

24 October 1979

Some qualms were expressed at the Annual Meeting about the accuracy of the Membership List and, indeed, there have been several additions, deletions, and changes of address since the full list last appeared in the Autumn 1976 Newsletter. According the current list is included in this issue. This should facilitate the circulation of reprints or preprints by members who have sufficient copies to permit general circulation. Unfortunately the growth in the size of the group means that its numbers now exceed the number of free reprints provided (by such publishers as provide any).

Revision of the Membership List unfortunately delayed the despatch of reminders that contributions for this issue were due. Evidently these are essential because only 3 members did send their contributions by the deadline given in the Spring issue. But it would be a useful economy if members would diarise the appropriate date and then act at the right time.

The deadline for receipt of contributions for the Spring issue will be Monday 21st April 1980.

The Gordon Conference decided to ask for a third 'Polymer Colloid' Conference in 1981 with a preference for a week in July although it was observed that it had not been possible to meet preferences for either period or site in the case of the second conference! The Chairman of the A.C.S. Symposium on 'Emulsion Polymerisation' being planned for the San Francisco Meeting, 24-29 August, 1980 (Bassett and Hamielec) intend to include four invited lectures in the programme. Although common practice elsewhere, this will be an innovation for the A.C.S. It is likely to be generally welcomed by participants, however, since many who attend usually do so in the hope of gaining an impression of the state of knowledge in the field. The Chairman are asking for final manuscripts (presumably as camera-ready typescript) at the time of the meeting so it should be possible for the proceedings which are to appear in the A.C.S. Symposium Series to be published with the minimum delay.

The National Colloid and Surface Chemistry Symposium is to be held at Lehigh University 9-11 June 1980: one session will be on emulsion polymerisation. Further details follow.

John Vanderhoff was elected as Vice-chairman for the next Gordon Conference: Bob Fitch will be Chairman.

A two-day Symposium on 'Emulsion Polymerization of Vinyl Acetate' is to be held at Lehigh, April 10-11, 1980. Further details follow.

To mark the retirement of Professor C.H. Bamford, FRS, Macro Group UK is holding a three-day Symposium in Liverpool, 3-5 September 1980 on 'Polymerization Mechanisms'. Intending participants may display their work in a Poster Session provided notice is given by 29 February.

Andy Homola, who is now with IBM at San Jose, California has resigned from the Group because he is no longer working in the field of Polymer Colloids.

MINUTES of the ANNUAL MEETING of the POLYMER COLLOID GROUP held on Thursday, 5th July 1979 at 1.20 p.m. at Tilton School, Tilton, New Hampshire.

Present: Gary Poehlein (in the chair), Drs. Dunn, El-Aasser, Fitch, Klein, Krieger, Nomura, Ottewill, Piirma, Rowell, Saunders, Stone-Masui, Ugelstad, and Vanderhoff (14).

It was decided that a Microsymposium should be arranged in 1980. Experience had shown that it was not very practical to try to arrange this in conjunction with an A.C.S. Meeting and it was ultimately decided that this should be arranged for Lehigh in the week-end between the Short Course (scheduled for the first week of June 2-6) and the National Colloid Symposium (to be held in the second week of June 9-11): being at the height of the examination season in Britain, this date would necessarily preclude the possibility of the British academic members attending but nevertheless seemed the optimum choice in the circumstances.

Gary Poehlein said that it had not been necessary to select applicants to attend the Gordon Conference (as was necessary for some of the Conferences) but the total number of participants had reached 95 which represented a considerable increase on the attendance at the 1977 Conference and which meant that there was a prospect that the Conference could become a regular one. It was thought, however, that a biennial frequency was sufficient and that there would certainly be no point in asking for a Conference in 1980 when the topic of emulsion polymerisation would be featured in two meetings which had already been arranged - the National Colloid Symposium at Lehigh and the A.C.S. San Francisco Meeting.

It would be desirable to meet in Europe again as soon as possible and Gary Poehlein and Ron Ottewill undertook to investigate the possibility of holding a second N.A.T.O. Advanced Study Institute at Bristol in 1982 during the first fortnight of July.

Membership: it was noted that neither Watillon or Homola had ever provided a Newsletter contribution since their election and that Homola was now with IBM in California and no longer working in the field of polymer colloids. However, enquiries as to their intentions should be made before they were removed from the list.

It was agreed that Archie Hamielec, Derek Rance, and Tim Healey (of the University of Melbourne) should be invited to join the Group.

An updated Membership List should be included in the next issue of the Newsletter since the last list to have been generally circulated was now seriously out of date.

The meeting closed at 2.08 p.m.

North American Circulation

1. Dr E.A.Collins, Diamond Shamrock Corp., P.O. Box 348, Painesville, Ohio 44077, USA.
2. Dr R.M.Fitch, Department of Materials Science, The University of Connecticut, Storrs, Connecticut 06268, USA.
3. Dr J.L.Gardon, ~~Southfield Coatings & Chemical Research Center, 38701 Telegraph Road, Southfield, Michigan 48076, USA.~~ *The Shaw-Williams Co, 10909 So. Cottage Grove Avenue, Chicago, Illinois 60628.*
4. Dr A. E. Hamielec, Dept. of Chemical Engineering, McMaster University, Hamilton, Ontario, Canada, L8S 4M1.
5. ~~Dr A. Homela, IBM Corporation, San Jose Research Laboratory, 5600 Cottle Road, San Jose, California 95195, USA.~~
6. Dr A. Klein, Department of Chemical Engineering, Whitaker Laboratory, Lehigh University, Bethlehem, Pennsylvania 18015, USA.
7. Dr I.M.Krieger, Olin Building, Case-Western Reserve University, Cleveland, Ohio 44106, USA.
8. Dr S.G.Mason, Department of Chemistry, McGill University, P.O. Box 6070, Montreal, PQ, Canada, H3A 2A7.
9. Dr I. Piirma, Institute of Polymer Science, The University of Akron, Akron, Ohio 44325, USA.
10. Dr G.W.Poehlein, School of Chemical Engineering, Georgia Institute of Technology, Atlanta, Georgia 30332, USA.
11. Dr A.A.Robertson, Pulp and Paper Building, Department of Chemistry, McGill University, 3420 University Street, Montreal, PQ, Canada H3A 2A7
12. Dr R.L.Rowell, Department of Chemistry, University of Massachusetts, Amherst, Massachusetts 01003, USA.
13. Dr F.L.Saunders, Dow Chemical Co. Central Research, 1712 Building, Midland, Michigan 48640, USA.
14. Dr V.T.Stannett, Department of Chemical Engineering, Box 5035, North Carolina State University, Raleigh, North Carolina 27607, USA.
15. Dr M. El-Aasser, Institute for Emulsion Polymers, Lehigh University, Bethlehem, Pennsylvania 18015, USA.
16. (Associate) Dr D.J.Williams, Foster Grant Co. Inc., 289 North Main St., Leominster, Massachusetts 01455, USA.
17. (Associate) Dr S.L.Goren, Program Director - Solid and Particulate Processing Division of Engineering, National Science Foundation, Washington, D.C. 20550, USA.
18. (~~Provisional~~) Dr J.S.Dodge, B.F.Goodrich Co., Chemical Division Technical Center, Avon Lake, P.O. Box 122, Ohio 44012, USA.
19. Dr J.W.Vanderhoff, Center for Surface and Coating Research, Lehigh University, Bethlehem, Pennsylvania ~~18015~~, USA.

