

1 May 1979

The deadline for the arrival of contributions has come once again with an even greater dearth of material than usual particularly from the U.S. I can only suppose that since the deadline, 23rd April, was St. George's Day (and also Shakespeare's Birthday) which is the nearest thing England has to America's 4th July (although it is not a holiday) that it must have aroused some sort of political objection amongst our U.S. members! * May I remind academic members that we expect some news about their activities in each issue and that industrial members will also contribute whenever possible. The Annual Meeting may decide to expel members who persistently fail to comply with this primary requirement without excuse! This is a terrible fate because I gather that the Newsletter is much valued by most of the laboratories which receive it.

The International Polymer Latex Conference last November was very successful attracting 257 participants despite the £60 registration fee! The volume containing preprints of 38 Contributed Papers (but not of the 6 Plenary Lectures) may be obtained for £18, including postage by surface mail, from the Plastics and Rubber Institute, 11 Hobart Place, London SW1W 0HL who are also willing to supply copies of individual papers, abstracts of which have appeared recently in Chemical Abstracts. A report of the Conference has been published in the Institute's news journal 'Plastics and Rubber International'. Most of the papers should be ultimately published in the Institute's scientific journals 'Plastics and Rubber: Materials and Applications' and 'Plastics and Rubber: Processing'

Papers given at the 51st Colloid and Surface Science Symposium, Grand Isle, New York have been published by Marcel Dekker in a 344 page volume edited by P. Becher and M.N. Yudenfreund at S. Fr. 64. Authors include Krieger, El-Aasser, Poehlein, Vanderhoff, McHugh, and Rowell. The title is 'Emulsions, Latices, and Dispersions' ISBN: 0-8247-6797-7.

The details of the 1979 Gordon Research Conference on 'Polymer Colloids' appear below. Proceedings of Gordon Conferences are not published as a matter of policy. The Annual Meeting of the Group will be held during this Conference.

John Ugelstad has included a note on the 3rd International Conference on Surface and Colloid Science in his contribution to this issue. The Invitation Program may be obtained by writing to The Swedish Institute for Surface Chemistry, c/o Stockholm Convention Bureau, Strandvägen 7C, S-114 56, Stockholm, Sweden. Telex: S-11556.

The European Short Course on 'Advances in Emulsion Polymerization and Latex Technology' will be held at Davos, Switzerland during the following week (August 26-31). Lecturers are Vanderhoff, El-Aasser, McHugh, Collins, Poehlein, and Bonner. Details from Gary Poehlein at the Georgia Institute of Technology, Atlanta or Dr F.J. Bonner, Technisch-Chemisches Lab., Eidgenössische Technische Hochschule Zürich, CH-8092 Zürich, Switzerland. Presumably there will also be a course at Lehigh in June covering similar ground but I have no details of this year's arrangements.

* Or are they all stranded in Honolulu, thus preventing our Japanese members sending their contributions too?

MAKRO MAINZ 1979, the 26th International Symposium on Macromolecules is scheduled for 17-21 September 1979 but I do not know whether the programme will contain much of interest to polymer colloid enthusiasts. Details can be obtained from Dr W. Fritsche, c/o Gesellschaft Deutscher Chemiker, P.O. Box 90440, D-6000 Frankfurt/Main 90, West Germany.

David Bassett and Alec Hamielec have now been named as Co-Chairmen of the Symposium on Emulsion Polymerisation sponsored by the Division of Organic Coatings and Plastics Chemistry (with the Division of Polymer Chemistry as co-sponsor) which is to be held during the A.C.S. San Francisco Meeting August 24-29, 1980. Titles of proposed contributions are required by 1st September, 1979. The papers will be preprinted and texts will be required by 1st April, 1980. The topics which it is intended to cover include the nucleation, growth, and stabilisation of latex particles, the characterisation of latex particles, reaction kinetics and mechanism, latex reactor engineering including problems of coagulation and foaming. Offers of contributions to Dr D.R. Bassett, Technical Center 720-132, Union Carbide Corporation, P.O. Box 8361, South Charleston, West Virginia 25303, U.S.A. or Prof. A.F. Hamielec, Department of Chemical Engineering, McMaster University, Hamilton, Ontario, Canada.

Perhaps the Annual Meeting should consider whether it is not time that the job of collecting contributions for the Newsletter reverted to a member resident in North America who would be in a better position to harass dilatory members by use of the telephone. David Williams did always manage to extract a contribution from both John Vanderhoff and Gary Poehlein! In this event the present arrangement might be reversed by having the 'Rest of the World' copies produced from the originals Air Mailed from the U.S. in Europe or elsewhere to minimise postage costs and spread production costs. Whatever may be decided, members might fix Friday 14th September 1979 as a deadline for the despatch (by Air Mail) of their contributions for the Autumn issue. This should permit the issue to be distributed in early October.

GORDON RESEARCH CONFERENCE ON POLYMER COLLOIDS

July 2-6, 1979

The Tilton School, Tilton, New Hampshire
Chairman, Gary W. Poehlein (Georgia Institute of Technology)
Vice-Chairman, Robert Fitch (University of Connecticut)

PROGRAM

Monday Morning: David Basset (Union Carbide), Discussion Leader

"Analytical Purification Methods for
Polymer Colloids" Mohamad S. ElAasser
(Lehigh University)

"Particle-Particle Interactions in
Polymer Colloids" Ron Ottewill
(University of Bristol)

Monday Evening: Andrew Klein (Lehigh University), Discussion Leader

"Fluorescent Polymer Latexes" Milton Kerker
Josip Kratochzil
(Clarkson College)

Tuesday Morning: Ritchie Wessling (Dow Chemical), Discussion Leader

"Polymerization Rates for Emulsion
Copolymerization" Mamoru Nomura
(Fukui Univeristy)

"Swelling of Polymer-Oligomer Particles-
Polymerization with Initiation in
Monomer Droplets" John Ugelstad
(University of Trondheim)

Tuesday Evening: Carlton Force (Westvaco), Discussion Leader

"Glassy State Transport Processes
in Polymeric Colloids" Harold Hoffenberg
(North Carolina State Univeristy)
A. R. Berens
(B. F. Goodrich)

Wednesday Morning: John Vanderhoff (Lehigh University), Discussion Leader

"The Behavior of Emulsion Polymerization
Reactors" W. Harmon Ray
(University of Wisconsin)

"Water Soluble Polymers-Application
in Oil Recovery Processes" Edward J. Glass, Jr.
(Union Carbide)

Wednesday Evening: Edward Collins (Diamond-Shamrock), Discussion Leader

"Particle Chromatography" Anthony J. McHugh
(Lehigh University)

GORDON RESEARCH CONFERENCE ON POLYMER COLLOIDS

Thursday Morning: W. Wilson White (Uniroyal Chemical), Discussion Leader

"Use of Polyvinyl Alcohol as
an Emulsifier in Emulsion
Polymerization"

A. S. Dunn (Sandy)
(University of Manchester)

"Sterically Stabilized Nonaqueous
Dispersions"

M. D. Croucher
(Xerox, Canada)

Thursday Evening: Gary W. Poehlein (Georgia Tech), Discussion Leader

"Laser-Kerr Studies of Anisotropic
Colloidal Particles"

Robert L. Rowell
(University of Massachusetts)

Friday Morning: Pranab Bagshi (Eastman Kodak), Discussion Leader

"Particle Size Distributions in
Emulsions and Dispersions; Experimental
and Theoretical Considerations"

Robert Fitch
(University of Connecticut)

"Computer Simulation of
Colloid Dynamics"

C. T. Havens
J. A. Mann, Jr.
I. M. Krieger
(Case Western Reserve University)

The Conference Fee is \$ 185 which includes accommodation and meals from the evening of Sunday 1st July until lunch on Friday 6th July. Accommodation may also be booked for Guests (including children over 12) for a Fee of \$ 135. A chartered bus is provided to convey participants arriving at Logan International Airport, Boston to the Conference site leaving at 4.00 p.m. if booked in advance at a charge of \$ 8. Applications etc. should be addressed to

Dr Alexander M. Cruickshank
Director, Gordon Research Conferences

Before June 11

Pastore Chemical Laboratory,
University of Rhode Island,
Kingston,
Rhode Island 02881
U. S. A.
Telephone: (401) 783 4011

June 11 - August 24

Colby-Sawyer College,
New London,
New Hampshire 03257,
U. S. A.
Telephone: (603) 526 2870

POSSIBILITY OF PERIODIC BEHAVIOUR IN CONTINUOUS EMULSION POLYMERISATION REACTION SYSTEMS

118 APR 1979

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

Some experimental studies (e.g., 1,2) have indicated that, in certain circumstances, the ultimate behaviour of continuous emulsion polymerisation reaction systems can be such that the rate of polymerisation persistently oscillates. The origin of these oscillations is unclear. Gerrens and Kuchner⁽³⁾ have pointed out that variations in the rate of feed of the reactants could be one cause, but it should clearly be possible to eliminate fluctuations arising from this cause by carefully controlling the feed rates of the reactants. We have not been concerned with the possibility of fluctuations in rate of polymerisation arising from this cause. Our concern has been to examine a plausible model for a continuous emulsion polymerisation reaction, namely, that proposed by Brooks⁽⁴⁾, in order to ascertain whether it allows the inherent possibility of periodic fluctuations in polymerisation rate.

