registration form*

NAME : \_\_\_\_\_ TITLE : \_\_\_\_\_

AFFILIATION : \_\_\_\_\_ ADDRESS : \_\_\_\_\_

CONTRIBUTION : YES  NO

Title : \_\_\_\_\_

(Return this form to : J. GUILLOT/C. PICHOT - Laboratoire des Matériaux Organiques  
BP 24 - 69390 VERNAISON (France))

SCIENTIFIC COMMITTEE

- Pr M. S. EL AASSER - Lehigh University - BETHLEHEM (USA)
- Dr J. C. DANIEL - Rhone-Poulenc -AUBERVILLIERS(France)
- Pr A. S. DUNN - MANCHESTER University (United Kingdom)
- Dr A. GUYOT - CNRS - SOLAISE (France)
- Pr A. E. HAMIELEC - Mc Master University - HAMILTON (Canada)
- Pr M. LAMBLA - Ecole d'Application des Hauts Polymeres - STRASBOURG (France)
- Pr J. M. LIEGEOIS - Universite de Liege - LIEGE (Belgium)
- Dr J. F. PIERSON - Produits Chimiques Ugine Kuhlmann - CCURBEVOIE (France)
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- Dr R. A. WESSLING - Dow Chemical - MIDLAND (USA)
- Pr J. UGELSTADT - University of TRONDHEIM (Norway)

INVITED SPEAKERS

- Dr D.R. BASSETT - Union Carbide Corp.-SOUTH CHARLESTON (USA)
- Dr J. C. DANIEL - Centre de Recherches Rhone Poulenc - AUBERVILLIERS (France)
- Pr A.S. DUNN - MANCHESTER University (United Kingdom)
- Pr M. NOMURA - Fukui University - FUKUI (Japan)
- Pr M.S. EL AASSER - Lehigh University - BETHLEHEM (USA)
- Pr A.E. HAMIELEC - Mc Master University HAMILTON (Canada)
- Pr M.LAMBLA - Ecole d'Application des Hauts Polymeres - STRASBOURG (France)
- Dr G. LOHR - Hoechst Ag - FRANKFURT (west Germany)
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- Dr N. SUTTERLIN - Rohm GmbH - DARMSTADT (west Germany)
- Pr J. UGELSTADT - University of TRONDHEIM (Norway)
- Pr J.W. VANDERHOFF - Lehigh University - BETHLEHEM (USA)
- Dr B.R. VIJAYENDRAN - Celanese Polymer Speciality Co - JEFFERSONTOWN (USA)
- Pr V.I. YELISEEVA - Academy of Sciences of the USSR -MOSCOW (USSR)
- Dr h. WARSON - Solihull Chemical Services -SOLIHULL(United Kingdom)



PREPARATION AND PROPERTIES OF SYNTHETIC POLYISOPRENE LATICES FOR SIMULATION OF BEHAVIOUR OF NATURAL RUBBER LATEX

10 MAY 1968

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

Readers of this newsletter will know that in recent years we have examined several aspects of the behaviour of natural rubber latex in some detail. Our principal motivation has been the industrial and commercial importance of this latex, and the frequent lack of understanding of its behaviour by many who use it industrially. Aspects of the behaviour of natural rubber latex with which we have been particularly concerned include mechanical and chemical stability, heat-sensitivity zinc-oxide thickening, prevulcanisation, and coagulant dipping. However, we have been acutely aware that, useful and interesting though many of our results have been, their interpretation has been made difficult by the complicated nature of natural rubber latex. We have therefore been aware of the need to repeat much of our work using synthetic or artificial rubber latices whose compositions and characteristics are much better defined than are those of natural rubber latex, in order that the interpretation of the results may thereby be simplified.

Our first attempts to prepare well-defined latices of rubbery polymers were made using monomers such as butyl acrylate. Although some success was achieved in producing well-defined latices from monomers of this type by emulsion polymerisation under various conditions, the products were not entirely satisfactory. One problem was that the monomers tend to undergo partial hydrolysis during emulsion polymerisation. For various reasons, not least the chemical nature of the polymer, a more satisfactory model for natural rubber latex would be a synthetic or artificial latex of polyisoprene.

We have now produced several synthetic polyisoprene latices by the emulsion polymerisation of isoprene, and have shown that they can be used to simulate at least some of the aspects of the behaviour of natural rubber latex in which we are interested. Of course, the polymer produced by free-radical polymerisation of isoprene lacks the stereoregularity and linearity of the polyisoprene which is present in natural rubber latex. From this point of view, a better model for natural rubber latex would probably be an artificial latex prepared by dispersing a stereoregular synthetic polyisoprene in an aqueous medium. However, the emulsion polymerisation route was preferred because of the relative ease and simplicity of the process, and the ease with which properties such as particle size could be varied. We recognise that lack of stereoregularity and linearity may have important implications if synthetic polyisoprene latices are used as models for studying certain aspects of the behaviour of natural rubber latex, such as prevulcanisation, but believe that these deficiencies will be less serious when using synthetic polyisoprene latices as models for the colloidal behaviour of natural rubber latex.

Synthetic polyisoprene latices have been prepared by emulsion polymerisation at 60°C using the potassium salt of 4,4'-azobis-4-cyanopentanoic acid as initiator and potassium stearate as surfactant, and by emulsion polymerisation at room temperature using cumene hydroperoxide and tetraethylene pentamine as initiators and various potassium n-alkanoates as surfactant. We have found that latices of reasonably uniform particle size can be obtained by these methods if appropriate reaction conditions are chosen, and that the particles produced by the initial reaction can be grown by a seeding technique. Of the two emulsion polymerisation procedures, that carried out at room temperature is preferred, partly because of the high vapour pressure of isoprene at 60°C, and partly because partial hydrolysis of the cyano group of the initiator tends to occur at 60°C.

Preliminary experiments have shown that certain aspects of the behaviour of natural rubber latex can be simulated using polyisoprene latices prepared as indicated above. These latices can be prevulcanised in the same way as natural rubber latex, curves for the insertion of crosslinks as a function of time being of similar shape for the two latices. The responses of the two latices to coagulant dipping are similar. So also are the responses to continuous shearing in a Ferranti-Shirley viscometer. The latter responses are being investigated in some detail, because it is hoped that they will assist with the interpretation of the many results which we have for the mechanical stability of natural rubber latex and for the effects of variables which affect mechanical stability. We find that for both natural rubber latex and the synthetic polyisoprene latices the viscosity under continuous shearing progressively increases, and that the rate of increase in the case of the synthetic polyisoprene latices depends upon factors such as particle size and soap coverage. The effect of soap coverage is particularly interesting in that the rate of increase of viscosity falls as the soap coverage is increased; for a 205 nm. latex, the change in behaviour is particularly marked as the soap coverage is increased from 55% to 65%.

\* \* \* \* \*

Members of the Group may care to note that the work described in two papers on the emulsion polymerisation of styrene which have recently appeared under the sole authorship of S.M. Hasan (J. Polym. Sci: Polym. Chem. Ed., 1932, 20(10), 2969-2973 and 1932, 20(11), 3031-3063) was carried out here by Mr. Hasan under the the joint supervision of Dr. W. F. H. Burgar, myself and Dr. B. D. Phillips of BP Chemicals, South Wales. The work was supported by a Research Assistantship provided by this Polytechnic. Mr. Hasan has chosen to publish the work without consulting us, inviting us to participate as co-authors. We understand that a note concerning the circumstances surrounding the publication of these papers will appear in J. Polym. Sci: Polym. Lett. Ed. in due course. This note will include a statement to the effect that Dr. Burgar and myself should be considered as co-authors of the papers, but that we do not necessarily agree with everything which is said in them.



Dr A. S. Dunn

Department of Chemistry

The criterion for the cessation of nucleation in emulsion polymerisation and for renucleation in seeded emulsion polymerisation.

The Smith-Ewart-Gardon theory works well for styrene provided the values of the constants used are chosen judiciously but nevertheless some of the basic postulates now seem not to be justified e.g. the criterion for the cessation of particle nucleation is taken to be that the total surface area of the latex particles should have increased sufficiently to adsorb all the surfactant present in a saturated monolayer. Absence of micelles of emulsifier is not a sufficient condition for the avoidance of renucleation in seeded polymerisations and it is possible to find conditions in which micelles remain at the end of an ab initio polymerisation despite an Interval II with constant rate of polymerisation being observable. The possibility ought to be considered that the number of latex particles remains constant in Interval II because a steady state has been reached in which the rate of particle nucleation is equal to the rate particle coalescence. Coalescence certainly occurs in the early stages of the polymerisation of the more water-soluble monomers and in the polymerisation of styrene using emulsifier concentrations below the c.m.c. when monodisperse particle size distributions are obtained. Increasing emulsifier concentration would reduce the rate of coalescence and it could be that the distributions of particle sizes observed above the c.m.c. are the result of variable rates of coalescence between particles of different sizes and not of the differing lengths of time which the particles have had to grow from the time at which they were nucleated in Interval I as has been generally been maintained hitherto. This could explain our observation that similar adsorbed concentrations of different emulsifiers produce similar final particle size distributions despite a considerable increase in the duration of Interval I as the alkyl chain length of homologous emulsifiers is decreased (cf. Dunn & Al-Shahib in Fitch ed. 'Polymer Colloids II', p. 619, Table I and Fig. 2).

During his sojourn in Bristol in 1931, Don Napper presented the results on the evolution of particle size distributions with time which had been obtained at Sydney: the details of this work have now been published in the January 1933 issue of the Journal of Polymer Science, Polymer Chemistry Edition 21 (1933) 269-91 [1]. The outstanding conclusion of this work is that the particle size distribution early in Interval II can only be accounted for if, contrary to all previous expectation, the particle nucleation rate in Interval I is an increasing function of time. The assumption that nucleation ceases at the end of Interval I is, however, maintained in this work. In order to explain the increasing nucleation rate and the cessation of nucleation at the end of Interval I it is necessary to postulate that primary particles formed by oligomeric precipitation or from monomer-swollen micelles do not polymerise as fast as secondary particles formed by coalescence of the primary particles but that, once all the surfactant has been adsorbed, coalescence of primary particles with secondary particles becomes dominant over the mutual coalescence of primary particles. Although this is plausible enough, the critical test will be to see if this theory can be made quantitative which is the authors' professed intention.