Circulation to the Rest of the World

20. Dr D.C.Blackley, National College of Rubber Technology, Northern Polytechnic, Holloway, London N7 8DE, England.
21. Dr A.S.Dunn, Department of Chemistry, UMIST, P.O.Box 88, Manchester M60 1QD, England.
22. Dr F.K.Hansen, Dyno Industrier A/S, Lillestrøm Fabrikker, Svellevæien, P.O.Box 160, 2001 Lillestrøm, Norway.
23. Dr ~~P.W.Haley~~ ^{N. Furlong}, Département of Physical Chemistry, University of Melbourne, Parkville, Victoria 3052, Australia.
24. Dr. C.-C. Lin, Department of Chemical Engineering, National Taiwan University, Taipei, Taiwan.
25. Dr D.H.Napper, Department of Physical Chemistry, The University of Sydney, Sydney, New South Wales 2006, Australia.
26. Dr S. Muroi, New Product Developing Laboratory, Asahi Chemical Industry Co. Ltd., 2-1, Samejima, Fuji-City, Shizuoka, Japan.
27. Dr M. Nomura, Department of Industrial Chemistry, Fukui National University, Fukui, Japan.
28. Dr R.H.Ottewill, School of Chemistry, University of Bristol, Cantock's Close, Bristol BS8 1TS, England.
29. Dr D.G.Rance, I.C.I.Ltd., Plastics Division, P.O. Box 6, Bessemer Road, Welwyn Garden City, Hertfordshire AL7 1HD, England.
30. Dr P.J.Stenius, The Swedish Institute for Surface Chemistry, Drottning Kristinas väg 45, S-114 28, Stockholm, Sweden.
31. Dr J. Ugelstad, Institutt for Industriell Kjemi, Norges Tekniske Høgskole, 7034, Trondheim-NTH, Norway.
32. Dr ~~A. W. Hill~~ ^{J. Stone-Matsui}, Université Libre de Bruxelles, Service de Chimie Analytique et Minerale, 50 av. F.D.Roosevelt, Bruxelles 5, Belgium.
33. Dr V.I. Yeliseyeva, Institute of Physical Chemistry, Academy of Sciences of the U.S.S.R., Leninsky Prospekt 31, 117312 Moscow, U.S.S.R.

5. Dr J.W. Goodwin, School of Chemistry, University of Bristol, Bristol BS8 1TS, England

North American circulation (continued)

34. Dr F. Bagchi, Research Dept, Chemical Division B87 Eastman Kodak Co, Kodak Park, Rochester NY 14650, USA
35. Dr T. van der Ven, Pulp and Paper Building, Dept of Chemistry, McGill University, Montreal, PQ Canada H3A 2A7
36. Dr D. Bassett, Union Carbide Corporation, Technical Center 720-130, South Charleston West Virginia 25303, U.S.A.



Diamond Shamrock

T. R. Evans Research Center

16 OCT 1979

J O B O P P O R T U N I T Y

Polymer Colloid Science opening for senior scientist to work in area of polymer surface science. Position is in Corporate Research. Background training and/or experience in polymerization, polymer compatibility, and morphology is highly desirable.

For further details, contact:

*Dr. E. A. Collins
Associate Director
of Research
Corporate Polymers*

A TWO-DAY SYMPOSIUM
ON
EMULSION POLYMERIZATION OF VINYL ACETATE

APRIL 10-11, 1980

EMULSION POLYMERS INSTITUTE
FRANCIS MACDONALD SINCLAIR MEMORIAL LABORATORY
LEHIGH UNIVERSITY
BETHLEHEM, PENNSYLVANIA 18015, USA

The Emulsion Polymers Institute at Lehigh University is sponsoring a two-day symposium on various aspects of the emulsion polymerization of vinyl acetate. The following topics will be discussed:

1. Mechanism and Kinetics of Vinyl Acetate Emulsion Polymerization
2. Colloidal Stability of Poly Vinyl Acetate and Vinyl Acetate Copolymer Latexes
3. Surface and Morphological Properties of Poly Vinyl Acetate Copolymer Latexes and Films

The speakers who have tentatively agreed to participate are:

Dr. Wiley Daniels (Air Products), USA
Dr. S. Dunn (UMIST), England
Dr. A. Hamielec (McMaster Univ.), Canada
Dr. A. Klein (Lehigh Univ.), USA
Dr. M. Litt (Case Western Reserve Univ.), USA
Dr. C. Pichot (CNRS), France
Dr. V. Stannett (North Carolina State Univ.), USA
Dr. J. W. Vanderhoff (Lehigh Univ.), USA
Dr. B. R. Vijayendran (Celanese), USA
Dr. H. Warson (Consultant), England
Representative from E. I. duPont deNemours Co., USA
Representative from Union Carbide, USA

Other papers are invited in the above areas of the emulsion polymerization and copolymerization of vinyl acetate. Papers should be submitted to the co-chirman indicated on the following page.

SYMPOSIUM CO-CHAIRMEN

Dr. J. W. Vanderhoff
Sinclair Lab., #7

Dr. M. S. El-Aasser
Whitaker Lab., #5

Lehigh University
Bethlehem, Pa. 18015

Phone: (215) 861-3589

Phone: (215) 861-3598

FEE

\$250 for the two days, including extended abstracts of the papers, two luncheons, and four coffee breaks. Checks payable to "VAC-SYMPOSIUM, LEHIGH UNIVERSITY" should accompany applications, or presented on first day of Symposium. The Symposium fee will be waived for the speakers. Each member of the Industrial Liaison Program may send one representative without charge. Please reserve early as registration is limited to the capacity of our auditorium (capacity 130).

DEADLINE FOR PAPER SUBMISSION

December 15, 1979	Titles
February 15, 1980	Two-Page Abstract

54TH
COLLOID AND SURFACE SCIENCE SYMPOSIUM
JUNE 15-18, 1980
LEHIGH UNIVERSITY, BETHLEHEM, PENNSYLVANIA 18015

CALL FOR PAPERS

FOR

SPECIAL SYMPOSIUM ON THE SCIENCE AND
TECHNOLOGY OF EMULSION POLYMERS

Papers are invited in all areas of the science and technology of emulsion polymers, including the preparation, characterization, properties, and applications of emulsion polymers. Papers should be submitted to the Co-Chairman designated for each of the following categories:

1. Analytical Chemistry of Emulsion Polymers - determination of latex particle size distribution; particle morphology; surface characterization; serum analysis; electrokinetic properties (Dr. John W. Vanderhoff).
2. Stabilization of Emulsion Polymers - theoretical and experimental studies of the stabilization of latex particles; measurement of various types of latex stability; stability problems in latex formulations (Dr. Mohamed S. El-Aasser).
3. Mechanism and Kinetics of Emulsion Polymerization - kinetics of emulsion polymerization; mechanism of particle nucleation and growth; correlation of reactor operation with emulsion polymer properties; reactor and process engineering (Dr. Gary W. Poehlein).

4. Applications of Emulsion Polymers - mechanism of latex film formation; mechanisms by which emulsion polymers function in practical applications; correlation of latex properties with application performance; new applications of latex (any of the Co-Chairmen listed above).

This Special Symposium should be of interest to academic and industrial scientists and engineers who work with emulsion polymers. We look forward to your participation.

SYMPOSIUM CO-CHAIRMEN

Dr. John W. Vanderhoff
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DEADLINES FOR SUBMISSION OF PAPERS

December 15, 1979
February 15, 1980

Titles of Proposed Presentations
Extended Abstracts (two-three pages)

A NEW METHOD FOR DETERMINING THE GELATION TEMPERATURE AND TIME FOR HEAT-SENSITIVE LATICES

D. C. Blackley, National College of Rubber Technology, The Polytechnic of North London, Holloway, London N7 8DB.

A latex is said to have been "heat-sensitised" if, although it is stable at room temperature, it coagulates rapidly when the temperature is raised above some threshold value. Usually coagulation takes the form of gelation. Rubber latices which have been made heat sensitive by the addition of suitable compounding ingredients are of considerable industrial importance. They find application, for instance, in processes such as latex foam rubber manufacture, the foam backing of carpets, and the production of articles by latex dipping. A matter of some importance in connection with such latices is the temperature at which (or the temperature range over which) the latex undergoes the transformation from liquid to gel, together with the associated time required for the completion of gelation. This contribution is concerned with a new method which we have recently developed for determining the gelation temperature and time for heat-sensitive latices. The method depends upon the reasonable assumption that the heat transfer properties of a latex gel differ somewhat from those of the latex from which it was derived. An advantage of the new method over older procedures for determining the gelation temperature of a heat-sensitive latex is that, unlike the older procedures, the identification of the gel point does not call for an element of subjective judgement. In the new method, the gel point is located by means of a reasonable, objective and quantitative criterion, namely, the differences between the heat-transfer properties of the fluid latex and those of the gel derived from it. That such differences should exist is reasonable, because the thermal conductivity of a disperse system is determined mainly by that of the continuous phase, and it is the nature of the continuous phase which changes at the gel point.