The emulsion polymerisation reaction is assumed to be taking place in a single well-stirred reactor, so that effects arising from macro-heterogeneity within the reaction system can be neglected. Reactants are assumed to be fed into the reactor at steady rates, the reaction product being removed at a steady rate such that the volume of reactants in the reactor remains constant. The monomer and surfactant are assumed to be fed in separately from the initiator solution, so that polymer particles can be assumed to be absent from the feed. The monomer is assumed to be only sparingly soluble in water, and the surfactant to be present in the initial feed at a concentration above its critical micelle concentration. Particles are assumed to be formed exclusively by micellar nucleation; complications arising from the simultaneous occurrence of homogeneous nucleation are ignored. The monomer is assumed to be completely miscible with its polymer, and to be present in sufficient quantity as always to ensure that an excess of monomer is present as droplets at all stages of the reaction.

It has been claimed by Brooks, Kropholler and Purl⁽²⁾ that the Brooks model does permit the possibility of oscillations in polymerisation rate. Under the assumed reaction conditions, this amounts to a claim that the number of particles present in the reaction system can fluctuate periodically. The root cause is said to be that the incoming surfactant micelles participate in two competing processes, namely, the nucleation of new particles and dissolution into the aqueous phase as monomolecular surfactant molecules. The tendency for the second of these processes to occur arises because the concentration of monomolecular surfactant has been reduced below its critical micelle concentration owing to the removal of surfactant molecules by adsorption at the surface of older particles which are growing in the reactor. If the rate of increase of particle surface area due to growth is greater than the rate at which particle surface is lost from the reaction system by efflux of particles from the reactor, then the adsorption area available to surfactant molecules in the reactor will increase, and the rate of production of new particles will be expected to decrease. The rate of polymerisation would then fall. It is postulated that, in some cases, the reduction in particle number may be such that the particle number "under-shoots" the steady-state value, and then subsequently increases to, and remains at, the steady-state value. In other cases, the particle number can continue to oscillate with respect to time. Brooks states that it may be difficult to distinguish in practice between these two types of behaviour. It is not entirely clear what are the factors which determine whether or not a steady-state is eventually achieved. However, if sustained oscillations do occur, their cause is attributed to a feed-back effect which the products of the reaction (the particles) have upon the reaction process.

The Brooks model gives the following equations for the rate of change with time (t) of number of particles (N) and number of micelles (N_m) in unit volume of aqueous phase of the reaction system:

$$\frac{dN}{dt} = \frac{k_2 R_i N_m}{k_2 N_m + k_3 N} - \frac{N}{T} \quad \dots\dots\dots (1)$$

$$\frac{dN_m}{dt} = \frac{N_{m0}}{T} - \frac{N_m}{T} - k_1 N_m - \frac{k_2 R_i N_m}{k_2 N_m + k_3 N} \quad \dots\dots\dots (2)$$

where R_i is the rate of acquisition of radicals from the aqueous phase by both the particles and the micelles which are present in unit volume of aqueous phase, k_1 is the rate coefficient for the dissociation of micelles into monomolecular surfactant molecules, k_2 and k_3 are rate coefficients for the processes of radical capture by micelles and by particles respectively, N_{m0} is the number of surfactant micelles present in unit volume of the surfactant solution which is being fed into the reaction system, and T is the mean residence time of the reactants in the reactor. Putting $\tau = t/T$, $\alpha = k_3/k_2$, $\beta = 1 + k_1 T$, and $\gamma = R_i T$, these equations become respectively

$$\frac{dN}{d\tau} = \frac{\gamma N_m}{N_m + \alpha N} - N \quad \dots\dots\dots (3)$$

$$\frac{dN_m}{d\tau} = N_{m0} - \beta N_m - \frac{\gamma N_m}{N_m + \alpha N} \quad \dots\dots\dots (4)$$

Unfortunately, no general solution to this pair of simultaneous non-linear differential equations is readily available. However, there is a substantial corpus of essentially qualitative theory which is applicable to pairs of simultaneous differential equations of this type. By the application of this theory, it is possible to draw some significant conclusions concerning the behaviour of reaction systems which conform to the Brooks model. In this theory, N and N_m are regarded as defining orthogonal Cartesian axes in a two-dimensional space, called the "phase plane". Solutions of a given pair of differential equations will trace out paths ("trajectories") in this plane as time elapses, and these trajectories will represent the behaviour of the reaction system as time elapses. Two conclusions which we have been able to draw by application of this theory are as follows:

- (i) the steady state for the Brooks model must always be stable, so that periodic fluctuations of rate of polymerisation about the steady-state value are not possible; and
- (ii) the physically-significant region of the phase plane cannot contain closed trajectories, and therefore the Brooks model does not allow the possibility of sustained cyclic behaviour of any reaction system which conforms to it.

The first of these conclusions follows by re-writing equations (3) and (4) in terms of the new variables

$$\theta = N - \bar{N} \quad \text{and} \quad \phi = N_m - \bar{N}_m \quad \dots\dots\dots (5)$$

where \bar{N} and \bar{N}_m are the steady-state values of N and N_m respectively, and then examining the nature of the trajectories which are predicted by the linear approximations to the resultant equations (applicable, of course, at $\theta, \phi \rightarrow 0$). The linear approximations are found to be

$$\frac{d\theta}{dt} \cong - \left\{ 1 + \frac{\alpha}{\gamma} \frac{\bar{N}^2}{\bar{N}_m} \right\} \theta + \frac{\bar{N}}{\bar{N}_m} \left\{ 1 - \frac{\bar{N}}{\gamma} \right\} \phi \quad \dots\dots\dots (6)$$

and

$$\frac{d\phi}{dt} \cong \frac{\alpha}{\gamma} \frac{\bar{N}^2}{\bar{N}_m} \theta + \left\{ \frac{\bar{N}^2}{\gamma \bar{N}_m} - \frac{\bar{N}}{\bar{N}_m} - \beta \right\} \phi \quad \dots\dots\dots (7)$$

The general solution to these equations is (in matrix form)

$$\begin{bmatrix} \theta \\ \phi \end{bmatrix} = c_1 [A_1] e^{\lambda_1 \tau} + c_2 [A_2] e^{\lambda_2 \tau} \quad \dots\dots\dots (8)$$

where c_1 and c_2 are arbitrary constants, λ_1 and λ_2 are the eigenvalues of the matrix

$$\begin{bmatrix} -1 - \frac{\alpha}{\gamma} \frac{\bar{N}^2}{\bar{N}_m} & \frac{\bar{N}}{\bar{N}_m} \left\{ 1 - \frac{\bar{N}}{\gamma} \right\} \\ \frac{\alpha}{\gamma} \frac{\bar{N}^2}{\bar{N}_m} & \frac{\bar{N}^2}{\gamma \bar{N}_m} - \frac{\bar{N}}{\bar{N}_m} - \beta \end{bmatrix}$$

and $[A_1]$ and $[A_2]$ are the corresponding column eigenvectors. Examination of the equation which determines λ_1 and λ_2 shows that inevitably the real parts of λ_1 and λ_2 are negative. Equation (8) then shows that the steady state must always be stable, since the trajectory for any system slightly disturbed from the steady state must always be such that the system tends to return to the steady state.

The second of the above conclusions follows from the observation that the quantity

$$\frac{\partial}{\partial N} \frac{dN}{dt} + \frac{\partial}{\partial N_m} \frac{dN_m}{dt}$$

is negative throughout the entire region of physically-relevant values of N and N_m . This observation leads to the conclusion that the physically-significant region of the phase plane cannot contain closed trajectories, and therefore that the Brooks model does not allow the possibility of sustained cyclic behaviour of any reaction system which conforms to it.

A more detailed discussion of these ideas and conclusions is planned for publication in due course.