One important observation in this work is that the unswollen diameter of the smallest particles observed at the earliest time of sampling (at 10 % conversion after 7 min. polymerisation) is about 16 nm diameter. After further polymerisation

the size of these particles has increased; no smaller particles which might not have been resolved in the original specimen appear after growth. 16 nm may therefore be the size of the smallest particles which are large enough to have appreciable stability under these conditions (50 °C,  $K_2S_2O_8 = 1.54 \times 10^{-2} \text{ mol dm}^{-3}$ ,  $2.66 \times 10^{-2} \text{ mol dm}^{-3}$  sodium dodecyl sulphate (about 3 x c.m.c.),  $5 \times 10^{18}$  latex particles per  $\text{m}^3$  water - this initiator concentration [and consequently the ionic strength] is relatively high).

The Smoluchowski rate constant for rapid coalescence,  $k_0 = \frac{4}{3}(kT/\eta) = 1.1 \times 10^{-17} \text{ m}^3 \text{ s}^{-1}$  at this temperature, giving a half-life for the latex  $t_{1/2} = 1/k_0 N = 1.8 \text{ s}$  at this (relatively low) particle concentration. Taking  $t_{1/2} = 24 \text{ h}$  as a criterion for stability, a value of the Fuchs Stability Ratio  $W > 10^6$  is required: this corresponds to a barrier height,  $V_{\text{max}} > 17 kT$  or  $7.6 \times 10^{20} \text{ J}$ . The amount of surfactant present is about 3 times that required to saturate the total surface area of the particles present so the surface of the monomer-swollen particles may be taken to be completely covered with adsorbed surfactant at this stage (although at a later stage, when all the surfactant has been adsorbed, the coverage, and consequently the stability of the particles, will decrease). The area occupied in a saturated monolayer by a sodium dodecyl sulphate molecule on a monomer-swollen polystyrene particle at this temperature can be estimated as  $61.5 \text{ \AA}^2$  from Piirma & Chen's work (J. Coll. Interface Sci. 74 (1980) 90). Assuming this to be independent of particle size, the surface charge density would be  $26 \mu\text{C cm}^{-2}$  if the adsorbed layer were completely ionised. But counter ions are extensively bound by highly charged particles (micelles, proteins, or latex particles). The Lehigh group (e.g. Wu, El-Aasser, Micale, and Vanderhoff in P. Becher & M.N. Yudenfreund ed. 'Emulsions, Latices, and Dispersions' Decker, New York, 1978 p. 71) have determined the degree of dissociation of the ionisable surface groups on large polystyrene latex particles from a combination of measurements of electrophoretic mobility, conductivity, and conductometric titration. However the conclusion seems to be that counter ion binding is only important at very low ionic strengths ( $< 10^{-5} \text{ mol dm}^{-3}$ ) and should be negligible at the relatively high ionic strength prevailing in these experiments. If this is so, the corresponding surface potential would be 175 mV. However to get a value of  $V_{\text{max}}$  of the right order of magnitude for 16 nm particles to be at the boundary between stability and instability requires a surface potential of about 90 mV when the value for the Hamaker constant for polystyrene in water is taken as  $A = 7 \times 10^{20} \text{ J}$ . This implies a degree of ionisation of only about 20%. The explanation of the discrepancy may be that the Lehigh particles have only a low surface charge so that much higher ionic strengths would be needed to overcome counter-ion binding on particles with a high surface charge.

In an earlier paper from Sydney, Hawke, Gilbert, & Napper (J.C.S. Faraday Trans. I 76 (1980) 1323) found that in order to prepare a monodisperse latex using a micelle-free solution of an emulsifier with a high c.m.c. ('Aerosol' MA) at a high temperature (90 °C) to get a high rate of initiation from persulphate, it was essential not to deoxygenate the emulsion to get a monodisperse latex, quite contrary to good practice in radical polymerisations.

The explanation of this curious observation is now clear. When using a similar recipe, Mr S.A. Hassan finds the order of mixing of the deoxygenated solutions to be vital. The normal procedure of first emulsifying the monomer and finally adding the initiator to start the polymerisation does not give a really monodisperse latex although the particle size distribution is narrow whereas adding styrene (not preheated) to a preheated aqueous solution of initiator and emulsifier does produce a perfectly monodisperse latex.

The vital difference is the avoidance of any particle formation from the styrene polymerising thermally in emulsion before the initiator is added which can be achieved either by permitting oxygen inhibition or by adding the initiator first.

11.

EFFECT OF POLARITY AND PHYSICAL STATE OF COMPOSITE POLYMER  
ON ITS MORPHOLOGICAL CHANGE DURING EMULSION POLYMERIZATION

V.I. Eliseeva, N.V. Titova

We have found that during polymerization of chloroprene (Chl) in the presence of butylmethacrylic latex as a "seed" the obtained polychloroprene (PChl) penetrates into the seed particles. This process is accompanied by desintegration of the acrylic component and its emergence on the particle surface. In terms of thermodynamics this phenomenon can be explained by a change in free energy of transition from aqueous medium-PCl-PEMA system to the system aqueous medium-PEMA-PChl and accounted for by polymethacrylate greater polarity, that makes it migrate to the interface with polar medium-aqueous phase- and polychloroprene greater hydrophobity, that makes it penetrate into the hydrophobic medium of polymeric particles.

According to the kinetics of phase transitions along with the difference in polarity of both polymers a physical state of the seed latex polymer also plays an important role in realization of such transitions during emulsion polymerization. It is evident, that a decrease in free interface energy, resulting in "sucking" of hydrophobic polymer inside a particle, can only be realised when macromolecules of the seed polymer have sufficiently high translation mobility, i.e. when polymerization temperature ( $T_p$ ) exceeds its glass transition temperature ( $T_g$ ).

In this connection we have investigated the mechanism of formation of the composite polymer particles, obtained by a two-step polymerization of monomers, that differs in their properties, namely polymerization of chloroprene in the presence of seed latexes of EA, MMA, St polymers. The polymer polarity was characterized by the value of interface energy of the corresponding monomers at the water interface; the polymer physical state was characterized by the difference between  $T_g$  and  $T_p$  (313 K). The Table lists the corresponding characteristics of the polymers used in seed latexes. It can be seen that under conditions of polymerization the selected polymers are either in the same

physical state--in a glassy state--but differs in polarity (PMMA, PSt), or one of them is in a glassy state, while the other is in a viscousflow state--but their polarity is practically the same (PMMA, PEA).

Two-step latexes were synthesized under similar conditions with persulfate as initiator; conversion of the monomer in the seed latexes was 95%; the second step of the process was carried out on gradual introduction of chloroprene into reaction mixture with a rate providing for a deep conversion during polymerization. The morphology of particles, generated at different stages of the second step was observed using electron micrographs. The electron micrographs were obtained by contrasting with  $\text{OsO}_4$ .

The electron micrographs have demonstrated that introduction of Chl into reaction system initially results in formation of new polychloroprene particles, which have a darker colour in microphotographs. These particles are suspended in the aqueous phase, but due to their lesser stability they display a tendency to weak agglomeration with larger particles of seed latexes. At the final stages of the process the behaviour of PChl particles differs in dependence of the nature of seed latex polymer. With PSt-PChl composition they form a separate fraction, which consists from floccules of the initial PChl particles. In the case of PMMA-PCP composition, the PChl particles, being adsorbed by the particles of the seed latex, form on their surface a dense, although nonuniform shell. With PEA-PChl composition we observed a phenomenon similar to that observed with PChl-PBMA system (1); the chloroprene particles penetrate into the volume of seed particles and some kind of phase reversion takes place.

The difference in the behaviour of PChl particles, generated in the second stage of the process in the presence of PSt and PMMA, is certain to be related to the difference in polarity of the polymers of the seed latexes (no difference in  $T_g$  is observed for both polymers). Due to considerably different chemical nature of PSt and PChl the particles of the latter in the process of flocculation form a separate fraction, displaying no tendency to being adsorbed on the surface of PSt particles. On the contrary, such tendency can be observed with PChl and PMMA particles (MMA and Chl are known to copolymerize in emulsion systems (2)). It

results in more dense contacts and possibly in formation of transitional layer of intermediate chemical composition between both polymers. The latter consideration is substantiated by the results of investigation of mechanical properties of the films of composite latexes, obtained from the mixture of corresponding latexes (PChl + PSt and PChl + PMMA) and from latexes obtained in a two-step process (PChl - PSt and PChl - PMMA).

The behaviour of PChl particles in the presence of seed PEA particles is different in comparison with the first two cases: the PChl particles generated at the beginning of the second stage of polymerization in the form of separate fraction, form in the end of the process a separate phase, penetrating inside PEA particles. The polarity of the latter polymer is close to that of PMMA, although in the process of polymerization the PEA particles are in a viscous flow physical state. That is why the thermodynamically advantageous process of "sucking in" the PChl particles in the hydrophobic volume of seed particles is not prevented by deformation of the seed polymer, which is characterized by a high translation mobility at polymerization temperature. With PMMA seed particles, which are under conditions of polymerization in a glassy state such process cannot be realized.

The data presented suggest that the mechanism of formation of particles in the process of two-stage emulsion polymerization cannot be sufficiently described as a colloidal process only, but the polymer structural changes, affecting its practically valuable properties should also be taken into account.

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Table

| Polymer | Interphase energy<br>at monomer/water<br>interface, mJ/m <sup>2</sup> | T <sub>g</sub><br>of poly-<br>mers<br>K | T <sub>p</sub> - T <sub>g</sub><br>K |
|---------|---|---|--------------------------------------|
| PEA     | 16.9  | 253                                     | +60                                  |
| PMMA    | 17.8  | 378                                     | -65                                  |
| PSt     | 35.0  | 373                                     | -60                                  |



COLLOID RESEARCH AT MCMASTER UNIVERSITY - RECENT DEVELOPMENTS

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by  
Archie Hamielec

1. McMaster Institute for Polymer Production Technology

Search for sponsor companies for the Institute has begun in earnest. To date 6 companies have agreed to join. The target figure is 30 sponsor companies.