The new method depends upon the measurement at various times of the temperature of a latex at a fixed distance from a heated former which is immersed in the latex and maintained at a constant temperature which is well above the gelation temperature of the latex. The theory of the method gives the following equations:

$$\theta_a = \frac{\theta^*}{\operatorname{erfc}(\lambda)} \operatorname{erfc}\left(\frac{x}{\sqrt{4\alpha_a t_a}}\right) \dots\dots (1)$$

$$\theta_b = \theta_i - \frac{\theta_i - \theta^*}{\operatorname{erf}(\lambda\sqrt{\alpha_a/\alpha_b})} \operatorname{erf}\left(\frac{x}{\sqrt{4\alpha_b t_b}}\right) \dots\dots (2)$$

and
$$\frac{\alpha_a \theta^*}{\operatorname{erfc}(\lambda)} e^{-\lambda^2} = \frac{\alpha_b (\theta_i - \theta^*)}{\operatorname{erf}(\lambda\sqrt{\alpha_a/\alpha_b})} \sqrt{\frac{\alpha_a}{\alpha_b}} e^{-\lambda^2 \alpha_a/\alpha_b} \dots\dots (3)$$

where θ_i is the temperature of the former and θ^* is the gelation temperature of the latex, both relative to the initial temperature of the latex as zero, θ_a is the temperature of the latex (on the same scale) at the fixed distance x from the former and at time t_a whilst the latex is still fluid, θ_b is the temperature of the latex at the same distance x and at a subsequent time t_b after gelation

has occurred, α_a is the thermal diffusivity of the fluid latex, and α_b is the thermal diffusivity of the gelled latex. λ is a constant parameter which is defined by the equation

$$\lambda = \frac{x^*}{\sqrt{4\alpha_a t^*}} \dots\dots (4)$$

where t^* is the time at which the plane separating gelled latex from fluid latex (the "gel plane") has reached a distance x^* from the surface of the former.

It is not possible to give exact analytical solutions for the set of equations (1) - (3). It is, however, possible to solve them numerically by an iterative procedure with the aid of a computer if θ , x and α_a are known. (The value of α_a is known from other work on the thermal properties of rubber lattices in the fluid condition which we have recently carried out.) The first step in our numerical procedure is to assume a value for λ , and then calculate θ^* by means of equation (1) using the measured value of $\theta_a(x, t_a)$ and the known values of x, t_a and α_a . We then calculate α_b by means of equation (2) using the same value of λ , the measured value of $\theta_b(x, t_b)$, and the known values of x and t_b . We now have values of all the quantities necessary to calculate values of the two sides of equation (3). This we do, and of course, find that in general the two values differ significantly. We now repeat the process using a different value of λ , and, by successive iterations of this kind, eventually obtain a value of λ (and also of θ^* and α_b) such that the difference between the values of the two sides of equation (3) is less than 5% of the smaller of the two sides. Although the iteration could be continued to give even closer concordance between the values of the two sides of equation (3), we regard this degree of concordance as being sufficiently satisfactory for our purposes. Having obtained a satisfactory estimate of λ , and hence also of θ^* and α_b , it is then possible to estimate the value of t^* for the point $x^* = x$, i.e., to estimate the time which must elapse from the beginning of heat transfer for the gel plane just to have reached the point at which the measurements of θ were made. t^* can then be estimated from equation (4) as $x^2 / (4\lambda^2\alpha_a)$.

We have applied this method with some success to prevulcanised natural rubber latex which has been heat-sensitised by the addition of polyvinyl methyl ether. Some interesting results have been obtained. It can be seen from the foregoing outline description of the method that, besides giving estimates of θ^* and t^* (corresponding to $x^* = x$), it also gives an estimate of α_b , the thermal diffusivity of the latex gel. This latter property may prove to be a useful index of the structure of a latex gel, since it is to be expected that it will depend upon the number of inter-particle contacts and the extent to which inter-particle coalescence has occurred.



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Effect of Emulsifiers on the Thermal Initiation Rate of Styrene

As a M.Sc. Dissertation project, Mr S.A.Hassan has been following up Said's work on the energy of activation for the thermal polymerisation of styrene in emulsion using a different emulsifier - sodium dodecyl benzene sulphonate. Unlike potassium stearate and sodium dodecyl sulphate which accelerate the rate of thermal initiation at 60 °C by a factor of 100 or thereby (and sodium tetrapropylene benzene sulphonate used by Ashara et al. for which the effect is even larger) this emulsifier (or at least the sample of it which was used) does not accelerate thermal initiation of styrene. In the mechanism proposed by Mayo and by Pryor for the thermal initiation of styrene polymerisation, styrene dimer (AH) is supposed to be formed by Diels-Alder addition and then, in a step described as Molecule Assisted Homolysis, to transfer a labile hydrogen atom to a styrene monomer molecule to initiate polymerisation:



It has not yet been possible to isolate the dimer, AH, but model compounds have been made containing similar structures with labile hydrogens. Some of these do accelerate the rate of thermal initiation of styrene in bulk but others do not, presumably depending on whether their labile hydrogens are more or less labile than that in AH. If an emulsifier molecule is going to enter into this mechanism, it must presumably do so either by accepting a hydrogen atom from AH more readily than styrene monomer or by itself having a labile hydrogen atom more labile than that of AH which can be donated to a styrene monomer molecule to initiate polymerisation. Neither of these possibilities seems likely for an emulsifier with an n-alkyl chain the sodium tetrapropylene benzene sulphonate has an extensively branched alkyl chain so that the catalysis could be attributable to the loss of labile tertiary hydrogen atoms. It seemed possible that the stearic acid and the alkyl chain of the sodium dodecyl sulphate might be synthetic and might therefore contain a minor proportion of branched-chain isomers (since the criterion of acceptability would primarily be that the proportion was low enough to avoid foaming of sewage-works effluent). We obtained a sample of Triton X-100 (notorious for having a labile hydrogen): this however proved not to accelerate polymerisation. Examination of the reagent bottle dealt a final blow to the labile hydrogen theory: the material used proved not to be the B.D.H. Specially Pure grade (labelled 99% by GIC) as I had thought but a old Hopkin & Williams' sample which whilst labelled 'Pure' was also specified as containing no more than 7% palmitic acid and no more than 3% oleic acid which appears to indicate quite clearly that the material used had been prepared from vegetable oil and even if not pure stearic acid would be free from branched-chain isomers. The concentrations of all the emulsifiers used were well above their c.m.c. so the effect seems to be connected with the specific properties of the emulsifier rather than the presence of micelles. At this stage, it would clearly be desirable to screen as wide a variety of emulsifier types as possible to classify them into accelerating and non-accelerating groups to see if any common features emerged in each group. This is an aspect which has also been neglected in studies of the micellar catalysis of other reactions.

Contribution from Dr. Finn K. Hansen,
Dyno Industrier, Lillestrøm, Norway.

51 MAY 1978

First I must express my gratitude for the honour it is to be elected into the Polymer Colloid Group, and hope to fulfill the requirements. The last year I have been working with Egon Matijević at Clarkson in the U.S.A. on some very interesting heterocoagulation experiments. We have treated the heterocoagulation between particles of widely different size as an adsorption process and are thus able to calculate directly the potential energy change at coagulation. In these experiments small polymer particles produced by emulsion co-polymerization of methyl methacrylate and methacrylic acid (diameter 80 nm) are adsorbed on large spherical metal (hydrous) oxide particles (aluminum and iron, diameter 500 nm). The adsorption rate is measured and found to be purely diffusion controlled if the hydrodynamic correction of the diffusion constant at close interparticle distances is included. Adsorption is performed in emulsifier-free systems at pH values (6 - 9) where the small and large particles are mainly oppositely charged and with different concentrations of neutral electrolyte. The adsorption isotherms are all of the Langmuir type with an adsorption energy fairly independent of coverage, increasing only 1 - 2 kT with increasing coverage. The maximum adsorption at high electrolyte concentration corresponds within 10% to a monolayer calculated from a hexagonal closest packing of small particles on the surface of the large ones, decreasing with decreasing electrolyte concentration (10^{-2} - 10^{-5} M). The adsorption energy at pH 6 is about -14 kT (10^{-2} M electrolyte) decreasing to about -11 kT at the isoelectric point of the metal (hydrous) oxide particles. The same result is obtained for both oxides. The -11 kT at the i.e.p. seems a very reasonable value for the Van der Waal's energy at a particle separation of ≈ 5 Å, then leaving about -3 kT for the electrostatic part. If the well known expression of Hogg, Healy and Fuerstenau is applied, energies of -150 kT or more are calculated (using zeta potentials). However, we were also able to compute values by means of the recent model developed by Barouch et al. (at Clarkson) based on the complete two-dimensional Poisson-Boltzmann equation, resulting in a reduction in the theoretical V_R to -3 to -5 kT, in excellent agreement with experiments. Also other results at Clarkson indicate that the main reason for the great overestimation of V_R by HHF and the DLVO-theory for spherical particle interaction stems from the approximations introduced in the Derjaguin method. The Barouch-expression also seems to bring the stability ratios (W) down to the values measured experimentally. The above work is submitted for publication in the J. Chem. Soc., Faraday Trans.