References

1. J. J. Owen, C. T. Steele, P. T. Parker and E. W. Carrier, *Ind. Engng Chem.*, 1947 39, 110
2. B. W. Brooks, H. W. Kropholler and S. N. Puri, *Polymer*, 1978, 19, 195
3. H. Gerrens and K. Kuchner, *Br. Polym. J.*, 1970, 2, 18
4. B. W. Brooks, *Br. Polym. J.*, 1973, 5, 192



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Oil-phase Initiation of Emulsion Polymerisation

Dr Al-Shahib, who is now at the College of Education of the University of Baghdad, hopes to present a paper at the Stockholm Surface and Colloid Chemistry Conference in August entitled 'Emulsion Polymerisation of Styrene using an Oil-soluble Initiator'. Although water-soluble initiators are usually more efficient and are generally preferred, oil-soluble initiators are also effective in promoting emulsion polymerisation and have often been used by Russian workers particularly. Their use might be desirable if the presence of hydrophilic end-groups in the product had to be avoided. The use of an emulsifier is, of course essential when oil-phase initiation is used. Oil phase initiation may be advantageous for monomers less soluble in water than styrene for which water-soluble initiators may prove ineffective. As pointed out some years ago by B.M.E. van der Hoff, emulsion polymerisation using oil-phase initiation depends on the escape of one of a pair of radicals initially formed by decomposition of the initiator into the aqueous phase leaving an isolated radical in the oil-phase. The escape of radicals is not usually particularly efficient and rather large initiator concentrations are required to generate numbers of particles comparable to those obtained with water-phase initiation. Possibly escape of radicals could be promoted by use of an emulsifier with a high transfer constant and a high rate of exchange between adsorbed and dissolved molecules. Conditions can be found under which the same number of latex particles is formed as when water-phase initiation is used. The rates of initiation must then be equal. If it is assumed that persulphate decomposes in the aqueous phase at its standard rate and that the efficiency of the radicals produced in nucleating latex particles is 100%, the efficiency of particle nucleation by an oil-phase initiator (azodiisobutyronitrile) can be calculated since its rate of decomposition is known. The results show that only 4% of the radicals produced in the oil-phase are effective in nucleating latex particles. Under conditions in which the same number of latex particles is formed, the rate of Interval II polymerisation using an oil-phase initiator is lower than when water-phase initiation is used. This is probably because the rate of escape of radicals falls as particle size increases being lower from the latex particles than from the initial micelles and is too low to maintain $n = \frac{1}{2}$. Our results are consistent with $\bar{n} = 0.3$. When thermal initiation is used in the emulsion polymerisation of styrene it seems to be impossible to achieve more than about 80% conversion probably because the rate of escape of radicals has fallen to zero by that stage.

Structure and Properties of Polyvinyl Alcohol

Mr Naravane is well on the way to creating a record for the time taken to compose a Ph.D. thesis working full-time! However he is making some real progress in interpreting his results. Evidently the different carbon atoms in polyvinyl alcohol are subject to somewhat different Nuclear Overhauser Effects which may enhance the intensity of a resonance by a factor of up to 2.98 and this partly accounts for the differences in the relative intensities of the resonances. This makes quantitative analysis based on the intensities of the n.m.r. peaks unreliable but does not affect the fact that the relative intensities in two similar specimens found to have conspicuously different properties do differ indicating the existence of differing amounts of branching although it prevents a quantitative

assessment of the extent of the branching. We are indebted to Dr F.S. Heatley for the operation of the n.m.r. spectrometer: by accumulating a really immense number of spectra, he has now been able to locate a signal attributable to tertiary or quaternary carbons constituting branch points although the concentration of these is certainly lower than we had thought it might be earlier. It is possible to prepare linear polyvinyl acetate by photopolymerisation at very low temperatures as was shown by Burnett, George, and Melville (J. Polym. Sci. 16 (1955) 31) so the next step would seem to be to prepare some genuinely linear incompletely hydrolysed polyvinyl alcohol to examine its properties but we may not be able to do this unless we can succeed in getting some support for this specific project from somewhere. Light scattering measurements (which have not so far been at all popular with polyvinyl alcohol) might be capable of being developed to provide a rapid method for characterising the extent of branching.

Faraday Discussions of the Chemical Society No. 65 (1978) 'Colloid Stability' has now been published containing the papers presented and the discussions on them from the Lunten meeting last April. Several of the papers are concerned with the use of polyvinyl alcohol as a steric stabiliser and its suitability as a subject for studies of a theoretical nature attracts some pointed comments from Waite, Osmond and others pp. 328 et seq.

Review

At the instance of Professor R. N. Haward of Birmingham (as editor), I have written a review on 'Developments in Emulsion Polymerisation' which will appear in one of Applied Science Publishers Ltd 'Developments' Series 'Developments in Polymerisation - II' which is now due for publication in about July this year at £25. The other articles are on Free Radical Polymerisation (Bevington & Ebdon), Condensation Polymerisation (I. Goodman), Transition Metal Polymerisation (P.J.T. Tait), and Template Polymerisation (Bamford & Ledwith). The topics discussed in the review are the theory of emulsion polymerisation including Medvedev's theory which recent work by Ryabova et al. in Leningrad seems to have disposed of finally at last, continuous polymerisation processes, the core-shell controversy, the preparation of monodisperse and surfactant free latex particles, initiation of polymerisation in monomer droplets, and initiation of emulsion polymerisation by radiation. The writing was completed in May 1978.

Can Micellar Catalysis affect initiation in Emulsion Polymerisation?

Smith-Ewart kinetics may be applicable to the emulsion polymerisation of styrene with oil-phase initiation provided the low efficiency of particle nucleation is taken into account. If the efficiency is independent of temperature, the energy of activation for initiation can be deduced from an Arrhenius plot of the logarithm of the number of latex particles formed against the reciprocal of the absolute temperature. Then since $N \propto R_i^{0.4}$, $E_N = 0.4 E_i$. In the thermal emulsion polymerisation of styrene, Said finds $E_N = 12 \text{ kcal mol}^{-1}$ giving $E_i = 30 \text{ kcal mol}^{-1}$ which is the same as the value (28 kcal mol^{-1}) found for the thermal bulk polymerisation of styrene within the experimental error suggesting that none of the steps in the thermal initiation mechanism are subject to micellar catalysis which would probably reduce the activation energy below the bulk value. However in these experiments the particle numbers are calculated from \bar{d}_w measured by our light scattering method which inevitably gives low particle numbers for polydisperse samples. The products of thermal emulsion polymerisation are very polydisperse. This may not matter for calculating activation energies but it will introduce an error if the breadth of the particle

size distribution varies with temperature. To check on this and other qualms about residual monomer etc., Said is now in the course of determining the required average particle diameter by electron microscopy.

An alternative procedure for determining E_i in thermal emulsion polymerisation was introduced by Asahara, Seno, Shiraishi, and Arita (Bull. Chem. Soc. Japan, 46 (1973) 249). This depends on measuring the dependence of the degree of polymerisation on temperature. They used viscometric molecular weight determination and Said has also done this although, on reflection, the same sort of difficulty may arise if the breadth of the molecular weight distribution changes with temperature and it might have been wiser to attempt to determine \bar{M}_n , which is what is really wanted, since we do have an Automatic Osmometer which is believed to be in working order. With sodium tetrapropylenebenzenesulphonate as emulsifier and thermal initiation, Ashara et al. find $E_p = -5.2 \text{ kcal mol}^{-1}$ when they deduce $E_i = 12.6 \text{ kcal mol}^{-1}$ which would suggest that micellar catalysis does occur with this emulsifier. Using potassium stearate as emulsifier (which was also the emulsifier used in determining E_p above), Said finds $E_p = -12 \text{ kcal mol}^{-1}$, whence E_i would be $21.4 \text{ kcal mol}^{-1}$ according to Ashara et al's calculation, significantly lower than found by the particle number method. If micellar catalysis does occur the activation energy found would be expected to depend on the emulsifier used. However Ashara et al. seem to have confused termination of the polymer chain with termination of the kinetic chain and neglected all transfer steps whereas it is generally believed that the molecular weight of polystyrene obtained by thermal bulk polymerisation is limited by transfer to monomer and, in emulsion, transfer to emulsifier is a further possibility (which will also be influenced by the nature of the emulsifier). They write

$$\bar{P} = \frac{R_p}{R_t + R_f}$$

which is correct, but equate this to R_p/R_i whence $E_p = E_D - E_i$ which is only correct if transfer reactions are all negligible. If this assumption is not justified, I don't, at the moment, see how to extract a value of E_i from an Arrhenius plot of $\ln \bar{P}$ against $1/T$. Although the above results would indicate the occurrence of micellar catalysis if they are valid, they most probably merely reflect the results of failing to taken account of transfer and that the transfer constant for the two emulsifiers is different!

The Newsletter

I am glad to say that several items from U.S. members have arrived during the past week. All had been posted on 18th April so that they might reasonably have been expected to arrive by the 23rd, since Air Mail from New York does reach Manchester in 3 days under favourable circumstances. The delay may be a result of a 'go-slow' which is said to be affecting some London Postal Sorting Offices.

A. S. D.
30 April 1979

R. M. Fitch:

"Polymer Colloids II", comprised of most of the papers from the Miami Beach Symposium, will be published by Plenum Publishing Corp. sometime this summer. Manuscripts and reviews often have been slow in coming in, but typing and final editing are now in full swing.