2. Semi-batch and continuous emulsion polymerization - adhesives

Models are being developed for the emulsion polymerization of vinyl acetate/acrylic acid, vinyl acetate/2-EH acrylate/acrylic acid and n-butyl acrylate/i-butyl acrylate/2-EH acrylate.

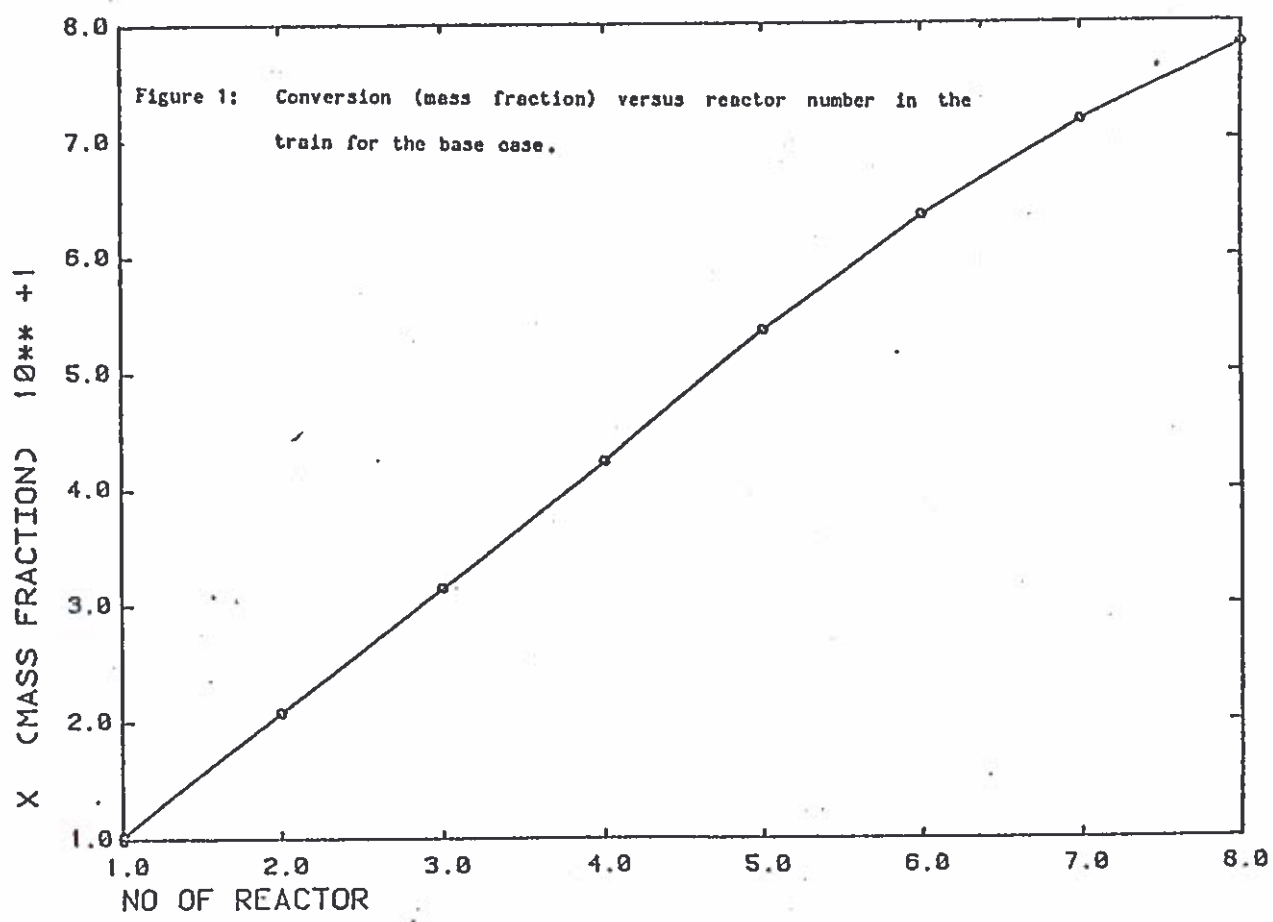
3. Semi-batch and continuous emulsion polymerization of styrene/  
butadiene

Steady-state and dynamic reactor models have been developed for the manufacture of cold SBR in a continuous commercial CSTR train. Simulations for a commercial train of 5000 gal reactors with a production capacity of 50-100 tons/train/day of SBR are shown in Figures 1-4. The terminal conversion of monomers in the train is limited to about 63 wt.% to minimize long chain branching and maintain processability. These reactor models are being used to identify reactor train operations during startup, reactor switching for cleaning and steady-state manufacture, which are safe, give higher production rates and higher quality copolymer.

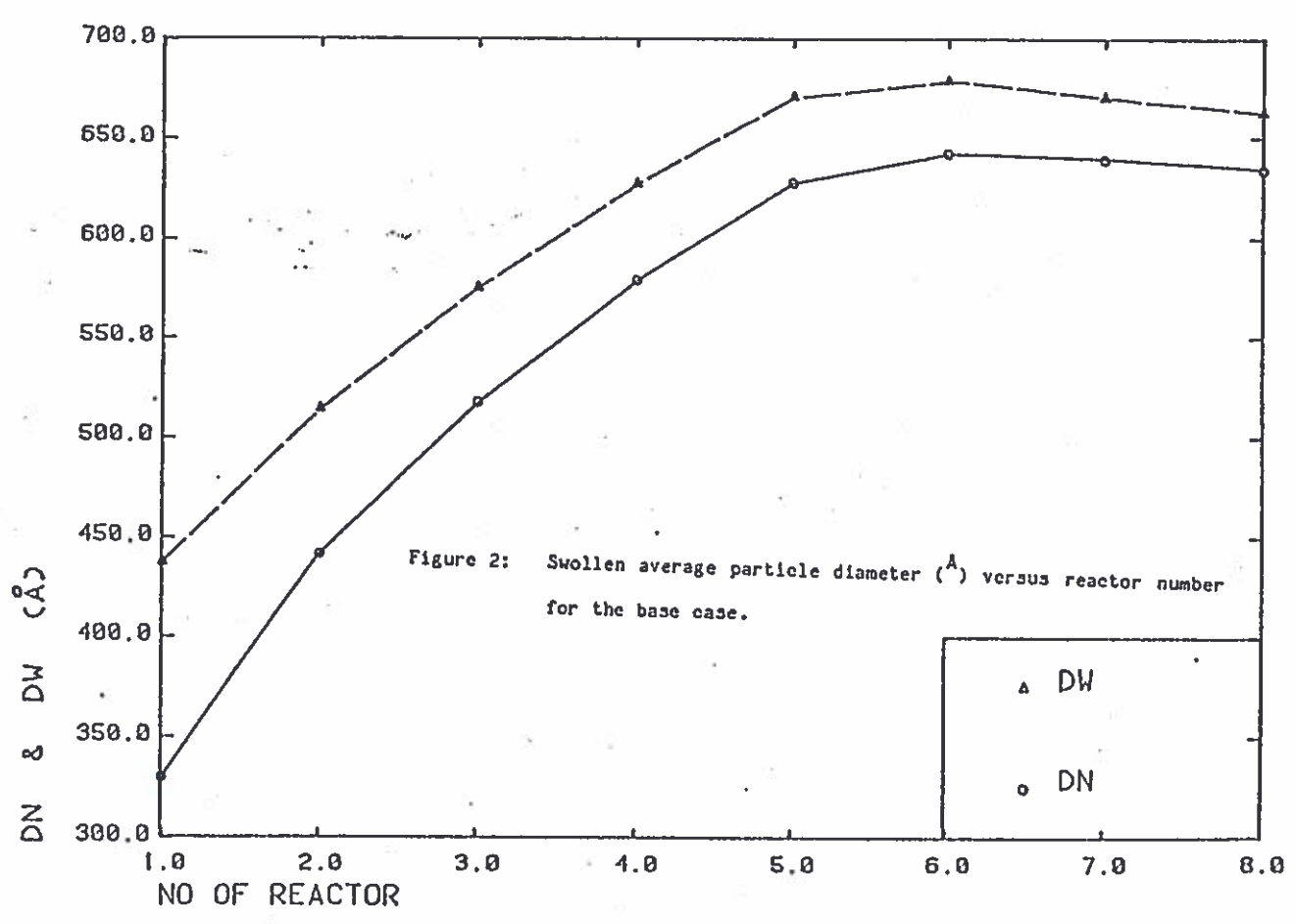
4. Semi-batch emulsion polymerization of styrene/acrylonitrile

No significant progress to report.