Finn K. Hansen

Contribution to the Polymer Colloid Group
Newsletter

28 SEP 1979

M. S. El-Aasser, A. Klein, and J. W. Vanderhoff

Our group was accused and rightly so, of not contributing to the previous Newsletter (Vol. 9, No. 1, May 1, 1979). We have decided to wash our sins once and for all. Consequently, our contribution this time is Volume Number 12 of our Graduate Research Progress Reports. The 75-page Report summarizes the progress in 17 active research projects in our institute. The titles of these projects are given in the index of that Report which is included with this write-up. Copies of the report will be mailed directly to the members of the Polymer Colloid Group, as soon as we get an up-to-date membership list.

Four events are scheduled to take place at Lehigh University during 1980:

- i. A two-day symposium on the "Emulsion Polymerization of Vinyl Acetate", April 10-11, 1980.
 - ii. Lehigh's short course on "Advances in Emulsion Polymerization and Latex Technology", June 9-13, 1980.
 - iii. A special symposium on "The Science and Technology of Emulsion Polymers," which is part of the 54th Colloid and Science Symposium, June 15-18, 1980.
 - iv Annual Meeting and Microsymposium of the Polymer Colloid Group June, 14-15, 1980.
- Announcements and Call for Papers on events (i) and (iii) are enclosed with this write-up.

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Influence of Monomer Preemulsification on Formation of Particles from Monomer Drops in Emulsion Polymerization

D. P. DURBIN, M. S. EL-AASSER, G. W. POEHLEIN, and J. W. VANDERHOFF, *Lehigh University, Department of Chemical Engineering, Bethlehem, Pennsylvania 18015*

Synopsis

Evidence was obtained supporting the theory that monomer droplets can become a locus of initiation and propagation in emulsion polymerization. This was done by reducing the size of the monomer droplets prior to initiation of polymerization using different preemulsification techniques for a typical latex recipe containing a common anionic surfactant. Monomer droplet size reduction caused an increase in the total surface area of the monomer droplets and thereby increased the competitiveness of these droplets for capturing active free radicals which are generated in the aqueous phase. As the total surface area of the monomer droplets was increased by preemulsification, a corresponding increase in the number of large particles formed by polymerization of these monomer droplets was experimentally measured. This work shows that monomer droplets are a locus of emulsion polymerization. However, the importance of monomer droplet polymerization is limited by their total surface area because of the competition for free radicals with other surfaces and/or particle nucleation processes. The results offer a basis for explaining why broad, and sometimes bimodal, particle size distributions are obtained in some commercial processes where the reactants are preemulsified prior to being charged into a reaction vessel.

POLYMER COLLOID NEWSLETTER CONTRIBUTION

CASE WESTERN RESERVE UNIVERSITY

22 OCT 1979

Equilibrium and Transport: Charles Havens completed his doctoral dissertation on Computer Simulation of Colloid Dynamics, working with Professors J. A. Mann, Jr. and I. M. Krieger. The thesis contains two principal advances: a thorough analysis of phase equilibria in colloidal fluids, and a practicable method to treat transport properties. Havens points out that, for a stable colloid, the maximum in the DLVO potential is so high that the region of the primary minimum is of no interest. The potential curve at attainable interparticle spacings resembles the familiar Lennard-Jones potential, with the DLVO secondary minimum playing the role of the equilibrium spacing. The depth ϵ of this minimum, however, is very sensitive to electrolyte level.

By analogy with the statistical-mechanical analysis of molecular fluids, there should be a critical temperature T_c of the order of ϵ/k , where k is Boltzmann's constant. The actual critical transition should be unobservable, however, due to the low concentrations of colloidal particles and the resultant large fluctuations in relative density near the critical point. The gas-liquid transition should, however, be observable at temperatures below T_c , although it may be interpreted as settling or creaming. The order-disorder transition is a fluid-solid transition.

In approaching the problem of calculating transport properties, Havens notes that Monte Carlo techniques such as that of van Megen and Snook are limited to equilibrium properties. Dynamic simulation methods must take into account the interactions between the particles and the molecules of the medium, as well as molecule-molecule interactions. Since there are ca. 10^9 molecules for every colloid particle, this approach is not practical for concentrations where particle-particle interactions become significant. Havens chooses instead to use Langevin's equation, in which the effect of the medium is included through a viscous drag $-\beta\dot{\underline{u}}$ and a random force $\underline{A}(t)$. If \underline{X} is the body force exerted on a particle by the other colloidal particles, then the velocity \underline{u} is given by

$$m \frac{d\underline{u}}{dt} = \underline{X} - \beta\underline{u} + \underline{A}(t).$$

Havens first shows that integration of Langevin's equation yields radial distribution functions and equation-of-state data consistent with those obtained by van Megen and Snook. He then applies this method to obtain the mean-square displacement $\overline{x^2}$, and from this the diffusion coefficient

$$D = \frac{\overline{x^2}}{2t}.$$

His results show a decrease in D with particle concentration, with D dropping rapidly as the effective volume fraction approaches that of packed spheres.

Polyelectrolyte in Latices: One of the methods which we have studied for obtaining latices with high surface charge is the sulfonation of a poly-(vinylbenzyl chloride) latex. Much of the apparent charge, calculated from conductometric titration of the deionized latex with base, is due to water-soluble polyelectrolyte. Yohannes Chonde reported a quantitative study of this problem at the Gordon Research Conference on Polymer Colloids in August. By ultracentrifuging latices and analyzing the sera using gel permeation chromatography (GPC), he showed that most latices contain significant concentrations of water-soluble polymers of low molecular weight (1000 to 4000). He prepared a radioactive soluble polymer by solution polymerization of sodium vinylbenzyl sulfonate containing ^{35}S . He added this radioactive polymer to latices, and determined the properties of serum and residue after successive centrifugations. He found that ultracentrifugation followed by GPC analysis of the serum is a useful way to detect and determine water-soluble polymers in latices, and that successive ultracentrifugation is an effective method to remove them.

R.M.Fitch - University of Connecticut

Telegraphed apologies, but refers members to a recent publication in the Journal of Colloid & Interface Science, Fitch, Gajria, & Tarcha "Acrylate Polymer Colloids: Kinetics of Autocatalysed Hydrolysis" August, 1979 issue.

As presaged by Robertson in the Spring Newsletter, the August and September, 1979, issues of the 'Journal of Colloid & Interface Science' constitute a Festschrift in honour of Stan Mason's 65th birthday and consequently contain many articles likely to be of interest to Group members.

Other recent items in the literature

F.K.Hansen & J. Ugelstad "The Effect of Desorption in Micellar Particle Nucleation in Emulsion Polymerisation" MaKromol. Chem. **180** (1979) 2423-34 (10)

Following Nomura $N \propto (S - S_{\text{cmc}})^z (I)^{1-z}$: as radical desorption becomes more important z increases from 0.6 to 1. Inter alia, the authors calculate the factor ξ = the efficiency of capture of radicals by a micelle relative to a latex particle of the same size is 0.6 for styrene and 1.6×10^{-4} for vinyl acetate

R. L. Zollars (on work done at Union Carbide but now at Washington State University) 'Kinetics of the Emulsion Polymerization of Vinyl Acetate' J. Appl. Polym. Sci. **24** (1979) 1353-70 (5), addresses himself to reconciling the conflicting results in the literature on the order of the vinyl acetate emulsion polymerisation with respect to initiator which varies between 0.5 and 1. He reproduces both the results obtained by Friis & Nyhagen at 50 °C and by Litt, Stannett, & Patsiga at 60 °C and largely succeeds in reconciling the conflicting evidence.

POLYMER COLLOIDS AT SYDNEY UNIVERSITY

Reporter: D. H. Napper

8 OCT 1979

Polymers at Interfaces

Monte Carlo calculations have demonstrated empirically the slow convergence of the characteristic ratio ($C_n = \langle r^2 \rangle_0 / nl^2$) of linear polymer tails. Whereas most chains in free solution attain a C_n value within 2% of their C_∞ value by $n=250$, the corresponding C_n value for tails is usually 10% lower than the C_∞ value. To obtain a value of C_n for attached polymethylene within 2% of its C_∞ value requires n to be greater than 2000.