The main emphases of our current work are: (1) nucleation kinetics by time-dependent light scattering, an extension to much shorter times of our work recently published in J. Colloid. Int. Sci.; (2) swelling kinetics and equilibria of latex particles of various M and γ , in cooperation with John Ugelstad; (3) adsorption thermodynamics and kinetics of surface active molecules onto liquid and polymeric substrates; (4) synthesis of model colloids; and (5) heterogeneous catalysis by polymer colloids. Some of these are reported on by the people involved:

Prakash Kasargod:

Polystyrene latices containing surface sulfonate groups have been synthesized using a new initiator, Disodium Bis-(4-sulfomethyl benzoyl) peroxide. The ion-exchanged latices in the H^+ form will be investigated as heterogeneous catalysts for the hydrolysis of polysaccharides. The rate of hydrolysis will be followed using a glucose probe. The effects of variation of substrate and H^+ concentrations, temperature and latex particle size on the rates of hydrolysis will be studied and compared to the rates obtained using conventional ion-exchange resin beads in the H^+ form and simple homogeneous acid catalysts.

G. R. Traut:

We are seeking a way to produce model fluorocarbon polymer colloids stabilized with sulphonate groups. Our plan is to initiate polymerization by sulfite ion radicals in the absence of surfactant or organic materials that may function as transfer agents.

Experiments have been run with styrene to evaluate methods for effectively producing sulfite ion radicals. McCarvill and Fitch earlier reported work with a ferric ion-bisulphite ion system that required large amounts of sulfonate stabilizer to prevent coagulation by the Fe^{2+} and Fe^{3+} ions.

We have found with styrene that $Ag(NH_3)_2^+$, $Cu(NH_3)_4^{2+}$ and $Cu(CN)_4^{2-}$ are capable of oxidizing sulfite ion to form initiating radicals. The resulting stable polymer colloids when purified by ion exchange resin and conductometrically titrated show high surface charge densities and strong acid surface groups that totally resist hydrolysis at $98^\circ C$. A designed experiment was run to compare the variables of temperature, oxidizer concentration, ratio of sulfite ion to oxidizer, and ratio of complexing agent to oxidizer.

TABLE 1

Run Number	37A	37B	39A	39B	46
Styrene, m moles/liter	3.6	3.6	3.6	3.6	5.4
Cu Cl ₂	8	8	0	0	0
KCN	32	32	0	0	0
AgNO ₃	0	0	8	8	8
NH ₃	0	0	16	16	64
Na ₂ SO ₃	16	16	16	16	16
NaNO ₃	0	0	0	0	56
Oxidizer addition method	at start	gradual	at start	gradual	at start
Temperature °C	60	60	60	60	78
% Conversion	9.1	6.3	69	80	45
Particle size nm	360	320	300	300	846
Surface charge density μ coulomb/cm ²	3.6	3.9	3.8	2.1	41.5±.5
Surface charge density after 24 hrs./98°C					41.5±.3

NOTE: All of the above had a narrow particle size range by HOTS and were stable.

A.R.M. Azad:

We have continued the work on particle formation in suspension polymerization. The presentation given at Miami Beach will be published in Polymer Colloids II as "Particle Size Distributions in Suspension Polymerizations: Effect of Added Low Molecular Weight Compounds". We also plan to do some studies on molecular weight distributions of suspension polymers. A study of the adsorption-stabilization characteristics of water-soluble polymers in suspensions and emulsions has just been started. The adsorption would be studied as a function of the nature of the interface for various polymeric stabilizers.

Shu-Jan Liang:

Monodisperse polymer colloids have been prepared in order to investigate their swelling rates and swelling capacities. Seed latexes were made by emulsion polymerization. Subsequent polymerization of these with different amounts of initiator, chain transfer agent and monomer gave large, uniform particles of polymer or oligomer. This procedure was repeated to obtain a series of several larger particle size latexes. HOTS and sedimentation experiments are used to check the particle size distributions.

These monodisperse colloids were subsequently swollen with various concentrations of organic solvent in aqueous solution in a photometer cell. The intensity of monochromatic light at specific angles was recorded as a function of time. From computations of the Mie-Debye equations, light intensity as a function of particle size and refractive index is provided, so that swelling ratios can be calculated. Finally, general models for the swelling process in high polymers, oligomers and low molecular weight compound may be obtained.

The Emulsion Polymerization Kinetics and its Reactor Design III. A Mathematical Model for Continuous Flow Operation

CHEN-CHONG LIN¹ AND WEN-YEN CHIU²

Department of Chemical Engineering, National Taiwan University
Taipei, Taiwan, R.O.C.

Journal of The Chinese Institute of Chemical Engineers, 1978, Vol. 12, pp. 169-175.

Abstract—An approach to modeling of the emulsion polymerization of styrene in continuous flow operation is proposed and analysed in detail using the experimental conditions and numerical values of Nomura et al⁽⁴⁾. The results obtained in this model are compared with those obtained in Nomura's model based on the generating polymer particles. The assumption of a zero-order reaction has been found normally to be valid for the continuous flow operation. It is also found that the MWD of a continuous emulsion polymerization has an unique feature but shifts to the shorter chain length range as the mean residence time increases. Moreover, the conversion always never exceeds in a greater value in spite of a long residence time.

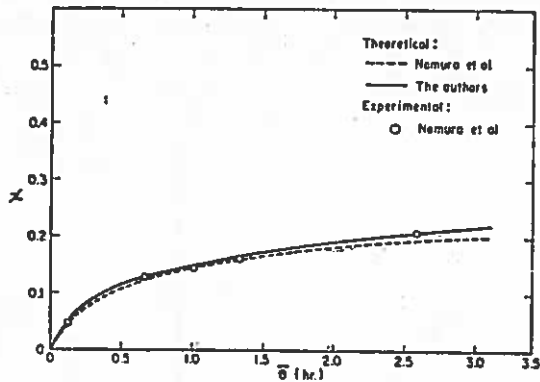


Fig. 1 Relationship between conversion and mean residence time

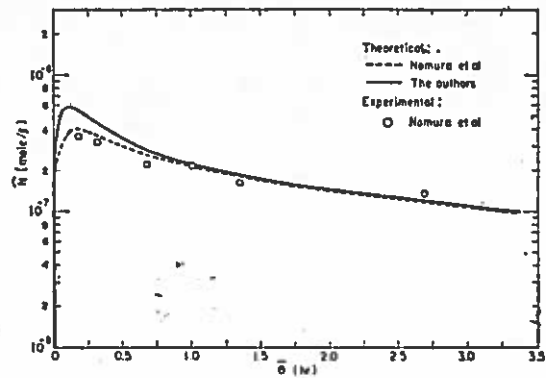


Fig. 2 Relationship between number of polymer particles and mean residence time

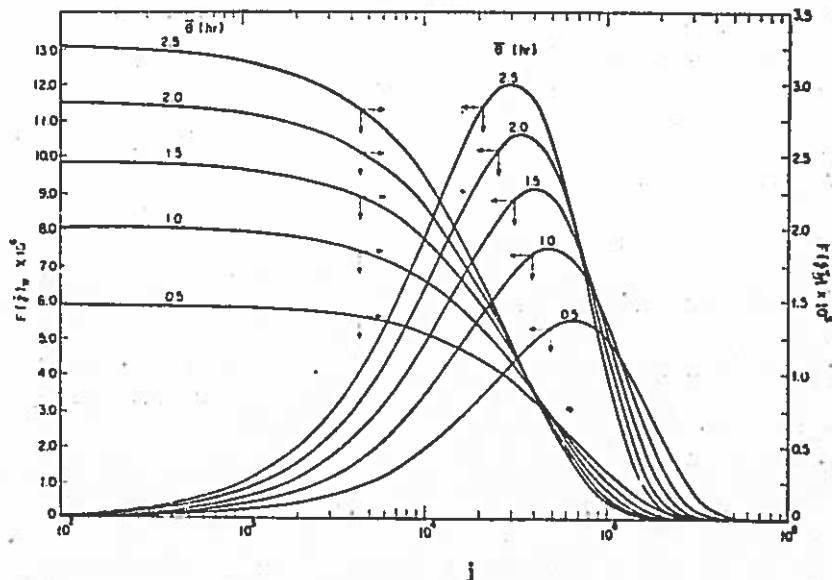


Fig. 4 The MWD as a function of mean residence time

POLYMER COLLOID NEWSLETTER

R.H. Ottewill
J.W. Goodwin

30 APR 1979

Our apologies for not contributing to the last Polymer Newsletter, but life has been very hectic with teaching and conferences.

In order to bring people up-to-date with our activities, we give below a short resume of papers published and current research topics.