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



FIG



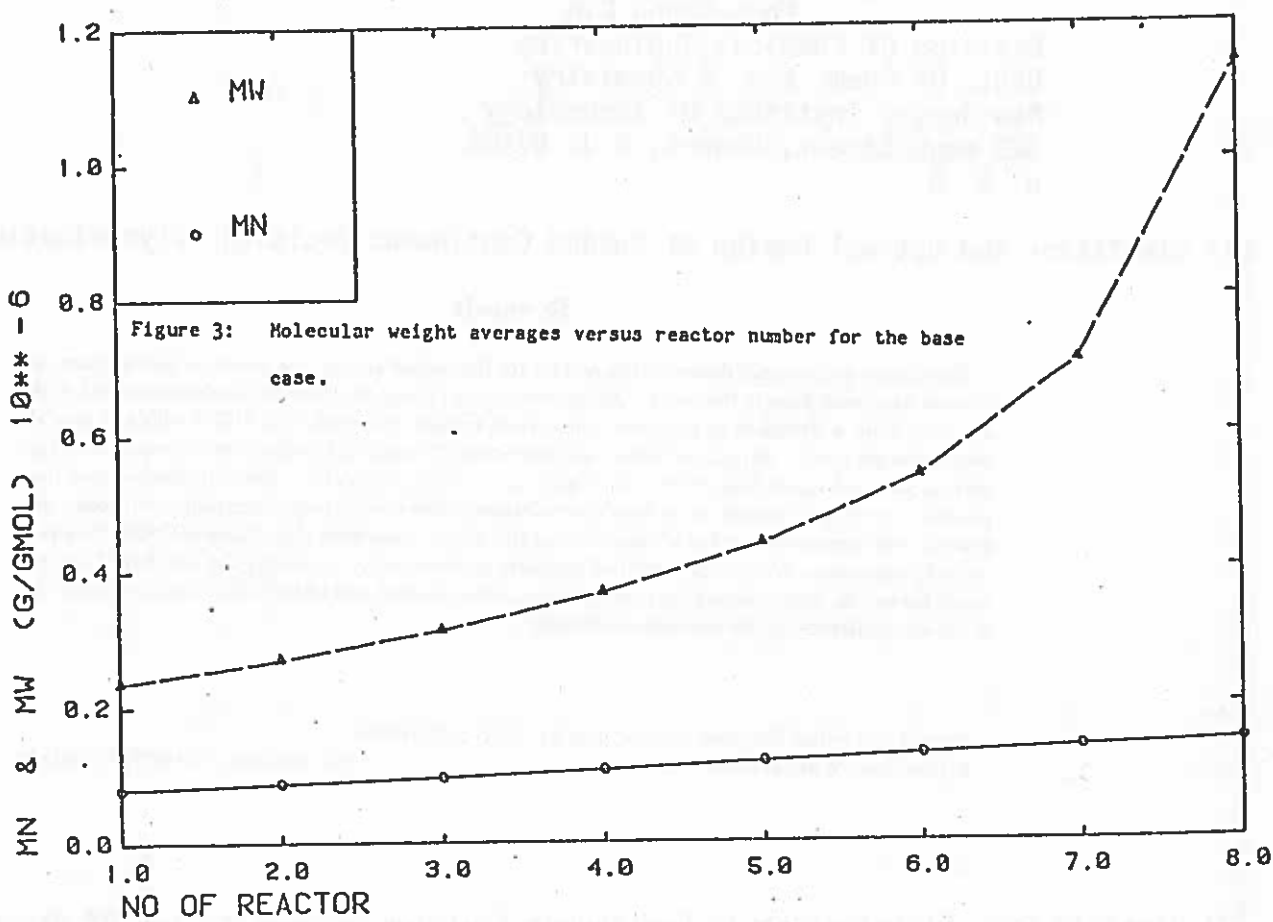
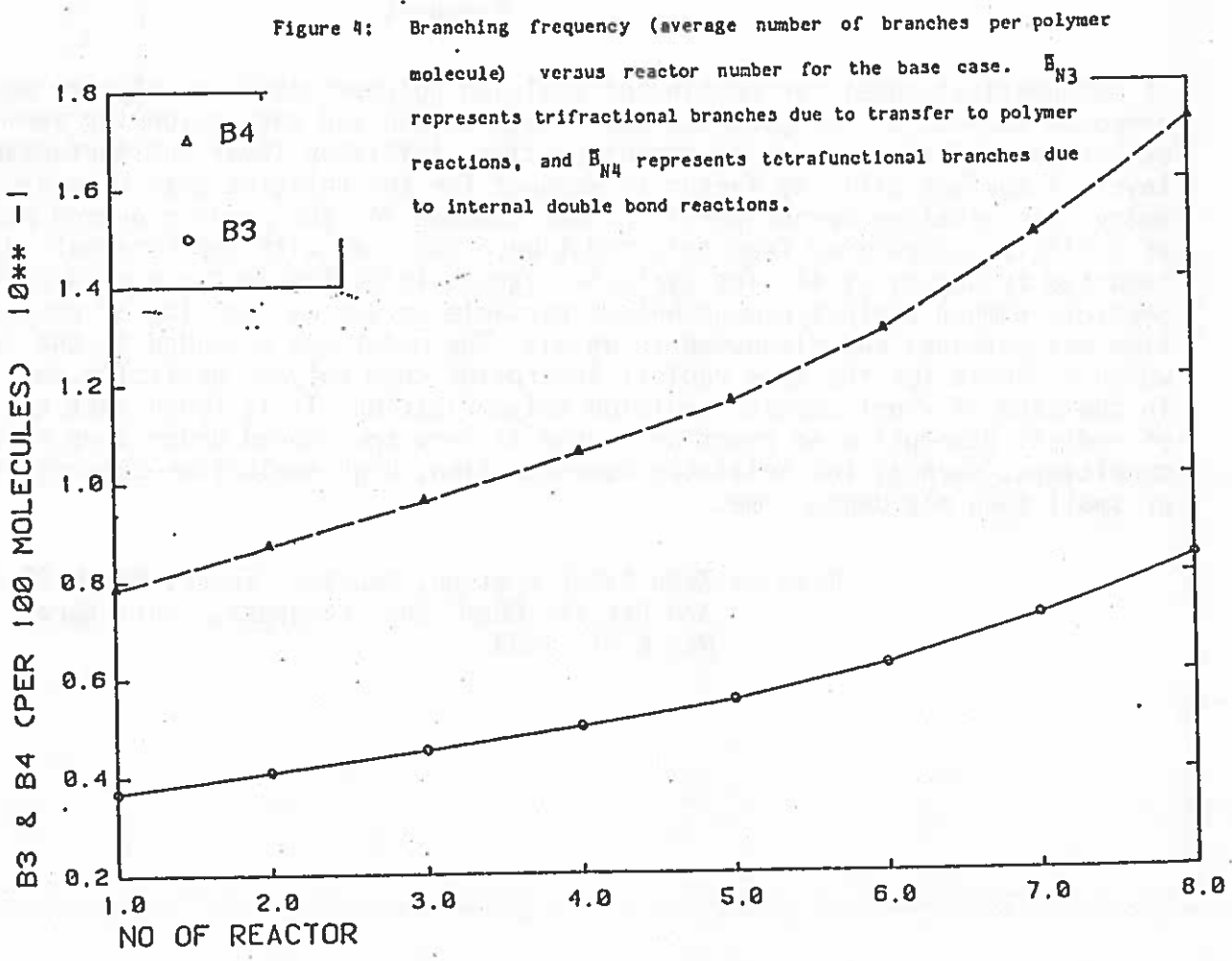


FIG 4



Polymer Colloid Group Newsletter  
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13 11 83

(1) Simulation and Optimal Design of Seeded Continuous Emulsion Polymerization Process

Synopsis

Simulation and optimal design of the reactor for the seeded continuous emulsion polymerization process have been done in this work. An internal mixer (Toray Hi-Mixer) as seeder connected with a stirred tank is designed to correlate conversion, molecular weight, and MWD with the model simulation proposed. An optimal mean residence time of seeder ( $\bar{\theta}_1$ ), is found to lie between  $(\bar{\theta}_1)_{opt}$  and  $t_{in}$ , where  $(\bar{\theta}_1)_{opt} = (3aS_0/2r_i\eta N_A\alpha)^{3/5}$  and  $t_{in} = 1.57(aS_0/r_i\eta N_A)^{3/5}$ . The optimal design of the process is performed according to the above relations under several polymerization conditions. In general, the increase in number of stages inside the seeder can reduce the volume of CSTR for a required production. Molecular weight of products is increased by increasing the number of stages inside the seeder, by decreasing the concentration of the initiator, and by increasing the concentration of the emulsifier under the optimal conditions.

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(2) Particle Size Distribution In Continuous Emulsion Polymerization Of Styrene

Synopsis

A mathematical model for continuous emulsion polymerization of styrene was proposed to predict the particle size distribution and conversion for various operation conditions, such as residence time, initiator level and surfactant level. A surface affinity factor to account for the relative ease of radical entry into micelles versus particles was considered. The conversion and number of particles calculated from this model were compared with experimental data reported by Nomura et al. The particle size distribution in terms of differential particle number against dimensionless particle volume as function of residence time was obtained and discussed in detail. The model was extended to the system which accounts for the free radical desorption from polymer particles such as in the case of vinyl acetate emulsion polymerization. It is found that the effect of radical desorption on reaction course is very pronounced under some reaction conditions, such as low initiator concentration, high emulsifier concentration, or small mean residence time.

Read at 76th AIChE Meeting, Houston, Texas, March 27-31, 1983  
3rd Pacific Chem. Eng. Congress, Seoul, Korea,  
May 8-11, 1983

POLYMER COLLOIDS AT SYDNEY UNIVERSITY

Reporter: D. H. Napper

MORE ON HYDROCARBON DILUENTS

Kinetic relaxation studies using <sup>60</sup>Co as the initiating source have shown that certain hydrocarbon diluents, such as ethylbenzene, toluene and cyclohexane, increase the rate of exit of free radicals from seeded emulsion polymerizations, although others, e.g. benzene, do not. The results can best be interpreted in terms of not only the rate of transfer of free radical activity to the diluent but also the chemical reactivity of the diluent free radicals with monomer. Many diluent free radical species appear to react quite slowly with monomer. This increases the time available for escape of the unreacted free radical from the latex particle and hence increases its probability of exit. Diluent free radical reactivities can be calculated from the experimental data.

At high chemical initiator concentrations, the average number of free radicals per particle in a seeded emulsion polymerization of styrene is ca. 1/2 and inert diluents exert little effect, apart from the expected dilution of monomer within the latex particles. At low initiator concentrations, however, a very complex pattern of behaviour appears. Much of this pattern can be interpreted by measurement of the rates of entry and exit of free radicals from the seed particles using the slope and intercept method. The results so obtained for the exit rate coefficient agree with the relaxation measurements. What is most surprising is that certain inert diluents at low volume fractions are able to increase the entry rate coefficient. This effect appears to be related to the observation by Blackley that inert diluents can drastically reduce the latex particle size in the ab initio emulsion polymerization of styrene. At high volume fractions, however, all diluents reduced the rate of polymerization considerably more than expected on the basis of dilution of monomer in the particles. This effect may be associated with the depletion of monomer in the aqueous phase. This would reduce the rate of production of free radical species capable of entering the particles, leading to a slower rate of polymerization. It is apparent that hydrocarbon diluents can exert a complex manifold of effects on emulsion polymerizations.