To explore the reasons for this, we have developed an analytical expression for C_n for random flight chains attached to an inert interface. This shows that whereas C_n for the random flight chain in free solution converges instantaneously, the characteristic ratio of the attached chain is only a slowly converging function. This slow convergence can be traced to the bias that is introduced into the direction normal to the interface as a result of the presence of the interface. These analytical predictions are in good agreement with the Monte Carlo results on the same model.

Contribution to Polymer Colloid Group Newsletter

by

Mamoru Nomura
Department of Industrial Chemistry
Fukui University
Fukui, Japan

22 OCT 1979

On the Rate Coefficient of Radical Desorption and Absorption in Polymer Particles in Emulsion Polymerization

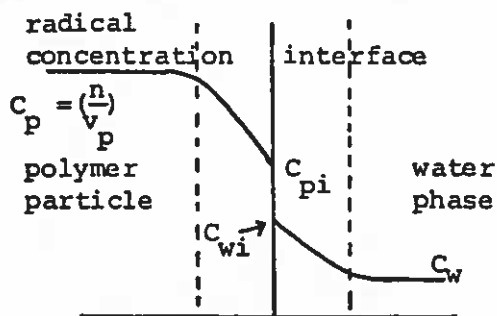
Radical desorption and absorption processes are, for example, expressed by the following formula¹⁾ in the emulsion polymerization system where the respective polymer particle contains at most one radical.

$$-\frac{dN^*}{dt} = k_f N^* - k_2 C_w N^* - k_2 C_w N_0 \quad \text{-----(1)}$$

where N^* denotes the number of polymer particles with polymerizing radical, N_0 , the number of polymer particles without radicals, C_w , the concentration of radicals in the water phase.

Ugelstad et al used k_d and k_a instead of k_f and k_2 , respectively²⁾. The first term of the right hand side of Eq.(1) shows the rate of radical desorption from polymer particles, the second term is the rate of radical termination by radical entry if instantaneous termination is assumed and if instantaneous termination is on the contrary, not assumed, this term means the increasing rate of the number of polymer particles with two radicals. The third term indicates the production rate of polymer particles with one radical by radical entry into polymer particle without radicals.

Let's consider here the physical meanings of k_f and k_2 in Eq.(1). According to the two-film theory developed by Lewis and Whitman³⁾ for mass transfer between two phases, the following concentration gradients (in the strict sense, activity gradients) near a phase boundary can be assumed.



- C : radical concentration in polymer particle.
- n : the number of radicals in polymer particle.
- C_w : radical concentration in water phase.
- v : volume of a polymer particle.
- a_p : surface area of a polymer particle.
- subscript "i" means interface.

The rate of radical desorption from the polymer particles which contain radicals is expressed by:

$$N_A = \frac{d(v_p C_p)}{dt} = k_p a_p (C_p - C_{pi}) = k_w a_p (C_{wi} - C_w) \quad \text{-----(2)}$$

where k_p is particle-side-film mass-transfer coefficient and k_w is water-side-film mass-transfer coefficient.

It is assumed that concentrations at equilibrium can be given by the following expression:

$$C_{pi} = m C_{wi} \quad \text{----- (3)}$$

where m denotes partition coefficient of desorbing radicals between phases. By using Eqs. (2) and (3), we get:

$$N_A = \frac{C_p - C_{pi}}{\frac{1}{k_{pa}}} = \frac{C_{wi} - C_w}{\frac{1}{k_{wa}}} = \frac{C_p - mC_w}{\frac{1}{k_{pa}} + \frac{m}{k_{wa}}} = K_p a_p (C_p - mC_w) \quad \text{--- (4)}$$

$$= \frac{C_p/m - C_w}{\frac{1}{mk_{pa}} + \frac{1}{k_{wa}}} = K_w a_p (C_p/m - C_w) \quad \text{----- (5)}$$

whence, $\frac{1}{K_p} = \frac{1}{k_{pa}} + \frac{m}{k_{wa}} \quad \text{---- (6)}$ $\frac{1}{K_w} = \frac{1}{mk_{pa}} + \frac{1}{k_{wa}} \quad \text{----- (7)}$

These state simply that the overall resistance is the sum of the two individual resistances. K_p and K_w are called the overall mass-transfer coefficients.

It is clear from Eqs. (6) and (7) that:

$$mK_p = K_w \quad \text{----- (8)}$$

Physical Meaning of k_p and k_w

There are many reports regarding mass-transfer coefficient around single sphere. One of the famous works is the following semitheoretical equation given by Ranz and Marshall⁴⁾.

$$Sh = 2 + 0.6 R_e^{1/2} S_c^{1/3} \quad \text{----- (9)}$$

As such small particles as polymer particles will move with eddies of the fluid, there will be no relative velocity between the surface of polymer particles and the fluid where the polymer particles suspend. Therefore, it will be reasonable to consider that the value of R_e , reynolds number is nearly zero.

\therefore Sherwood Number, $Sh = \frac{k_w d}{D_w} = 2 \quad \therefore \quad k_w = \frac{2D_w}{d_p} \quad \text{----- (10)}$

where D_w is diffusion coefficient of radicals in the water phase and d_p is diameter^w of polymer particle.

On the other hand, k is assumed to be $2D_w/d_p$ by analogy with Eq. (10). Another derivation of the form of k is as follows: when $C_w = 0$ and therefore, $C_{pi} = 0$, Eq. (2) is written as;

$$N_A = \frac{d(v.C)_{pp}}{dt} = k_{pa} C_p \quad \text{----- (11)}$$

The average time spent by the radical in the polymer particle \bar{t} is;

$$\bar{t} = \frac{(v.C)_{pp}}{N_A} = \frac{v_p}{k_{pa}} = \frac{d_p}{6k_p} \quad \text{----- (12)}$$

If Einstein's diffusion equation is applied to calculate \bar{t} , we get:

$$\bar{t} = \frac{d_p^2}{2D_p} \text{ (maximum time)} \quad \text{-----(13)}$$

If the treatment by Litt⁵⁾ et al. is used, we get:

$$\bar{t} = \frac{d_p^2}{4D_p} \sim \frac{d_p^2}{5D_p} \quad \text{-----(14)}$$

Therefore,

$$\bar{t} = (0.2 \sim 0.5) \frac{d_p^2}{D_p} \quad \text{-----(15)}$$

Comparing Eqs. (12) and (15), we have:

$$k_p = \frac{\zeta D_p}{d_p}, \left(\frac{1}{3} \leq \zeta \leq 2 \right) \quad \text{-----(16)}$$

By introducing Eq. (16) into Eqs. (6) and (7), we get:

$$K_p = \frac{2D_w}{md_p} \left[1 + \left(\frac{2D_w}{\zeta m D_p} \right)^{-1} \right] = \frac{2D_w \delta}{md_p} \quad \text{-----(17)}$$

and from Eq. (8),

$$K_w = \frac{2D_w \delta}{d_p} \quad \text{-----(18)}$$

where δ is $\left[1 + \left(\frac{2D_w}{\zeta m D_p} \right)^{-1} \right]$ and D_p is diffusion coefficient of radicals in the polymer particles.

Physical Meaning of k_f and k_2

Above theory is applied to an emulsion polymerization system where polymer particles contain at most one polymerizing radical. Let N^* be the number of polymer particles containing one radical, N_0 be the number of polymer particles containing no radical and N_T be the total number of polymer particles. Therefore, $N_T = N^* + N_0$.

The desorption rate of radicals from polymer particles will equal the decreasing rate of the number of polymer particles with radical.

Therefore,

$$-\frac{dN^*}{dt} = \bar{K}_p a_p \left(\frac{1}{v_p} - mC_w \right) N^* + \bar{K}_p a_p \left(\frac{0}{v_p} - mC_w \right) N_0 \quad \text{---(19)}$$

We must use \bar{K}_p , the average value of K_p instead of K_p , because desorbed radicals are different in chain length and hence, the overall mass-transfer coefficient vary with the chain length of desorbing radicals.