Recent Papers Published

1. D.E. Yates, R.H. Ottewill and J.W. Goodwin, Purification of Polymer Latices, J. Colloid and Interface Sci., 1977, 62, 356-358
2. R.H. Ottewill and D.G. Rance, Studies on Polytetrafluoroethylene Latices. Part 1. Coagulation by Non-hydrolysed Electrolytes, Croatica Chemica Acta 50, 65-75 (1977)
3. J.W. Goodwin, R.H. Ottewill, R. Pelton, G. Vianello and D.E. Yates, Control of Particle Size in the Formation of Polymer Latices, British Polymer Journal, 10, 173-180 (1978)
4. F.W. Cain, R.H. Ottewill and J.B. Smitham, Direct Measurements of the Interaction between Adsorbed Macromolecular Layers, Faraday Disc. Chem. Soc., No. 65, 1978, 33-42
5. J.W. Goodwin, R.H. Ottewill and R. Pelton, Studies on the Preparation and Characterization of Monodisperse Polystyrene Latices. V. The Preparation of Cationic Latices, Colloid and Polymer Sci., 257, 61-69 (1979)

Copies have already been sent to some members. Other copies are available on request.

Current Research Topics

1. Seeded growth of polymer latices.
2. The adsorption of fluorocarbon and hydrocarbon surface active agents on to polytetrafluoroethylene latices
3. Kinetics of swelling polystyrene latices by deuterated monomers using neutron scattering.
4. Preparation of polymer latices using deuterated monomers.
5. Studies on the interaction of polymer latex particles by, time average light scattering, intensity fluctuation light scattering and small angle neutron scattering.

26th April 1979



McGill
University

Department of Chemistry
Pulp and Paper Building

118 APR 21 1979

Contribution to the Polymer Colloid Group Newsletter

April 1979

S.G. Mason and A.A. Robertson

Dr. S.G. Mason reached the conventional age for retirement in March of this year, an event which is being marked in several ways, including a Festschrift in the Journal of Colloid and Interface Science and a Symposium in his honor at the ACS meeting in Washington in September. His association, however, with the Pulp and Paper Research Institute of Canada and with the Department of Chemistry of McGill University will continue and his work with his graduate students and post-doctoral fellows can be expected to produce further contributions to the knowledge of polymer colloids and to his several other fields of interest.

Recent activity and progress related to polymer colloids include the following:

Takamura has continued to study the effect of interparticle forces upon interactions between spheres in shear flow in order to explain the stability, coagulation and flocculation of flowing suspensions of colloidal dispersions.

Trajectory equations developed by van de Ven and Mason show that the paths of the centers of two equal-sized spheres during encounters in shear flow are governed both by hydrodynamic and interparticle forces. The interparticle force F_{int} , which is one of the most important factors governing the stability of hydrophobic colloids, can be obtained from a detailed analysis of shear-induced two-body collisions between colloidal-size spheres. Such analysis has previously been used, and reported in earlier newsletters, to study the formation of permanent doublets of polystyrene latex spheres in the aqueous solutions of simple electrolytes and polyelectrolytes undergoing Poiseuille flow in the traveling microtube apparatus. It was evident that doublets were formed as a result of van der Waals attraction and/or polymer-bridge formation but the magnitude of F_{int} could not be calculated. The microtube technique has now been used to study the flow behavior of transient or separating doublets in 50% aqueous glycerol solution at various KCl and polyelectrolyte concentrations through detailed measurements of the paths of approach and recession of spheres. The results were analysed in terms of the above-mentioned trajectory equations assuming that F_{int} is given by the DLVO theory of colloid stability.

Cont....

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The following is a summary of the conclusions drawn from the measurements on a total of 18 transient doublets of 2.6 μm diam polystyrene latex spheres at 1 and 10 mM KCl and 100 $\mu\text{g dl}^{-1}$ Cat-floc (cationic polyelectrolyte).

1. During collisions of spheres in 10 mM KCl, an attractive force between them can be measured when the separation distance between the surfaces is in the range of 30 to 200 nm. At shorter distances repulsion was observed, proving the existence of a secondary energy minimum.
2. Using the DLVO theory, the best fit of the measured trajectory is obtained when a value of 0.006 aJ is used for the Hamaker constant of the polystyrene latex in aqueous glycerol (assuming a London wavelength of 100 nm).
3. When Cat-floc was adsorbed on the latex surfaces, the adsorption thickness d of the polymer was computed to be of the order of 15-25 nm. The calculation was made assuming the above theory to apply but that repulsion occurs between the two adsorbed polymer surfaces whereas attraction was between the polystyrene surfaces.

Further plans include (1) study of the collision paths of transient doublets of latex spheres at various degrees of surface coverage of Cat-floc, and (2) extension of these measurements to study heterogeneous coagulation using spheres of different surface charge density and sign.

Labib has been studying the synthesis and characterization of model latexes and has recently been looking at the applications of conductometric titrations. Conductometric titrations of cleaned latexes having strong (SA) and weak (WA) acid surface groups have been made in the presence and absence of added strong and weak acids to determine the effect of contaminant on the titration curve. Added strong acids are titrated with the strong acid surface groups and give a linear titration curve with a single slope; the salt resulting from neutralization determines the conductance at the SA-WA end point. Added weak acids, if free, appear as a separate linear branch in the titration curve located between the strong acid and surface weak acid branches while adsorbed weak acids are titrated with surface weak acid to give a non-linear titration curve.

The conductometric titration curves of emulsifier-free copolymer latexes made with functional comonomers were determined before and after cleaning and have been interpreted in the light of the model titrations described above. In this way both adsorbed and free strong-acid and weak-acid impurities have been detected in the crude latexes. Only strongly acidic titratable impurities were detected in emulsifier-free homopolymer latexes. Large amounts of neutral electrolyte were shown in both crude copolymer and homopolymer latexes by the high conductance at the SA-WA end point.

Ion-exchange resins have limitations in cleaning emulsifier-free copolymer and homopolymer latexes and high molecular weight acidic impurities, whether free or adsorbed, are not completely removed. However diafiltration cleaning followed by treatment with ion-exchange resins has been shown to be efficient.

Cont....

Recent publications include the following:

Kinetics of Flowing Dispersions XI. Dielectric Constants of Streaming Suspensions of Spheruloids. A. Okagawa, R.G. Cox and S.G. Mason. J. of the Chemical Soc., Faraday Trans. I, 74, 1942, 1253 (1978).

Memory Impairment in Flow Suspension. I. Some Theoretical Considerations. A. Okagawa, G.J. Ennis and S.G. Mason. Can. J. Chem., 56, 2815-2823 (1978).

Memory Impairment in Flowing Suspension. II. Experimental Results. G.J. Ennis, A. Okagawa and S.G. Mason, Can. J. Chem., 56, 2824-2832 (1978).

Deposition of Cationic Styrene and Styrene-Butadiene Latex Particles on Cellulose Fibres. B. Alinec, M. Inoue and A.A. Robertson. J. Colloid Interface Sci., 65 (1) 98 (1978).

Colloidal Aspects of the Retention of Positively Charged Additives. B. Alinec and A.A. Robertson. Tappi 61 (11), 111 (1978).

Application of a Diafiltration Technique in Latex Studies, M.E. Labib and A.A. Robertson. J. Colloid Interface Sci., 67 (3), 543-547 (1978).

POLYMER COLLOIDS AT SYDNEY UNIVERSITY

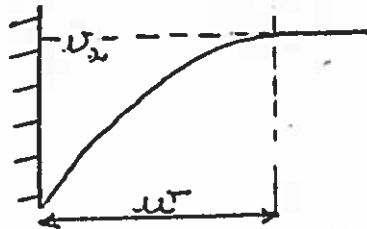
Reporter: D. H. Napper

28 MAR 1970

STABILIZATION BY FREE POLYMERS

It should, in principle, be possible to stabilize colloidal particles by adding free polymer to the continuous phase if it is a good solvent for the polymer. I stress 'free' because this phenomenon has nothing to do with steric stabilization which depends upon attached polymers.

The idea, developed in this lab. by Robert Feigin, is as follows. Because of the loss of configurational entropy when a polymer is close to an interface, the volume fraction of free polymer near to an inert interface can be shown to be thus:



Only when the distance from the interface is ca. the width of the polymer w , does the polymer volume fraction approach the bulk value. For two flat plates separated by a distance d , the bulk volume fraction will only be reached in the interparticle region provided $d > 2w$.