Latex Particle Nucleation Ab initio emulsion polymerizations of styrene have been performed in an ultrasonic field. Fewer particles are formed but these are of a larger size and more polydisperse. The results are in conformity with a coagulation mechanism for nucleation but are difficult to explain by a micellar entry mechanism.

\* CONTROL OF SURFACE AND STRUCTURAL PROPERTIES IN EMULSION COPOLYMERS

B. EMELIE, C. PICHOT and J. GUILLOT

With the objective of understanding the effect of introduction method on the distribution of a functional monomer in a latex system, studies were investigated on [methyl methacrylate (MMA) - butyl acrylate (BuA) - carboxylic acid] emulsion copolymers. A kinetic study was initially performed on batch [MMA-BuA] emulsion copolymerization using sodium dodecyl sulfate as an emulsifier and  $S_2O_8K_2$  as an initiator. With the same recipe, this copolymerization was carried out in the presence of acrylic (AA) or methacrylic acid (MAA). The introduction of the ionic comonomer makes the final particle size to decrease (as expected) but the polymerization rate was not much affected. Using serum replacement and ion exchange techniques, it was found that the distribution of the carboxylic acid comonomer in the latex system is largely dependent on the comonomer hydrophobicity and of the introduction method. Some experimental results were obtained on the particle structuration (using the soap titration method to characterize the particle surface composition) which seems to reveal a BuA rich particle surface in the case of 50/50 (MMA-BuA) batch copolymers compared to a MAA rich one in the case of carboxylated copolymer latexes. Moreover a simulation model based on thermodynamic considerations allowed to account for a particle composition gradient within these batch emulsion copolymer particles.

\* STRUCTURE PROPERTY RELATIONSHIPS IN ACRYLONITRILE - ACRYLATE EMULSION COPOLYMERS

B. ROCCHETTI, J. GUILLOT, A. GUYOT

Acrylonitrile (AN) - Butyl Acrylate (BuA) and AN - 2-Ethyl Hexyl Acrylate (2.EAH) emulsion copolymerizations have been studied using batch and semi-continuous processes. (AN-2.EAH) copolymer syntheses were found more sensitive to the AN solubility and emulsifier concentration than for (AN-BuA) ones. Different particle structures were consequently observed (hard or soft core) with AN-2.EAH copolymer latexes, with the result of differences in filmability for these latexes. Results were interpreted by assuming a competition between two kinds of particle nucleation (homogeneous [AN] and micellar [2.EAH]) in the batch process, and nucleation of new particles, fastly adsorbed by already growing ones in the semi-continuous process.

(These two papers were presented at the AIChE Symposium on Polymer Colloids - March 1983 - Houston USA)



\* DIELECTRIC BEHAVIOR OF LATEX IN MICROWAVES : A WAY FOR CHARACTERIZING THE SURFACE PROPERTIES OF POLYMER PARTICLES

(Cooperation between A. Kamel - Lehigh University USA  
F. Henry - CNRS Thiais France  
C. Pichot - CNRS Vernaison France)

A new measurement technique for the dielectric study of solutions and suspensions in microwaves was recently reported by F. Henry et al. Based on the first order perturbation theory, it allows a continuous measurement of the constant  $\epsilon'$  and  $\epsilon''$ . This technique was used for investigating the characterization of surface properties in the case of polymer latexes; the study was more concentrated on cleaned and well characterized latexes, carrying different types of surface end groups.

From  $\epsilon'$  and  $\epsilon''$ : values, the volume of hydrated particles was derived in order to determine the exact volume of water bound to the particles. In the case of polystyrene latexes, it was found a lower  $\epsilon'$  value for the sulfate ended particles compared to the carboxylated or hydroxyl ended ones. Results are explained in terms of polarity of the surface functional groups and its effect on the water structuration around polymer particles. The variations of  $\epsilon'$  and  $\epsilon''$  with temperature also shows differences in the dielectric behavior of these PS polymer particles. More experiments are actually investigated in order to work out the feasibility of this technique and to confirm the above results with polymer particles of different surface characteristics.

\* OLIGOMERIC EMULSIFIERS

C. PICHOT, J. GUILLOT, R. PELLICER, P. GROSSETETE

Abstract of a third paper accepted for publication in "Die Makromolekulare Chemie"

The synthesis of amphiphilic oligomers through the radical polymerization of hydrophilic monomers in the presence of long hydrocarbon chain thiols as transfer agents was simulated using a model based on a kinetic scheme similar to that proposed by Ikeda (7). Taking into account the solvent as a secondary transfer agent, weight fractions of different oligomer molecules and average polymerization degrees versus conversion were determined as a function of (thiol)/(monomer) molar ratios and solvent transfer constant values.

A relatively good agreement was found between these theoretical values and experimental ones derives from acrylic acid (AA) and acrylamide (Am) oligomerizations. It was particularly pointed out that oligomers terminated with unexpected structure (namely coming from the solvent) could compete with the thiol-terminated oligomers. An interesting application was deduced from this study : by modifying the simulation model, it was possible to estimate the amount of thiol necessary to keep constant the composition of the reactant mixture during synthesis, which eliminates the drift in the oligomer composition at high conversion.

\* INVERSE EMULSION COPOLYMERIZATION STUDY

- HOMOPOLYMERIZATION OF ACRYLAMIDE  
C. GRAILLAT

Preliminary work on the inverse emulsion polymerization of acrylamide was investigated in order to emphasize the main specific features of the process. The following recipe was used : organic phase = toluene ; aqueous phase = 40/60 acrylamide ; water - initiator = AIBN ; surfactants = mixture of Montane 83 (sorbitan sesquiolate) - Montanox 80 (polyoxyethylene sorbitan) or acrylamide oligomer. Temperature = 40 °C. Kinetics carried out by gas chromatography analysis was found to follow bulk or solution conditions. Efforts were done on the knowledge of the partition of AIBN in the organic and aqueous phases (owing to UV analysis). The AIBN concentration in aqueous phase was found to increase in the presence of acrylamide and to decrease when Montane 83 was added. Particle size of the final latexes was around 250 nm. Experimental conditions have been optimized in order to eliminate gel formation and secondary reactions, and to increase molecular weight.

- COPOLYMERIZATION OF ACRYLAMIDE WITH METHACRYLIC  
ACID

V. GLUKHIKHE

Using these experimental conditions defined for acrylamide (Am) homopolymerization, copolymerizations with methacrylic acid (MA) were performed as a function of methacrylic acid concentration and aqueous phase pH. Reactivity ratios of the system were determined under basic conditions (pH = 10) and the obtained values ( $r_{AM} = 0.54$  and  $r_{MA} = 0.15$ ) were found slightly different from those derived under solution conditions.

Analysis of sequence distribution in copolymers through  $^{13}C$  NMR showed that under acidic pH, mixture of homopolymers would be formed, whereas a better incorporation of MA units would be obtained under basic pH. These results can be explained on the basis of different partition of methacrylic acid in organic and aqueous phases as a function of pH. Indeed, under acidic conditions, the large concentration of MA in toluene (around 75 %) leads to assume that polymerization would occur in both phases.

Particle size measurement using QELS methods showed that an increase in MA concentration makes the initial aqueous droplet size to increase, due to poor stability. Particle diameters of the final inverse latexes were found to be smaller than for the initial emulsion droplets. Stability of the latex as well as molecular weight ( $< 3 \cdot 10^6$ ) can be enhanced by using acrylamide oligomer surfactants. From this "model" system, studies are actually directed in view of getting more information on the polymerization mechanism and particle formation in inverse emulsion copolymerization.

The following are abstracts of papers to be presented at upcoming meeting. The acrylamide polymerization paper is in the program of the 57th Colloid and Surface Science Symposium for June 13, 1983.

POLYMERIZATION OF ACRYLAMIDE IN WATER-IN-OIL MICROEMULSIONS. I. Piirma and M. M. Wu, Institute of Polymer Science, The University of Akron, Akron, Ohio 44325.

Microemulsion flooding is one of the processes of using surfactants for tertiary oil recovery. The microemulsion slug can be oil-external or water-external. In this process, a relatively small pore volume (about 3 to 20%) of the surfactant slug is injected. The purpose of this research, polymerization of acrylamide in water-in-oil microemulsion, was to try to correlate the work indirectly with the emulsion flooding process. Polymerization of acrylamide via photoinitiation of AIBN(2,2'-azo-bis(4-methylpropionitrile)) and ACVAK(4,4'-azo-bis(4-cyanovaleric acid)K at room temperature was conducted in a water-in-oil microemulsion system. This system contained a high volume fraction of interphase. The kinetics of the polymerization was found to follow the kinetics of bulk polymerization. The polymerization with ACVAK as the water-soluble initiator was found to have under comparable conditions, higher rates of polymerization than found in the polymerization with AIBN as the oil-soluble initiator. The molecular weight of the polyacrylamide reached a value as high as  $1.0 \times 10^6$ . The particle size of the microemulsion was found to control the molecular weight of the polyacrylamide, the molecular weight decreased with increasing particle size of the emulsion.

The following two are going to be presented at the National ACS Meeting in Washington, D.C. in August 1983. The papers have been submitted to the Polymer Preprints.

EMULSION POLYMERIZATION IN THE PRESENCE OF NONIONIC SURFACTANT. Taishih Maw and Irja Piirma. Institute of Polymer Science, The University of Akron, Ohio 44325.