Eq. (19) is rewritten as,

$$\begin{aligned} -\frac{dN^*}{dt} &= \bar{K}_p \left(\frac{a_p}{v_p} \right) N^* - \bar{K}_w a_p C_w N^* - \bar{K}_w a_p C_w N_0 \\ &= k_f N^* - k_2 C_w N^* - k_2 C_w N_0 \end{aligned} \quad \text{-----(20)}$$

This equation is equal to Eq. (1). Therefore, we get the following definition for k_f and k_2 in Eq. (1):

$$k_f = \overline{K}_p \left(\frac{a_p}{v_p} \right) = \frac{6\overline{K}_p}{d_p}, \quad k_2 = \overline{K}_w a_p \quad \text{-----(21)}$$

Let's look into the physical meaning of the term, $k_f N^*$ in more detail. From the definition of \overline{K}_p , we can write as:

$$k_f N^* = \left(\frac{6\overline{K}_{p1}}{d_p} \right) N_1^* + \left(\frac{6\overline{K}_{p2}}{d_p} \right) N_2^* + \dots + \left(\frac{6\overline{K}_{pj}}{d_p} \right) N_j^* + \dots \quad (22)$$

where N_j^* denotes the number of polymer particles with j-units radical and \overline{K}_{pj} is the overall mass-transfer coefficient for radicals with j-units.

We make the following assumptions for simplicity.

- (1) particles contain at most one radical.
- (2) radicals with less than s-units can escape and enter the polymer particles with the same rate.
- (3) Instantaneous termination takes place when another radical enter the particle which already contains a radical.
- (4) no distinction is made between radicals with or without an initiator fragment.

Considering the assumption (2) given above, Eq.(22) is rewritten as :

$$k_f N^* = k_{oI} N_I^* + k_o N_1^* + k_o N_2^* + \dots + k_o N_s^* \quad \text{-----(23)}$$

$k_{oI} N_I^*$ is the term for taking into account initiator radicals and $k_o = \frac{6\overline{K}_{p1}}{d_p}$.

Taking balances for the particles N_1^* and N_i^* containing an initiator radical and a radical with i-units, respectively, and assuming steady-state,

We have:

$$\frac{dN_1^*}{dt} = k_2 I^* N_o - (k_2 C_w + k_{mf} M_p + k_i M_p + k_{oI}) N_1^* = 0 \quad \text{-----(24)}$$

$$\frac{dN_i^*}{dt} = k_2 M_1^* N_o + k_i M_p N_I^* + k_{mf} M_p N^* - (k_2 C_w + k_{mf} M_p + K_{pp} M_p + k_o) N_i^* = 0 \quad \text{-----(25)}$$

$$\frac{dN_{i-1}^*}{dt} = k_2 M_{i-1}^* N_o + K_{pp} M_p N_{i-1}^* - (k_2 C_w + k_{mf} M_p + K_{pp} M_p + k_o) N_{i-1}^* = 0 \quad \text{--(26)}$$

$$\frac{dN_s^*}{dt} = k_2 M_s^* N_o + K_{pp} M_p N_{s-1}^* - (k_2 C_w + k_{mf} M_p + K_{pp} M_p + k_o) N_s^* = 0 \quad \text{--(27)}$$

where M_p = monomer concentration in the particles, k_{mf} = transfer rate constant to monomer molecules, k_i = initiation rate constant, k_{oI} = desorption rate constant for initiator radicals, M_i^* = the concentration of radicals with i-monomer units in the water phase and N_i^* = the number of polymer particles with radicals of i-units and K_{pp} is propagation rate constant. C_w , the total concentration of radicals in the water phase is written by:

$$C_w = I^* + M_1^* + M_2^* + \dots + M_s^* \quad \text{-----(28)}$$

Taking balances for the radicals in the water phase and assuming steady-state, we get:

$$\frac{dI^*}{dt} = r_i + k_{oI} N_I^* - k_2 I^* N_T = 0 \quad \text{-----(29)}$$

where r_i is the production rate of initiator radicals in the water phase.

$$\frac{dM_1^*}{dt} = k_{o1} N_1^* - k_2 M_1^* N_T = 0 \quad \text{----- (30)}$$

$$\frac{dM_i^*}{dt} = k_{oi} N_i^* - k_2 M_i^* N_T = 0 \quad \text{----- (31)}$$

$$\frac{dM_s^*}{dt} = k_{os} N_s^* - k_2 M_s^* N_T = 0 \quad \text{----- (32)}$$

Considering that high molecular weight polymers can be usually obtained in emulsion polymerization, it is reasonable to assume that:

$$k_2 C_w, k_{mf} M_p \ll K_{pp} M, k_i M_p \quad \text{----- (33)}$$

From Eqs. (24) and (29) and $N^* = \bar{n} N_T$, we get an approximate equation for N_I^* :

$$N_I^* = \frac{r_i (1 - \bar{n})}{k_{oi} \bar{n} + k_i M_p} \quad \text{----- (34)}$$

By a similar treatment we get expressions for N_1^* and N_i^* , respectively.

$$N_1^* = \left(\frac{k_{mf} M_p}{k_{o1} \bar{n} + K_{pp} M} \right) N^* + \left(\frac{k_i M_p}{k_{o1} \bar{n} + K_{pp} M} \right) N_I^* \quad \text{----- (35)}$$

$$N_i^* = \left(\frac{K_{pp} M}{k_{oi} \bar{n} + K_{pp} M} \right)^{i-1} N_1^* = \left(\frac{K_{pp} M}{k_{oi} \bar{n} + K_{pp} M} \right)^i \left[\left(\frac{k_{mf}}{K_p} \right) N^* + \left(\frac{k_i}{K_p} \right) N_I^* \right] \quad \text{----- (36)}$$

From Eq. (23) and Eqs. (34) to (36), we have:

$$k_f = k_{oi} \left(\frac{N_I^*}{N^*} \right) + k_o \left[\left(\frac{k_{mf}}{K_p} \right) + \left(\frac{k_i}{K_p} \right) \left(\frac{N_I^*}{N^*} \right) \right] \sum_{i=1}^s \left(\frac{K_{pp} M}{k_{oi} \bar{n} + K_{pp} M} \right)^i \quad \text{----- (37)}$$

Initiator radicals are usually so reactive that the number of polymer particles with I^* radical, N_I^* will be very small and hence, it will be reasonable to assume that the term N_I^*/N^* in Eq. (37) is negligible, especially if transfer to monomer molecules is dominant, that is, k_{mf}/K_p is larger. Further, $k_{oi} \bar{n}$ is far smaller than $K_{pp} M$ in an ordinary emulsion polymerization system, otherwise, high molecular weight polymer cannot be produced considering Eq. (36).

Then,

$$k_f = k_o s \left(\frac{k_{mf}}{K_p} \right) = \frac{12D_w \delta s k_{mf}}{m d_p^2} \left(\frac{k_{mf}}{K_p} \right) \quad \text{----- (38)}$$

If we assume that only monomer radicals can escape, the value of s should be unity and the values of m , D_w and δ should also be those for monomer.

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October 1979

S.G. Mason and A.A. Robertson
Department of Chemistry, McGill University

Mr. M.E. Labib has completed a thesis with the title "The Preparation and Characterization of Synthetic Latexes" and the following abstract.

"Several methods of preparing emulsifier-free homopolymer and copolymer latexes have been adapted or developed with the object of producing model colloids with controllable sizes and surface charges. Novel preparations of copolymer latexes with predictable sizes and charge densities were introduced. The diafiltration technique was introduced to clean the latexes with the advantages of efficiency and ease over conventional dialysis or ion exchange. Basic studies of the use of conductometric titrations to characterize the latexes have been made and the applicability of the technique was reconsidered by taking into account the presence of the electrical double layer, ion distribution between surface and bulk, and dissociation of surface groups. Consistent and practical extrapolation methods were developed for the forward and back titrations of latexes to determine stoichiometric amounts of surface charges. The conductometric method developed was applied to study the distribution of various impurities in latexes and criteria were set for latex cleanliness with different methods of cleaning. Oscillometric titrations of latexes were also used with excellent agreement with the conductometric technique. Electrophoresis studies have shown the presence and desorption of charged oligomers from the surface of emulsifier-free homopolymer latex with dilution or washing. The effect of the presence of these oligomers on the properties of the latexes was examined and found to limit the use of these latexes as model colloids. Comparative electrophoresis measurements of various latexes have shown results that are interpreted in terms of the structure of the latex surface layer. Emulsifier-free copolymer latexes produced in a methanol-water medium are monodisperse and appear to have stable predictable colloidal properties."