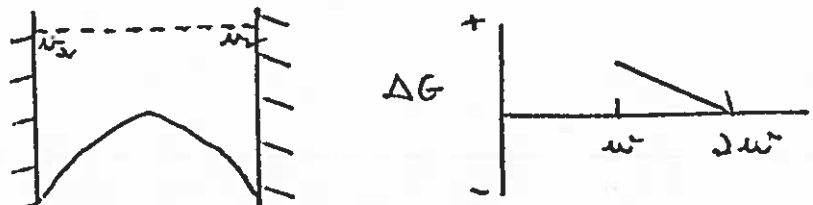
There are three domains of close approach:

i) $d \geq 2w$



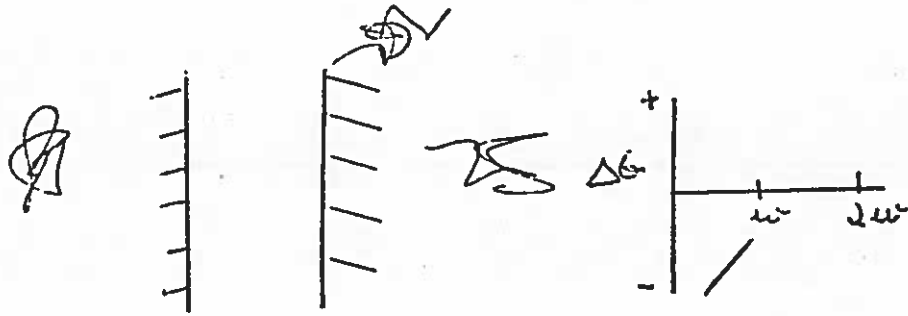
Here we push out polymer solution of bulk concentration from between the plates into bulk polymer solution outside the plates. No free energy required.

ii) $w < d < 2w$



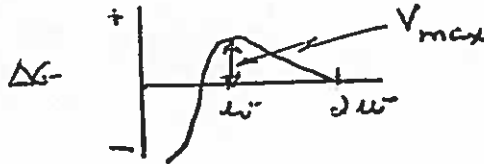
The volume fraction of polymer between the plates is less than that in bulk. To push more solution out requires a positive free energy because polymer solution (of near bulk concentration) is being pushed from a region of below bulk concentration into the bulk concentration. This is clearly against the natural entropic tendency of the chains in a good solvent to be distributed as uniformly as possible over the entire accessible domain.

iii) $d < w$



In principle, no chains exist between the plates. (Some do in practice but not many.) Closer approach squeezes water from between the plates into bulk solvent. As the solvent is a good one, this process is accompanied by a decrease in free energy

Quantitative calculations show that the free energy diagram for free polymer looks viz:



The maximum may be sufficient under suitable conditions to prevent flocculation occurring, i.e., free polymer chains can impart colloid stability to colloidal dispersions.

This phenomenon appears to account for both the flocculation and stability observed on adding polymer to a sterically stabilized dispersion.

Contribution to Polymer Colloid Group Newsletter

25 APR 1979

by M. Nomura

Dept. of Industrial Chemistry, Fukui University, Fukui, Japan

Our current work in the field of emulsion polymerization has been mainly centered on the kinetic study of emulsion copolymerization.

1. Emulsion Copolymerization of MMA and St

In my previous report, I proposed a mathematical model for the prediction of emulsion copolymerization rate and compared the theory with the experimental results of seeded emulsion copolymerization of MMA and St. Mr. Horie has continued the investigation on the swelling behavior of seed latex particles and found that:

(1) Contrary to my anticipation, the composition of polymer in the polymer particles (polyMMA/polySt), emulsifier concentration (interfacial tension between polymer particle and water phases) and ionic strength did not appreciably (in engineering sense) affect the swelling ratio of MMA and St monomers in polymer particles.

(2) MMA and St monomer concentrations in the polymer particles are solely determined by those in the monomer droplets in the water phase.

2. Vinyl Acetate Emulsion Polymerization-Effect of emulsifier type on the kinetics of vinyl acetate emulsion polymerization-

(Nomura, Fukui Univ., Litt and Chang, Case Western Reserve Univ.)

There is a controversy between two theories about the nature of VAc emulsion polymerization. One group (Nomura, Friis et al) uses a modified Smith-Ewart Case 1 approach, which states that all important reactions occur in the organic phase. The second theory (Patsiga, Litt et al) takes into account the interaction of the surfactant, polymer and radicals in the aqueous phase as well as considering the organic phase. The object of this work is to settle the controversy by running the polymerization using two different surfactants, that is, Na lauryl sulfate and a alkyl polyoxyethylene sulfate type surfactant. The former interacts strongly with polymer and the latter is non-complexing. If both surfactants give the same kinetics, the approach taken by the first group may be correct. If the kinetics differ significantly, the second theory may be valid.

The results of seeded emulsion polymerization carried out in CWRU was already presented by Dr. Litt at Miami Beach meeting and showed that there was no significant differences with two surfactants. I have continued this work after I came back and it was found that there was also no appreciable differences in unseeded emulsion polymerization of VAc with these different surfactants. It may be, therefore, concluded that the interaction of this kind does not affect the kinetics of polymerization.

Contribution to the Polymer Colloid
Group Newsletter
from University of Akron

25 APR 1979

Submitted by: I. Piirma

Experimental work carried out by: S. L. Fenske

The Effect of Surfactant Cation on the Emulsion Polymerization
Rate of Styrene Using Anionic Surfactants.

The cation effect of sodium oleate, potassium oleate, rubidium oleate and cesium oleate was studied in the emulsion polymerization of styrene at 50°C using potassium persulfate as initiator for a single polymerization recipe. Three variables which are likely to be influenced by the nature of the cation were examined both theoretically and experimentally in detail. The following observations are a result of this study:

a. The kinetics of the single particle in the emulsion polymerization under study are unaffected by changes in surfactant cation. Since the solubility of the polystyrene oligomer is low, it is expected that, while the cation might influence the absorption/desorption equilibrium of the oligomeric radical, the effect on the average number of radicals per particle during the constant rate period, Q , will be negligible.

The monomer concentration in the polymer particle, determined by noting the conversion at which the free monomer phase disappeared, was also found to be unaffected by a change in the surfactant cation.

b. The particle number obtained in the emulsion polymerization under study is unaffected by changes in surfactant cation.

c. Since the single particle kinetics and the particle number are unaffected by changes in surfactant cation, it is expected that the polymerization rate should also be unaffected. The rate data obtained for the emulsion polymerization under study confirms this proposal.

This research has failed to confirm that the electrostatic barrier present at the surface of particles stabilized with anionic surfactants has an influence on the rate of the persulfate ion-radical absorption. This conclusion is based on the fact that changes in the alkali metal cation of the oleate soaps do not result in measurable changes in the kinetics of the emulsion polymerization of styrene.

It is possible, however, that since styrene and its oligomers are essentially water insoluble, that even though there are large changes in the electrostatic barrier with changes in counterion, the differences are insufficient to have an influence on the extremely short life of the styrene oligomer radical in the aqueous phase. For this reason, it is suggested that future work in this area deal with monomers whose oligomers are soluble in the aqueous phase to a greater extent and that seed polymerization methods be used to study the possibility of hindered radical absorption.

It might also be fruitful to examine the counterion effect using additional counterions, such as lithium and ammonia, in order to increase the magnitude of the changes in the electrostatic energy barrier.

Contribution for the Polymer Colloid Group Newsletter

from R. L. Rowell

25 APR 1979

15. NEW APPROACHES TO THE CLASSIFICATION AND MEASUREMENT OF STABILITY. R. L. Powell, S. R. Vasconcellos and J. R. Ford. Department of Chemistry, University of Massachusetts, Amherst, Massachusetts 01003.

The accepted considerations of colloid stability are concerned with the availability of alternative states and the rates of transitions between states. In essence, the classical definitions are based on kinetics. We present a simple, conceptual approach based on fundamental thermodynamic ideas. To complement the thermodynamic framework we also present a classification of measurements for real systems based on the idea of an applied field. This allows the operational definitions of static, dynamic and reactive stability. As an alternative to the thermodynamic or macroscopic view, we distinguish the detailed-model approach which allows the definition of three main classes of stabilization: electrostatic, steric and matrix stabilization. The concept of matrix stabilization is discussed in relationship to the more familiar models of electrostatic and steric stabilization. Finally, in broad consideration of selected examples, it is shown that a statistical thermodynamic view is required with particular attention given to the distinction of system, ensemble and grand ensemble.

45. MEASUREMENT OF STABILITY IN COAL/OIL SYSTEMS. R. L. Powell, S. R. Vasconcellos and E. J. Marlov. Department of Chemistry, University of Massachusetts, Amherst, Massachusetts 01003 and S. Y. Tsai and S. K. Batra, New England Power Service Company, 20 Turnpike Road, Westborough, Massachusetts 01581.

Methods of measurement of stability in viscous opaque non-aqueous media are reviewed in connection with the problem of the stability of mixtures of ground coal in No. 6 fuel oil as a power plant fuel. Various sedimentation methods are discussed and it is shown that a sedimentation column employing direct measurement by bottom sampling is straightforward, versatile and effective. The sedimentation column allows direct measurement of partial specific volume as well as a rheological coefficient. The behavior of ideal and non-ideal systems is discussed in relation to sedimentation, subsidence, syneresis and rheological properties. The effect of water at low concentration is shown to have a pronounced effect on stability. Evidence for an interpretation of the results in terms of matrix stabilization is presented and the effect of particle size distribution is considered.