Monomer-nonionic surfactant-water system phase properties, and the effects of phase transitions on the emulsion polymerization, have been studied in terms of rate of polymerization ( $R_p$ ) and particle size distributions (PSD). It was found that at low polymerization temperatures and low monomer concentrations, the polymerization starts with an o/w emulsion, as expected for normal emulsion polymerization. At higher temperatures and higher monomer concentrations, however, the polymerization may start either with a w/o emulsion or a multiple emulsion, and invert back to o/w emulsion during the polymerization. This phase inversion during the polymerization will lead to a change in slope in the conversion vs. time curve and a second stage particle nucleation. In the emulsion copolymerization, different mole fractions of monomers in the monomer mixtures, may also lead to different types of emulsions, and therefore, different reaction kinetics and PSD.

THE EFFECT ON THE HLB VALUE OF THE NONIONIC SURFACTANT IN EMULSION POLYMERIZATION OF STYRENE. Tien-Chieh Chao and I. Piirma. Institute of Polymer Science, The University of Akron, Akron, Ohio 44325.

The chemical structure of a surfactant has great influence upon the kinetics of emulsion polymerization as well as the properties of the latex. Systematic studies on the kinetics of emulsion polymerization using nonionic surfactants and styrene were investigated. HLB number was used as the parameter for the selection of nonionic surfactants. Results showed that the polymerization rates differed in two orders of magnitude between the surfactants with high HLB numbers and those with low HLB numbers. For the former, i.e.  $HLB > 17$ , polymerization rates were proportional to the surfactant concentration of 0.6 to 0.9 power indicating that particle nucleation followed emulsion kinetics. As the HLB number decreased, rates became independent of the surfactant concentrations. At 50°C polymerization temperature bimodal distributions of particle sizes and molecular weights were observed with nonionic surfactants with an HLB number in the range of between 13 to 16. Monomer and surfactant concentrations both can affect the appearance of bimodality which occurred only within a certain range of monomer to surfactant ratio. Polymerization temperature was also found to control the appearance of bimodality which occurred only within a narrow range of temperatures.

HIGH SWELLING OF LATEX PARTICLES WITHOUT THE  
UTILIZATION OF SWELLING AGENTS

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The preparation of large latex particles with the use of various swelling agents has received much attention in the recent literature primarily because of the work of Ugelstad et al. and the space experiments of Vanderhoff, El-Aasser et al. Polymer particles which normally only swell with monomer by volume ratios of 3 to 6 are caused to swell by factors of 1000 or more by the presence of a water-insoluble swelling agent of modest molecular weight in the particles.

Two methods have been reported for incorporating these swelling agents into the latex seed particles. In the first, a second ingredient such as acetone, is added to the continuous phase to increase the solubility of swelling agent and facilitate its transport to the latex particles. The acetone is then removed by evaporation, trapping the swelling agent in the particles. Monomer is then added to achieve high swelling and the second-stage polymerization is carried out.

A second method involves the use of a transfer agent in a second-stage polymerization. With proper formulation a low molecular weight, water-insoluble swelling agent can be produced in the particles. This is followed by addition of monomer and a 3rd polymerization step to prepare large particles.

We have achieved some preliminary success in obtaining higher swelling by producing rather small droplet monomer emulsions. The equilibrium swelling ratios predicted by Morton, et al. and others are based on the assumption that the monomer is present in the form of large droplets (actually a planar surface). Higuchi and Misra presented a mathematical model for the diffusion destruction

of emulsions which can be modified to model mass transfer from small monomer droplets to polymer particles. This model predicts that large swelling ratios should be obtainable with small droplets. Figure 1, for example, shows the time required for 0.5  $\mu\text{m}$  polymer particles to be swollen by a factor of 100 with monomer droplets which start at a size of 0.5  $\mu\text{m}$ . Ugelstad et al. suggested this possibility in their Chapter in Dr. Piirma's book.

We have been successful in achieving swelling ratios of about 14 in two preliminary experiments with seed polystyrene latexes of 0.49  $\mu\text{m}$  diameter. The recipes for these experiments are given in Table 1. We believe that higher swelling ratios could have been achieved by simply using more monomer emulsion.

We prepared small monomer droplets by using additional emulsifier and agitation. Some new particles were nucleated in spite of the fact that we used oil-soluble initiator and, in one case, water-soluble inhibitor. This was not totally unexpected, but perhaps additional work will indicate how such nucleation can be avoided.

This third technique for achieving high swelling avoids the use of swelling agents and may offer some preparaiton and application advantages.



TABLE 1: POLYMERIZATION RECIPES

Experiment #1

Latex Seed Component:

60 ml latex seed (2.61 ml PS; D = 0.49  $\mu$ m)  
 100 ml H<sub>2</sub>O  
 23.6 ml acetone  
 0.115 gms SDS

Monomer Emulsion Component: (232 ml of an emulsion of the following composition was added to the latex seed component above, with stirring, over a period of 3 hours.)

90 ml acetone  
 200 ml styrene  
 600 ml H<sub>2</sub>O  
 0.04 gms SDS  
 2.0 gms benzoyl peroxide

Mixing Temperature = 25°C; Polymerization Temperature = 60°C.

Experiment #2

Latex Seed Component:

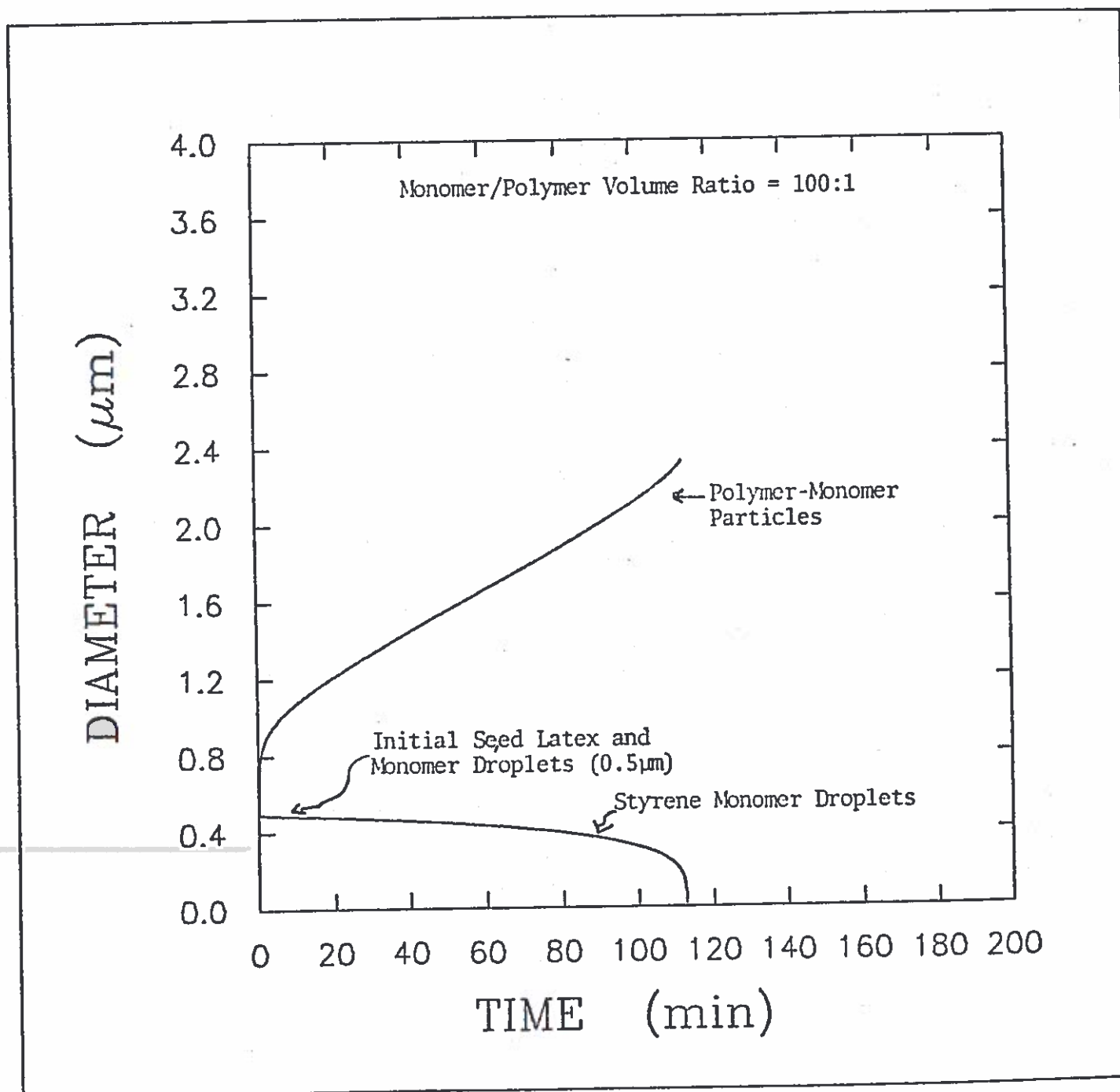
60 ml latex seed (2.61 ml PS; D = 0.49  $\mu$ m)  
 100 ml H<sub>2</sub>O  
 0.115 gms SDS  
 0.16 gms NaNO<sub>2</sub> (water phase inhibitor)

Monomer Emulsion Component: (209 ml of an emulsion of the following composition was added to the latex seed component above with stirring, over a period of 2 3/4 hours.)

100 ml styrene  
 300 ml H<sub>2</sub>O  
 0.40 gms SDS  
 0.40 gms AIBN  
 0.30 gms NaNO<sub>2</sub>

Mixing Temperature = 35°C; Polymerization Temperature = 80°C.

Figure 1. Transport of Monomer from Droplets to Latex Particles:  $J_m = 1$ ,  
 $\chi_{mp} = 0.50$ ,  $T = 323^\circ\text{K}$ ,  $D_w = 10^{-10} \text{ m}^2/\text{s}$ ,  $J_p = 100,000$ ,  $V_s = 10^{-4} \text{ m}^3/\text{mol}$ ,  
 $\gamma = 5 \times 10^{-3} \text{ n/m}$ ,  $C_{m\infty} = 6 \times 10^{-4} \text{ m/m}^3$  (Equilibrium monomer conc. above  
plane surface).