In an earlier newsletter a new technique developed by K. Takamura for studying shear induced two-body encounters between colloidal-size spheres was described. It involved measuring the paths of approach and recession of transient doublets of polystyrene latex spheres in Poiseuille flow using the travelling microtube MK II. The resulting particle trajectories in aqueous 50% glycerol were then analyzed by means of hydrodynamic theory in conjunction with the DLVO theory of colloid stability. It was found that the best fit of the experimental trajectories was obtained when values of the Hamaker constant A and the London wavelength λ of 0.003 aJ and 200 nm respectively, were used.

The same technique has now been applied to study the effect of adsorbed polyelectrolyte on the stability of the sols. From measurements of a total of 25 doublets of 2.5 μm diam. polystyrene latex spheres at 3, 6 and 100 $\mu\text{g dl}^{-1}$ Cat-floc (cationic polyelectrolyte) it appears that: (i) At the lowest Cat-floc concentrations the adsorbed molecules lie flat on the surface and there are no long range interactions between two latex spheres. (ii) Near the isoelectric point of Cat-floc at 6 $\mu\text{g dl}^{-1}$, there were still appreciable numbers of negatively charged Cat-floc-free sites. Here, polymer-bridges of lengths up to 1 μm were found; presumably with chains of Cat-floc molecules anchored at each end on different spheres. From the magnitude of the hydro-

dynamic force it was concluded that a single chain of Cat-floc molecules is strong enough to maintain a doublet of spheres of 3 μm diameter at shear rates up to 1000 s^{-1} .

Dr. K. Takano has been visiting the laboratory and has been conducting studies of the rheo-optical behavior of ordered lattices.

It has long been known (Osta, Krieger, etc.) that under certain conditions monodisperse latex dispersions exhibit interference colors (iridescence) in white light. Recent studies by Hachisu *et al* in Japan (with whom we have collaborated in the past) have indicated that this is an order-disorder phase transition: in well defined experiments with $\sim 2\mu\text{m}$ polystyrene latexes (particle density $> 1 \text{ g.ml}^{-1}$) in dilute aqueous electrolytes of appropriate ionic strength, phase separation occurs into an upper milky-white (disordered) and a lower iridescent (ordered) phase of higher solid fraction and hence higher density with the two phases separated by a sharp boundary. The iridescence was attributed to Bragg reflections of white light by an array of randomly oriented face-centered crystal lattices which act as a diffraction grating. Both phases are fluid. If the hypothesis of crystalline structure in the ordered phase is correct, such systems can be regarded as macroscopic versions of liquid crystals. It was considered therefore to be of great interest to examine the iridescence of such ordered phases under shear to see if the lattice structure is destroyed by the vorticity (rotation) caused by the fluid motion or whether it was reinforced by transforming the phase from an assembly of randomly oriented crystalline domains into a single lattice filling the whole sheared region.

Preliminary experiments performed in the macrocouette apparatus exhibited the Bragg diffraction patterns under various conditions of shear. It was observed that in the early stages of shear the lattices appeared to be destroyed after which they reformed progressively until a single large lattice was formed. This surprising result led to the question: did the single crystal fill the whole apparatus or was it simply confined to a thin layer extending inward from the glass wall of the apparatus? If the former, this meant that the velocity gradient traversed the whole system and (i) the individual spheres of the lattice were rotating independently like ball bearings at angular velocities = $1/2(\text{velocity gradient})$ or (ii) there is no rotation (vorticity) and shear motion consists of parallel crystalline layers sliding over one another like a riffled deck of cards. This question has not yet been completely answered.

Independent experiments were conducted in the Couette MK IV apparatus to determine the velocity distribution across the shear field. Under certain conditions (low concentrations) there was indeed nearly constant rate of shear across the system and under others (high concentrations) wall slip with zero shear in the portions away from the outer transparent cylinder, implying plastic flow. In both cases the system was iridescent with a single lattice when viewed from the outside. Unfortunately this work was interrupted by Dr. Takano's return to Japan; it is our hope, however, to continue this interesting work when help becomes available.

Contribution to the Polymer Colloid

Group Newsletter

from University of Akron

17 SEP 1979

Submitted by: I. Piirma

Experimental work carried out by: M.C. Chang

Emulsion Polymerization with Non-ionic Surfactant

Emulsion polymerizations of styrene in the presence of a non-ionic surfactant were carried out to investigate the kinetics and nucleation mechanism of such a system. A typical polymerization recipe was $K_2S_2O_8 = 0.188g$, BC-840 (tridecyl poly(ethyleneoxy) ethanol=2.0g, styrene=25g, $H_2O=50g$. The results are briefly discussed as follows:

The conversion-time curves of emulsion polymerizations of styrene using two emulsifier concentrations (curve A: BC-840 3.0g, Curve B: BC-840 2.0g) and in the absence of emulsifier (Curve C) are shown in Figure 1. With the exception of Curve C, both curves A and B, show two constant rate regions: i.e., conversion from 5% to 30%, and 45% to 80%.

Three possible explanations could be advanced for these abnormal conversion-time curves: (1) long induction time. (2) Trommsdorff's effect¹ (3) two-stages nucleation. In a conventional emulsion polymerization, the induction period usually diminished within 10% conversion. The polymerization rate in this period is accelerative, and the number of particles formed increases as the percent conversion increases, then remains constant during the so-called constant rate period. In this investigation, we found that the number of particles remains relatively constant throughout the first constant rate period. (Table 1)

Table I
No. of particles formed per cc. of aqueous phase

Conversion (%)	No of particle/cc. aq. phase $\times 10^{-13}$
4.64	8.10
9.33	7.02
14.03	7.84
17.86	8.19
20.01	7.83

When the Trommsdorff's effect is operative, it leads to a sharp decrease in the k_t and usually enhances the polymerization rate, and increases the molecular weight. It, however, should not have any influence on the number of growing particles. In our studies we found a sharp increase in the number of particles when the polymerization conversion approached 40%, i.e., was close to the inflection point of two linear lines in the conversion-time curve. Therefore, we conclude that the faster rate in the second region cannot be caused by the Trommsdorff effect.

A two-stage nucleation has been observed in the emulsion polymerization using seeded latex.² It was found that when the surfactant was charged at concentrations higher than its CMC, new particles were nucleated and competitively with the seed particles consumed monomer. Obviously, due to the secondary nucleation, the total number of growing particles increased and consequently the polymerization rate increased.

The histograms of particle sizes obtained from the electron microscopy data of latices at different conversions are shown in Figure 2. It can be seen that, below 40% conversion, there is only one particle size distribution, after 40% conversion, a bimodal size distribution appears. In order to make the comparison easier, the histograms are plotted as weight fraction vs particle sizes, instead of frequency of particles vs particle size. The number of particles generated in the second stage is much higher than that of the first stage. We conclude, therefore, that two constant rate regions in these emulsion polymerizations is caused by a two-stage nucleation.

It also has been pointed out that the molecular weights of polymers obtained from emulsion polymerization are closely related to the growing particle sizes. Based on Stockmayer³ treatment, the rate R_p and the degree of polymerization, P_n , can be expressed as:

$$R_p = Z \left(\frac{k_p^2}{k_t} f k_d [I] \right)^{1/2} [M]$$

$$P_n = Z \left(\frac{k_t}{k^2_p} f k_d [I] \right)^{-1/2} [M]$$

where Z , the subdivision factor, is given.

$$Z = \frac{\bar{n}}{a/4} \quad \bar{n} = \text{the average number of radical/particle}$$

$$a = 4 \left(\frac{f k_d [I]}{k_t} \right)^{1/2} N_s v$$

v = the volume of growing particles.

Qualitatively, this treatment suggests that molecular weights of polymers generated in small particles are higher than those generated in big particles.

The same series of latices that had been used for the electron microscopy studies were coagulated and analyzed by GPC. The results are shown in Figure 3. Viewing Figures 2 and 3 simultaneously suggests that the appearance of the high molecular weight portion (low elution volume) in the GPC is due to the participation of those particles nucleated after 40% conversion. At this point a clear explanation can be advanced for this two-stage nucleation. It is speculated that the total rate of capturing the initiated species from the aqueous phase is too slow for the particles generated in the first stage, and more and more are left behind to self-nucleate in the aqueous phase.

The emulsion polymerizations with ionic surfactants, as a rule, do not show this type of two-stage nucleation behavior. Comparison of ionic and non-ionic surfactants yields three important differences, namely: 1) the micellar sizes are much smaller for the ionic surfactants; and 2) the diffusion coefficient of ionic surfactant is much faster than for non-ionic surfactant; and 3) there is a charge and thus a higher hydrophobicity for ionic surfactants.