46. STABILIZATION OF SUSPENSIONS OF POWDERS VS. COLLOIDS: COAL/OIL VS. CARBON BLACK/OIL SYSTEMS. A.I. Medalia¹, B.S. Yarmoska^{1,2}, R.E. Cohen², R.L. Powell³, S.R. Vasconcellos³, R.J. Saia³. (1) Cabot Corp., Concord Fd., Billerica MA 01821; (2) Massachusetts Institute of Technology, Cambridge MA 02139; (3) University of Massachusetts, Amherst MA 01002.

Different mechanisms of stabilization are important in suspensions of powders and of colloids. These mechanisms are illustrated in the behavior of suspensions of powdered coal vs. carbon black in oil, as affected by various surfactants. Powdered coal is so coarse as to settle rapidly in dilute suspensions. In concentrated slurries (volume fraction 0.29) the coal undergoes subsidence to reach a final state of gravity packing. The addition of certain ionic surfactants prevents this subsidence, due to interparticle bonding (bridging); these surfactants thus act as stabilizers. At nearly the same volume fraction (0.15), carbon black forms a paste in oil, which is stabilized indefinitely by network formation. Surfactants which stabilize coal/oil slurries increase the viscosity of carbon black pastes, due likewise to increased bonding between the carbon black units in the network. In dilute suspensions of carbon black, these surfactants promote flocculation and rapid settling. Other surfactants have converse effects, such as reduced viscosity of carbon black pastes and stabilization of dilute suspensions of carbon black. Thus, surfactants which act as stabilizers for powder slurries, due to bridging, are flocculants for colloidal sols; and conversely.

Report from Vivian T. Stannett
Department of Chemical Engineering
North Carolina State University
Raleigh, North Carolina 27650

Goaded by the remarks of our worthy secretary in the October Newsletter the old Dean has sprung into action! The work reported earlier on the radiation initiated emulsion polymerization of styrene has now been completely written up and accepted for publication by The Journal of Colloid and Interface Science. Some more recent research on the grafting of styrene to large particle size crosslinked polybutadiene latex initiated both by radiation and $K_2S_2O_8$ has also been written up and submitted to the Journal of Macromolecular Science--Chemistry Edition. The abstracts of both papers are attached. Some further work will be reported in the next Newsletter!

KINETICS OF EMULSION POLYMERIZATION

27 APR 1979

KINETICS OF THE RADIATION INDUCED
POLYMERIZATION OF STYRENE IN EMULSION

V. Stannett, H. Shiota, H. Garreau and J. L. Williams

Department of Chemical Engineering
North Carolina State University
Raleigh, North Carolina 27650

ABSTRACT

The kinetics of the radiation induced polymerization of styrene in emulsion have been reexamined in a system which obeys the simple Case II Smith-Ewart kinetics with potassium persulfate initiation. The discrepancies found with other radiation emulsion systems were found to disappear and close agreement with the idealized simple theory was found.

The rate constants for propagation and the corresponding activation energy were found to be close to those reported in the literature. The termination rate constants were much smaller than the literature values for liquid systems but close to those reported for both chemical and radiation initiated emulsion systems. The lower values have been attributed to the higher viscosities encountered in the monomer-polymer particles. The efficiencies of the radicals both in initiating polymerization and in creating the number of monomer-polymer particles were found to be in the range of 0.3 - 0.5. The reasons for the low efficiencies are not clear but are consistent with results obtained by other investigators.

RADIATION AND CHEMICAL GRAFTING OF STYRENE TO POLYBUTADIENE LATEX

27 APR 1979

by

K. Yoshida,* K. Ishigure,** H. Garreau and V. Stannett
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North Carolina State University
Raleigh, North Carolina 27650

ABSTRACT

Earlier studies of the gamma radiation and potassium persulfate grafting of styrene to uncrosslinked small particle size polybutadiene latices have been extended to a commercial crosslinked large particle size latex. The larger size particles and high gel content of the substrate latex was found to lead to a more complicated pattern of behavior. The conversion curves and the molecular weights were found to be complex functions of the initial monomer concentration, number of particles and temperature with both methods of initiation. The simple Smith-Ewart theory did not, in general, apply to these systems and the k_p and E_p varied with conditions and were not in agreement with the generally accepted literature values.

The molecular weights of the extracted polystyrene homopolymer were lower in the case of radiation initiation, this is in agreement with the previous work and suggests that shorter but numerous grafted side chains are possible with radiation presumably due to the higher radical fluxes. (Some parallel experiments indicated that the molecular weights of the extracted homopolystyrene are similar to those of the grafted side chains.) This phenomenon also leads to somewhat lower graft efficiency with radiation initiation.

Nevertheless radiation was found to give grafting efficiencies of more than 80% under the best conditions. The conversions were also quite efficient with economical yields per radiation dose. These results coupled with the ease of control and other features of radiation make it a viable alternative method of initiation for industrial use.

WORK ON POLYMER COLLOIDS AT ÅBO AKADEMI AND THE SWEDISH
INSTITUTE FOR SURFACE CHEMISTRY

9 OCT 1978

Per Stenius

The Swedish Institute for Surface Chemistry, Stockholm, Sweden

Juhani Laaksonen, Kari Nurmi and Bengt Stenlund

Åbo Akademi, Åbo, Finland

EP of vinyl chloride without emulsifier

We have studied the mechanism of emulsifier-free emulsion polymerization of vinyl chloride by determination of the final particle size and characterization of the surface groups by conductometric titrations. The effect of the stirring conditions has also been studied.

Determination of particle diameters

The particle diameters were determined by electron microscopy. A diffraction grating (mean spacing 463 nm) was used for calibration. The number average diameter and the standard deviation was determined by measurements on about 30 particles on each micrograph.

Surface group analysis

The surface groups on the latex surface were determined by conductometric titration. The latexes to be titrated were purified by the method described by Vanderhoff immediately after the synthesis. About 1.5 g latex in 150 cm³ water was titrated with 2.6×10^{-3} mol dm⁻³ NaOH in a nitrogen atmosphere. The presence of acid impurities was checked by titration of 150 cm³ HCl solution with NaOH under identical conditions to those used in latex titrations; the results indicated a maximum concentration of weakly acid impurities of 10 µmol/dm³. The surface charge densities were calculated by combination of the EM diameter with the results from the conductometric titrations.

Results

The influence of the temperature and the concentrations of monomer, initiator and electrolyte on the particle size was studied using a simple three-level factorial plan consisting of four similar experiments on a central point (in order to estimate the experimental error) and eight experiments with each of the variables on two levels, one above and one below the central point. In the first series the ionic strength was adjusted with KCl. Very monodisperse (standard deviation of the order 1.5%) latexes were obtained; the reproducibility of the particle diameters was about 1%. From the results, the following linear equation for the diameter D as a function of the parameters may be calculated: ($[VCM]$ = concentration of monomer, $[KPS]$ = concentration of initiator, I = ionic strength)

$$\left(\frac{D}{\text{nm}}\right) = 1678 + 2 \left(\frac{[VCM]}{w/w\%}\right) - 15 \left(\frac{[KPS]}{\text{nmol/dm}^3}\right) - 8 \left(\frac{I}{\text{mmol/dm}^3}\right) - 3 \left(\frac{T}{K}\right) \quad (1)$$

The dependence of D on the parameters is in agreement with the work of other groups on other monomers except for the decrease with increased ionic strength. However, the number of experiments on which Equation 1 is based is fairly small and a linear model is probably too simple to give an adequate description, although the coefficients in Equation 1 are statistically significant when compared to the experimental uncertainty. The influence of ionic strength and counter ion charge was studied by using CaCl_2 and LaCl_3 as the electrolyte instead of KCl. The results are given in Figure 1, which shows the effect of increasing the electrolyte concentration under otherwise identical conditions of synthesis (given in the figure captions). The particle diameter increases linearly with the ionic strength and very sharply with the counter ion charge ($\text{La}^{3+} > \text{Ca}^{2+} > \text{K}^+$). The effect of increasing the concentration of K^+ is much smaller than that of Ca^{2+} or La^{3+} . Thus the unexpected sign of the coefficient for the ionic strength in Equation 1 may be due to the small contribution of I to D in this case.