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ACKNOWLEDGMENT

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STRUCTURE AND IMMUNOLOGICAL PROPERTIES  
OF POLYACROLEIN FORMED BY MEANS OF IONIZING RADIATION  
AND BY BASE CATALYSIS

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ABSTRACT

The kinetics of formation of polyacrolein microspheres by means of ionizing radiation (polymer I) were investigated. Its structure and reactivity were compared with polyacrolein microspheres prepared by base catalysis (polymer II). The study of Fourier IR spectra of polymer I and polymer II showed structural differences. The reaction of polyacrolein spheres with m-amino phenol indicated presence of conjugated groups. The reaction of antibodies with polyacrolein spheres was investigated as a function of pH, and the number of reactive aldehyde groups was determined by the nitrogen analysis of polyacrolein-hydroxylamine adducts.

Intensely fluorescent polyacrolein microspheres obtained by Coy irradiation in sizes from 100Å to 4µm have already found applications as immunoreagents for cell labeling and separation.

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STRUCTURE AND IMMUNOLOGICAL PROPERTIES  
OF POLYACROLEIN FORMED BY MEANS OF IONIZING RADIATION  
AND BY BASE CATALYSIS

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Polymerization of Acrolein in Aqueous Media

In the course of preparation of novel immunospheres, we investigated two methods of acrolein polymerization; namely those induced by ionizing radiation and those resulting from sodium hydroxide catalyzed condensation. Although the structures and reactivities of polyacroleins (PA) prepared by emulsion polymerization or by base catalyzed condensation were reported by Schulz<sup>1-5</sup> and other workers<sup>6-13</sup>, their findings are not sufficient for our needs. Knowledge of the covalent binding of antibodies or other proteins to the microspheres and the dependence on the morphological and structural factors resulting from variation of conditions prevailing during the polymerization are essential for our purposes. Moreover, some ingredients of recipes chosen by the previous workers could contaminate the final products making them unacceptable for biomedical applications.

The main results obtained from the present investigations are as follow:

1. Experimental conditions were established to prepare PA particles in the range of 100Å to 3µm in diameter.
2. Procedures were developed to produce intensely fluorescent PA microspheres of various sizes.

3. A comparison of the Fourier Infrared (IR) analysis and proton NMR (500 MH) of PA prepared by base catalysis and PA obtained by Co<sup>60</sup> polymerization<sup>20</sup> yielded evidence for a larger concentration of unreacted double bonds in base catalyzed PA and a lower concentration of functional groups capable of reacting with amines than in PA prepared by ionizing radiation. This evidence was substantiated by nitrogen analysis and reactivity studies with antibodies.
  4. Small amounts of PA on commercial polymeric spheres could be detected by a reaction with m-amino phenol which rendered the surface of spheres intensely fluorescent.<sup>14</sup>
  5. The amount of radioactive antibodies bound to PA prepared by the two methods was determined in the pH range of 4 to 10. The optimum pH for maximum binding was found to be of the order of 5.
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May 2, 1983

10 MAY 1983

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Manchester M60 1QD, England

Dear Sandy:

Current research in our group is centered around two areas:

1. Intrinsic volume and density of coal slurries.
  - a. Thermodynamic theory of binary mixtures.
  - b. Packing density of fine particles.
  - c. Density and specific volume of pulverized coal.
  - d. Influence of surface philicity on slurry concentration and rheology.
2. Properties of colloidal particles.
  - a. Optical anisotropy compared to geometric anisotropy.
  - b. Zeta potential and electrophoretic mobility.
  - c. Hydrodynamic diameter and geometric diameter.

The work is being carried out by three graduate students: Chyong-Hwa Chang from Fu-Jen Catholic University, Ana Morfesis from Chatham College and Robert Marganski from the University of Bridgeport. More recently, a Visiting Scholar, Zhong Zheng from the South China Institute of Technology, P.R.C., has joined our group and has brought his experience in the areas of stability and rheology of concentrated systems to bear with our efforts.

We will be presenting some of our results at the upcoming Colloid Symposium in Toronto and more at the ACS meeting in Washington in September.

Sincerely yours,

A handwritten signature in cursive script that reads "R. L. Rowell".

Robert L. Rowell  
Professor of Chemistry  
Acting Head

/h

## CONTRIBUTION TO THE POLYMER COLLOID GROUP NEWSLETTER

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

High Solids Latexes for Paper Coating\*

5 MAY 1983

R. L. Van Gilder, D. I. Lee, R. D. Purfeerst, J. L. Allswede  
Dow Chemical Co.; Midland, Michigan 48640

The pursuit of higher coating color solids is limited frequently by the solids level of the latex binder. Most current styrene-butadiene latex binders which are used in the blade coating application are in the 48 to 50 percent solids range and are relatively monodisperse. Many paper coaters prefer to use slurry clay for ease of handling and lower cost but are limited by the solids which can then be obtained in the formulated coating slurry. Since the remaining color component which could contribute to a significant solids increase is the synthetic latex, it would be desirable to have a high solids-low viscosity latex. In general, small particle size latexes are favored for blade coater runnability. However, as the average particle size of monodisperse latexes is decreased, the solids capability of the latex is lowered. To investigate these divergent effects of latex particle size on the latex viscosity-concentration relationship and the blade coater runnability of the corresponding coating color, a series of monodisperse carboxylated styrene-butadiene latexes of different particle size were prepared and the effect of particle size and distribution (bimodal blends) on the latex viscosity-solids relationship and high-shear paper coating color rheology determined. With high-solids monodisperse latexes from 720 to 2100 Å, the viscosity-concentration relationship increased with decreasing particle size. Bimodal blends of the 720 and 2100 Å particles showed a minimum in viscosity or a maximum in obtainable solids at a 75/25 blend of the 2100/720 Å latexes. This is attributed to an increase in packing efficiency of the bimodal blend compared with the monodisperse systems. This latex blend also produced a significant improvement in the high-shear rheology over the 2100 Å particle size latex coating color and comparable to a coating color prepared with a 1324 Å monodisperse latex. This study has demonstrated that a paper coating latex with a solids content of 60% or above with a workable viscosity can be obtained by blending and concentrating monodisperse latexes of two different particle sizes that permit high-solids clay-latex coating colors to be prepared from slurry clay which exhibit good high-shear rheology and blade coater runnability.

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\*This paper will be presented at the TAPPI 1983 Coating Conference May 15-19, 1983, San Francisco, Calif.

RADIATION INDUCED EMULSION POLYMERIZATION OF VINYL ACETATE IN A FLOW SYSTEM

9 MAY Recd

Contribution from Vivian Stannett, Department of Chemical Engineering, North Carolina State University (presently on leave with the U.S. Office of Naval Research, London)

The flow system designed and built by E.P. Stahel and his students in conjunction with the writer has been adapted to study vinyl acetate emulsion polymerization. Earlier studies were mainly concerned with styrene and vinyl acetate-chloride copolymerization. In addition some batch experiments were conducted. Earlier work with vinyl acetate has been reported by Woodard and Ransohoff, by Friis and by O'Neill and Hoigné.

The dependence of the rate on the emulsifier (sodium lauryl sulfate) concentration was found to be proportional to the  $0.38 \pm 0.09$  power with the flow system and  $0.29 \pm 0.12$  with the batch experiments. These results are in good agreement with the previously mentioned authors but contrary to the first power found earlier, and clearly, in batch experiments by Stannett et al. J. Appl. Poly. Sec. 13, 1175 (1969) and the close to zero power found by Sunardi et al. Rad. Physics and Chem. 18, 1109 (1981). The reasons for the discrepancies are not clear and suggestions are welcome!

The rates were found to decrease with increasing flow and agitation rates. The dose rate dependence was  $1.03 \pm 0.49$ . In spite of the scatter these results are within the range reported. Activation energies, molecular weights and other rate dependencies were similar to literature values.

Experiments were also conducted with nonionic (polyoxyethylene lauryl ether) and cationic (trimethyl dodecyl and octadecyl ammonium chlorides. The rates were high but lower then with sodium lauryl sulfate. Molecular weights were similar for all four emulsifiers. The full results will be presented at the A.I.CHE. meeting in Washington D.C. in November.

5 MAY 1961

We have undertaken a study of the competitive adsorption of mixtures, of a nonionic and an anionic surfactant, on polystyrene latex. The nonionic surfactant was an ethoxylated nonylphenol ether with ten ethylene oxide units (NP-E<sub>10</sub>) and the anionic surfactant was sodium dodecylsulphate (SDS).

Figure 1 shows the surfactant composition on the surface as a function of the surfactant composition in the equilibrium solution (the serum). The surfactant composition is defined as the amount nonionic surfactant divided by the total amount of surfactant. If the surfactant composition on the surface is the same as that in the surrounding solution, the experimental points would fall on the dashed line in the figure.

The figure reveals that the nonionic surfactant (NP-E<sub>10</sub>) is preferentially adsorbed on the latex surface. For example, a solution with a nonionic/anionic surfactant ratio of 10/90 is in equilibrium with a surface where the surfactant ratio is roughly 90/10. One conclusion therefore is that an analysis of the surfactant composition in the serum (the equilibrium solution) cannot give information on the surfactant composition on the latex surface.

There is, however, one rather simple way to obtain enough information to be able to estimate the surfactant composition on the surface. The only extra information needed is the critical micelle concentration of the pure surfactant.

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The calculation is based on the assumptions that (i) a complete surfactant monolayer on the latexes is achieved at the cmc and (ii) the surfactant monolayer forms an ideal mixture, i.e. there is no interaction between the two different surfactants. The latter assumption is, of course, rather crude but the effects of surfactant-surfactant interaction, at least in our case, are much smaller than the effect of the large difference in the cmc's of the two surfactants. The resulting equation is

$$B = \frac{\alpha \frac{C_a^*}{C_n^*}}{1 + \alpha \left( \frac{C_a^*}{C_n^*} - 1 \right)}$$

where B and  $\alpha$  are respectively the surfactant composition on the surface and in the equilibrium solution and  $C_a^*$  and  $C_n^*$  are the cmc's of the anionic respectively the nonionic surfactant. The results from such a calculation is shown as a dotted line in Figure 1. The agreement between experimental (from adsorption isotherms) and calculated surface composition is quite satisfactory.