Therefore, in the presence of ionic surfactant, the nucleation of particles is easier and faster than in the presence of non-ionic surfactant. From the Homogeneous Nucleation Theory, the main role of surfactant played in emulsion polymerization is to stabilize the particles. However, from this study, it is found that the micellar character is also an important factor in controlling the emulsion polymerization kinetics. An attempt to explain the observations with micellar nucleation or homogeneous nucleation alone cannot be successful. Further understanding of the behavior of non-ionic surfactant such as absorption-desorption of surfactant molecules on particles, the determination of the rate of capture of oligomeric radicals into particles, stability of sterically stabilized latices may be necessary for obtaining a complete picture of the emulsion polymerization in the presence of non-ionic surfactants. A possible mixed micelle formation between the oligomeric radicals and the surfactants cannot be ruled out.

References:

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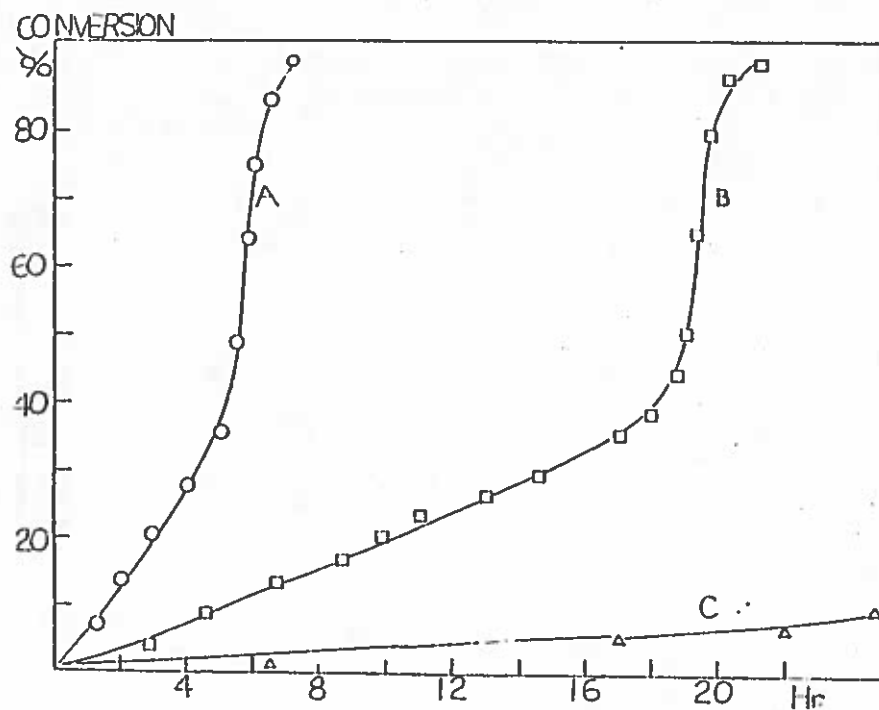


Figure 1. Conversion vs time. Polymerization recipe: 0.180g $K_2S_2O_8$, 25g styrene, 55g water, curve A 3.0g Eaulphogene BC-840, curve B 2.0g BC-840 and curve C no emulsifier.

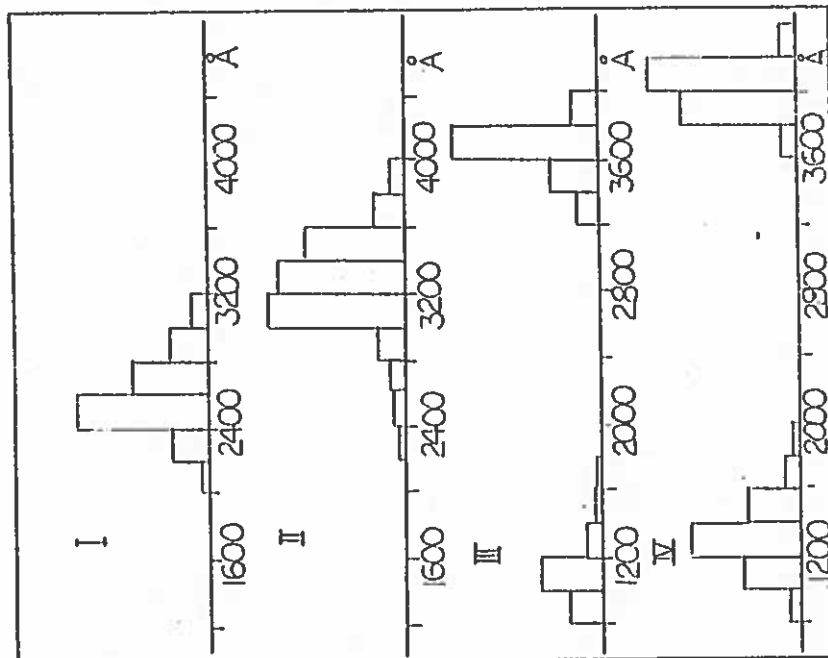


Figure 2. Histograms of latexes of same polymerization at different conversions. I 11.1%, II 21.3%, III 53.0%, IV 92.3%.

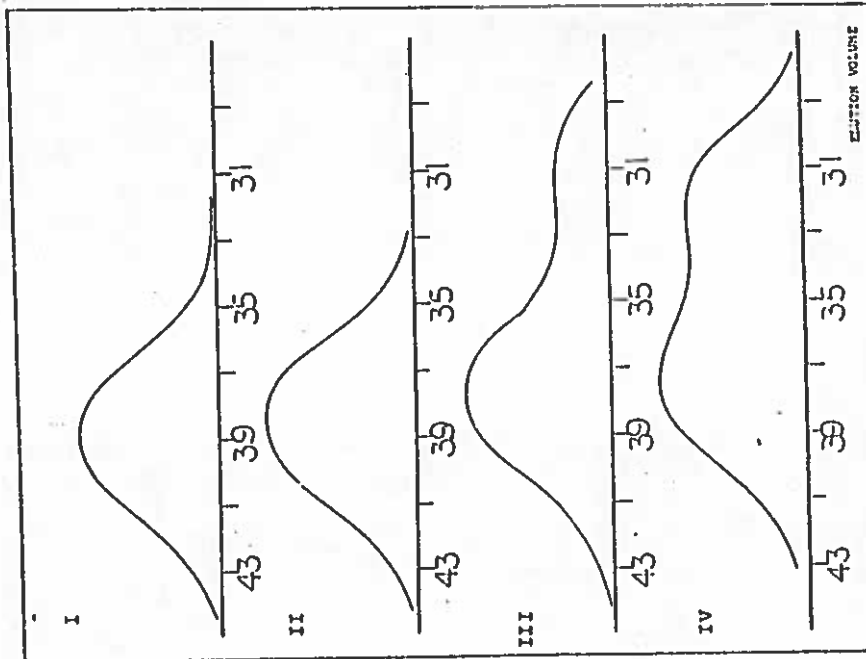


Figure 3. Gel permeation chromatography. Same polymerization at different conversions: I 11.1%, II 21.3%, III 53.0 IV 92.3



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Contribution to the Polymer Colloid Group Newsletter

by

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Notes on a paper entitled "Polystyrene Latex Particle Size by Electron Microscopy and Light Scattering" by R. L. Rowell, R. S. Farinato, J. W. Parsons, J. R. Ford, K. H. Langley, J. R. Stone, T. R. Marshall, C. S. Parmenter, M. Seaver and E. B. Bradford which was published in *J. Colloid Interface Science* 69, 590 (1979).

We have recently reported on the intercomparison of the determination of particle size distribution of a Dow latex as done in four independent laboratories each using an independent method. The four methods and laboratories are electron microscopy (Dow Chemical Co.), aerosol angular light scattering (Indiana University), Rayleigh linewidth (Department of Physics and Astronomy, University of Massachusetts), and suspension angular light scattering (Department of Chemistry, University of Massachusetts).

The work showed that an accurate measurement of particle size could be obtained by several methods provided that the experimental precautions of each method were observed. The work was encouraging in that the agreement of the modal size of the size distribution as determined by the several methods was sufficiently self-consistent that the differences may be attributed to differences in assessment of sample polydispersity and real differences in the state of aggregation of the latex as determined by each method.

The work was several years in preparation due to the fact that it was carried out in different laboratories and as an aside to other principal responsibilities of the workers involved. During that time considerable advances have been made in the linewidth technique so that it is now possible to obtain an improved characterization of sample polydispersity.