In a third series of experiments the same experimental plan as that used in the first series was repeated with CaCl_2 as the electrolyte instead of KCl . When Ca^{++} is used as the counter ion, the standard deviation in the particle diameters is somewhat larger and the reproducibility is not quite as good as with KCl . This probably reflects the greater sensitivity to bivalent cations of the stability of the particles formed in the primary coagulation. The following equation for the diameter may be calculated from the third series:

$$\left(\frac{D}{\text{nm}}\right) = 5923 + 8\left(\frac{[\text{VCM}]}{\text{w/w}\%}\right) - 28\left(\frac{[\text{KPS}]}{\text{mmol/dm}^3}\right) + 56\left(\frac{C_{\text{el}}}{\text{mmol/dm}^3}\right) - 16\left(\frac{T}{\text{K}}\right) \quad (2)$$

where C_{el} is the concentration of $\text{CaCl}_2 \cdot 2 \text{H}_2\text{O}$. In this case, the diameter increases strongly with ionic strength. This linear equation fits the results satisfactorily: introduction of quadratic terms does not give a significant improvement.

The results of the surface group analysis are given in Table 1; All titration curves showed two break points. We have interpreted these as representing neutralization of sulphate and carboxylic groups on the surface, respectively. Oxidation of the latexes with AgNO_3 resulted in a large increase in the amount of $-\text{COO}^-$ on latexes A and C, indicating the presence of $-\text{OH}$ groups on the surfaces of these latexes.

TABLE 1 - Surface group analysis of PVC latexes

$[\text{VCM}] = 15\text{w/w}\%$ for latexes A, C; $= 18 \text{ w/w}\%$ for latex B
 $[\text{KPS}] / [\text{VCM}] = 1:100$, temperature 65°C .

Latex	C_{el} g/dm ³	D nm	Surface charge density $\mu\text{C/cm}^2$			Conc. of -OH groups $\mu\text{mol/g PVC}$
			$-\text{SO}_4^-$	$-\text{COO}^-$	total	
A	-	395	1.72	0.92	2.64	2.42
B	0.17	535	2.60	0.85	3.45	-
C	0.31	555	2.69	3.27	5.96	0.78

The influence of stirring conditions on EP of VC without emulsifier

We have initiated a systematic study of the influence of stirring conditions (number of stirring blades, stirring velocity, stirrer geometry in relation to size of vessel) on the polymerization of vinyl chloride. So far, a simple two-blade stirrer, a six-blade stirrer and a stirring system with three four-blade stirrers on top of each other have been tested. In the polymerizations, the total amount of monomer was varied from 15 to 30%, the ratio $[KPS]/[VCM]$ was kept constant. The results are still being evaluated but the following conclusions can already be drawn.

- the reaction time for intervals I and II (up to 75% conversion) depends very little on stirrer geometry or speed while the reaction in interval III is very dependent on these parameters,
- it was difficult to keep temperature changes under control if the tip speed of the stirrer was < 1.5 m/s,
- the equation for the particle diameter given above are valid independently of the stirrer velocity or geometry for monomer concentrations $< 20\%$,
- the particle diameters become much larger than predicted when the monomer concentration is $> 21\%$; at the same time they become dependent on stirring conditions.

Polymer Newsletter. Contribution

John Ugelstad

University of Trondheim

23 APR 1979

We have continued our work with swelling of oligomer and oligomer-polymer particles both from a theoretical but mostly from a practical point of view. I am sending separately to the members a copy of our recent paper in Makromolekulare Chemie.

1. The two step swelling method.

As described in the paper sent separately the two step swelling method involves that we swell particles (eventually monodisperse) polymer particles first with a water insoluble relatively low molecular weight compound under conditions which allow the transport of the same through the aqueous phase. Then we change the conditions so that the transport of this compound is hindered, and then we add the low molecular weight compound (eventually a monomer). We have improved this method considerably and are now able to produce, I would say readily, monodisperse particles in the range up to 10 μm with a very narrow size distribution. When dried in a thin layer these particles form a nice pattern. A picture of a monodisperse polystyrene latex (optical microscope) with particle size 7 μm is shown below.

2. Theory of swelling.

In our first papers we have considered the partial free energy of swelling of the particles and showed that the presence of oligomer molecules in the particles would lead to a very large increase in swelling capacity of the particles for low molecular weight compounds. This was verified experimentally. Also it was pointed out that the theory predicted an even larger increase in swelling capacity. This was expected as we applied the Flory Huggins theory (with addition of the extra term for the interfacial energy). As pointed out the Flory Huggins theory which is based upon the concept of completely flexible chains will tend to give a too high entropy of mixing.

It might be that we, especially in the case that we apply oligomer molecules which are not too much larger in size than the low molecular weight compounds, would get a better approximation by assuming that the combinatorial entropy should be that of an ideal solution. This has been found to be the case for several systems up to molar volume ratios of 5-10. Also this is

expected in cases where the molecules are considered as rigid spheres, the free volume will only change little with change in molar volume.

Case I. Only compound 1 and 2.

Flory Huggins

$$(1) \quad \ln \frac{V_1}{V_1+V_2} + \left(1 - \frac{1}{j_2}\right) \frac{V_2}{V_1+V_2} + \left(\frac{V_2}{V_1+V_2}\right)^2 \chi + \frac{2\bar{V}_1\gamma}{rRT} = 0$$

Ideal entropy

$$(2) \quad \ln \frac{V_1}{V_1+V_2/j_2} + \left(\frac{V_2}{V_1+V_2}\right)^2 \chi + \frac{2\bar{V}_1\gamma}{rRT} = 0$$

V_2 is the volume of Compound 2 which is constant.

V_1 is the amount of 1 absorbed at equilibrium, $r = (V_1+V_2/V_2)^{1/3} r_0$.

\bar{V}_1 is partial molar volume of 1. The molar volume of compound 2 is set equal to $j_2\bar{V}_1$:

Eventually we could apply the Hildebrand expression for the interaction

term:
$$\frac{\bar{V}_1\phi_2^2(\delta_1-\delta_2)^2}{RT}$$

Equations (1) and (2) may be considered as representing the extreme case of completely flexible molecules and rigid spheres respectively.

Intermediate situation may possibly better be described by the equation

$$(3) \quad \ln \frac{V_1}{V_1+X_2V_2/j_2} + \left(1 - \frac{1}{X_2}\right) \frac{X_2V_2/j_2}{V_1+X_2V_2/j_2} + \left(\frac{V_2}{V_1+V_2}\right)^2 \chi_h + \frac{2\bar{V}_1\gamma}{rRT} = 0$$

where $1 \leq X_2 \leq j_2$ and X_2 increases in value as the flexibility of compound 2 increases.

Case II. Particles consists of oligomer (2) and polymer (3) molecules.

Flory Huggins

$$(4) \quad \ln \phi_1 + \left(1 - \frac{1}{j_2}\right)\phi_2 + \left(1 - \frac{1}{j_3}\right)\phi_3 + \phi_2^2 \chi_{12} + \phi_3^2 \chi_{13} \\ + \phi_2\phi_3 (\chi_{12} + \chi_{13} - \chi_{23}) + \frac{2\bar{V}_1\gamma}{rRT} = 0 \quad (\phi \text{ are volume fractions.})$$

Ideal entropy

$$(5) \quad \ln \frac{V_1}{V_1+V_2/j_2+V_3/j_3} + \phi_2^2 \chi_{12} + \phi_3^2 \chi_{13} + \phi_2\phi_3 (\chi_{12} + \chi_{13} - \chi_{23}) \\ + \frac{2\bar{V}_1\gamma}{rRT} = 0$$

where $j_3 = \bar{V}_3/\bar{V}_1$.

Also in this case an equation similar to (3) may be given:

$$(6) \quad \ln \frac{V_1}{V_1 + X_2 V_2/j_2 + X_3 V_3/j_3} + (1 - \frac{1}{X_2}) \frac{X_2 V_2/j_2}{V_1 + X_2 V_2/j_2 + X_3 V_3/j_3} \\ + (1 - \frac{1}{X_3}) \frac{X_3 V_3/j_3}{V_1 + X_2 V_2/j_2 + X_3 V_3/j_3} + \phi_2^2 x_{12_h} + \phi_3^2 x_{13_h} \\ + \phi_2 \phi_3 (x_{12_h} + x_{13_h} - x_{23_h}) + \frac{2\bar{V}_1 \gamma}{rRT} = 0$$

In the range of interest with swelling capacity $\geq \sim 50$, that is with $j_2 \leq \sim 20$ and $\gamma/r_0 \leq \sim 10^5 \text{ Nm}^{-2}$ the change to equation (2) resp. (5) does only lead to a small decrease in the calculated swelling capacities. A more comprehensive discussion of the problem of swelling will appear in a paper under preparation with M.A. Aziz as co-author.

3rd International Conference on Surface and Colloid Sciences,
August 20-25, 1979 Stockholm, Sweden.

At this conference there will (as you have been informed) also be a section on Polymer Colloids. There will be two main lectures by John Vanderhoff and Alex Rembaum. Besides there will at this section be about 25 short papers. Several group members will attend the meeting. From the preliminary programme I also can promise that there will be a lot of very interesting papers in the other sections which have important relations to problems in polymer colloids. The only problem is that expences in Sweden is perhaps even higher than in Norway.