Further work is pending in order to explore the general applicability of the above treatment, e.g. for systems where the cmc's of the pure surfactants are closer to each other.

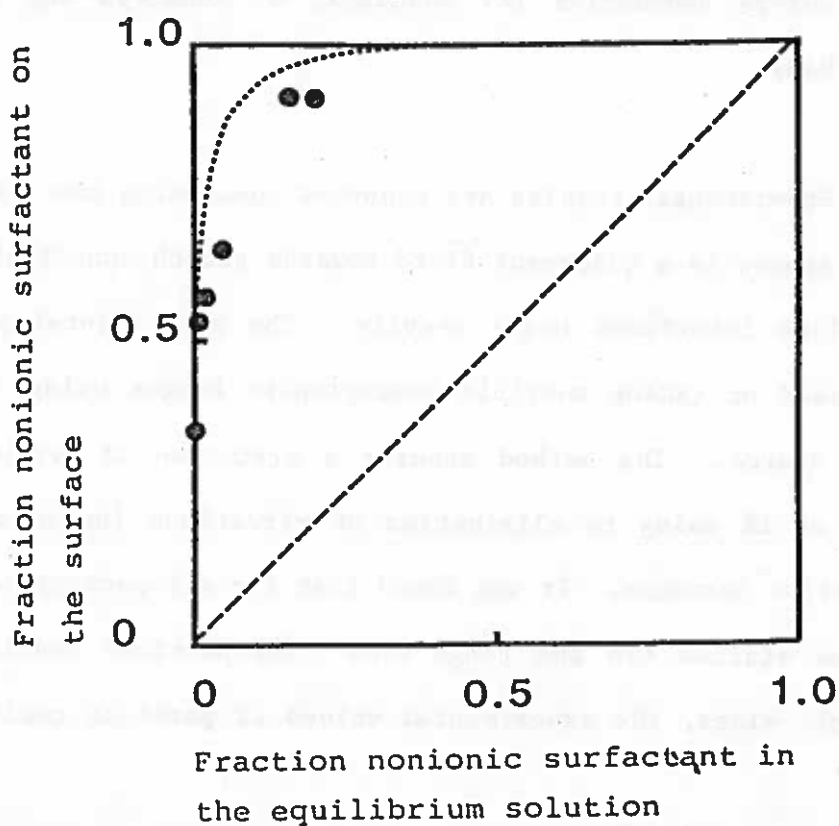


Figure 1

26 APR Recd

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 abstracts of two papers to be published in J.C.I.S. and J.P.C.S. and the contents of a note to be published in J.C.I.S.

1. Resistance coefficient of a solid sphere approaching plane and curved boundaries (Z. Adamczyk, M. Adamczyk and T.G.M. van de Ven).

Experimental results are reported concerning the slow motion of a solid sphere in a quiescent fluid towards smooth spherical, cylindrical and plane interfaces under gravity. The experimental procedure used was based on taking multiple photographic images using a stroboscopic light source. The method ensures a precision of measurement of the order of 1% owing to elimination of vibrations (no moving parts) and convective currents. It was found that for all particle-boundary separations studied (in the range 0.05 - 10 particle radii) and for all particle sizes, the experimental values of particle resistance coeffi-



cients agree with theory for systems for which theoretical predictions are available. The technique can provide accurate values of resistance coefficients of various shaped particles near curved boundaries. Such values are useful, e.g. in predicting mass transfer towards such boundaries, but are at present difficult or impossible to calculate theoretically.

2. A direct method for studying deposition of colloidal particles on solid surfaces (T. Dabros and T.G.M. van de Ven).

An experimental technique has been developed to study the deposition of colloidal particles under well controlled hydrodynamic conditions. The deposition process is observed under a microscope and recorded on video tape for further analysis. Fluid flow conditions in the experimental set-up were determined by numerical solution of the Navier-Stokes equations. Mass transfer equations were solved numerically (taking into account hydrodynamic, gravitational, electric double layer, and dispersion forces) for the stagnation point region. Also, some analytical solutions are presented. Deposition has been studied of 0.5  $\mu\text{m}$  polystyrene latex particles on cover glass slides used as collectors. From an analysis of the shape of the coating density vs. time curves and independently from the distribution of the particles on collector surfaces, it was found that one particle is able to block an area of about 20 to 30 times its geometrical cross section. The ini-

tial flux of particles to the collector for a given salt concentration was found to depend strongly on the method of cleaning the collector surface. In general the flux and the escape of particles to and from the collector surface are sensitive to the interaction energy at small separations. The direct method of observing particle deposition and detachment could lead to important insights into the nature of particle-wall interactions at near contact.

- 3. Flexible bonds between latex particles and solid surfaces (T.G.M. van de Ven, T. Dabros and T. Czarnecki).

Emulsion polymerization latices are regarded by many as model colloidal systems in which the suspended particles have well-defined surface properties (1). Here we want to report on some observations that cast doubt on the ideality of such systems, especially regarding their smoothness.

EXPERIMENTAL

Deposition of colloidal particles on transparent collector surfaces has been observed in a specially designed flow cell, in combination with a microscope and video equipment (2,3). The flow in the cell is a well-defined stagnation point flow and can vary from laminar to turbulent. With this technique the deposition process, typically on an area of  $10^{-2}$  mm<sup>2</sup>, can be followed directly.

As collector surfaces we used (i) glass (microscope cover glass slides), (ii) gold (a thin layer coated on glass), and (iii) a sapphire window.

Several latex samples, as well as a  $\text{TiO}_2$  sample, were used in the deposition experiments. Of the five latex samples used, four were polystyrene latices and one was a polyvinyl toluene latex. Of the polystyrene latices, two were prepared by Dow Chemical and two were soap-free polystyrene latices prepared according to classical recipes (4). The latices varied in size from 0.5 to 1.5  $\mu\text{m}$ .

All samples, prior to use, were diluted with distilled water (specific conductivity  $3 - 5 \times 10^{-6} \text{ } \Omega^{-1} \text{ cm}^{-1}$ ) and the ionic strength was varied by adding various amounts of NaCl.

#### OBSERVATIONS

Here we want to report on two observations which seem to indicate the presence of polymer segments protruding from the latex spheres.

1. Flexible bonds. We observed that a large fraction (sometimes up to 50%) of the latex particles deposited on a collector surface executed a type of oscillatory or "dancing" motion, especially when subjected to turbulent flow. Typically a latex particle moves irregularly over a certain site; its lateral motion can vary from a fraction of a micrometer to several micrometers. This motion was observed with all latices and all collectors used. In contrast,  $\text{TiO}_2$  particles of diameter 0.1 - 0.2  $\mu\text{m}$  did not show these flexible bonds, although some aggregates were able to rotate about an axis, however, without transla-

tional motion. Single  $\text{TiO}_2$  particles usually moved for a short time (< 1 sec) in an irregular fashion over the surface before becoming motionless.

For sapphire/latex systems the percentage of flexible bonds was pH dependent, increasing with increasing pH.

2. Anomalous deposition rates. A second observation we made is that for some systems, even in the presence of large energy barriers for which the DLVO theory (valid for perfectly smooth spheres and planes) predicts that no deposition should occur, the particles adhere to the surface with a rate characteristic of fast deposition, i.e., the deposition proceeds as if no energy barrier exists (3). For conducting surfaces (gold), changing the polarity of the surface by applying a voltage over the surface against a Pt counterelectrode immersed in the suspension, did not affect the deposition rate. The fast deposition seems to be affected by ionic strength. When  $[\text{NaCl}] < 10^{-3}$  M, little deposition was observed, in agreement with current theory (the glass/latex systems). No anomalies were observed for glass/ $\text{TiO}_2$  systems.

#### DISCUSSION

The motion of the particles over the surface seems to suggest that they are bound to the surface by a long invisible flexible connection as this motion is similar to the one observed by Pelton et al. (5) of glass and latex beads stuck to glass surfaces by high-molecular-weight polymers. However, in our systems no polymers were added to the system. Here one is reminded of an observation by one of us (6,7) that

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doublets of soap-free polystyrene latex spheres are occasionally bound together by invisible connections of up to several micrometers. The fact that the spheres of the doublet were in physical contact could be concluded from the rotation of the pair in shear flow.

From the observed motion of latex spheres tethered to collector surfaces (and to other spheres), it must be concluded that long chain-like structures exist in latex systems. The fact that flexible bonds were only observed with latices and not in  $TiO_2$  systems makes it highly unlikely that impurities in water or other artifacts could be responsible for this phenomenon.

Regarding the observation of fast deposition rates in the presence of energy barriers (according to DLVO theory), a likely explanation is the existence of "spikes" or "hairs" on the surface of the latex spheres, protruding from the surface up to distances comparable to the distance where the energy barrier occurs, typically of the order of 5 - 10 nm. The possibility that latices are "hairy" has been proposed by several people (see e.g., (8)) in order to explain anomalous behavior. Relevant to the explanation of "hairiness" is the work of Takamura et al. (9), who observed near-collisions of polystyrene latex spheres in glycerol water solutions. They observed that the particles ran into a large energy barrier at a separation of 12 nm. Hairs 5 - 10 nm long on the surface could explain this observation as well.

### Dangling Chain Model

We do not know whether the two observations reported in this note are connected. The long chains could conceivably be formed during the removal of excess monomer after the latex preparation; or they may be chains dangling from the latex particle prevented from collapsing on the surface due to the presence of surface charge groups (anchored or adsorbed). It is possible that some large tails are either lying very loosely on the particle surface causing a roughness of order 5 - 10 nm and coming loose on contact with another surface, or are dangling from the sphere, preventing contact in the absence of polymer bridging and forming flexible bonds otherwise. The presence of such loosely bound or dangling chains could explain both our observations. Such protrusions would not show up in electron micrographs as in a dry state they will collapse on the surface.

Whatever the explanation, from the observations reported in this note it seems clear that not all monodisperse emulsion polymerization latices can be uncritically considered model colloidal systems, especially in deposition and stability investigations.

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