

7 October 1977

Dr Tom R. Paxton died suddenly following a heart attack on July 16, 1977.

His contribution which appears in this issue of the Newsletter was intended for the Spring issue but unfortunately arrived just after copies had been sent out.

Dr Dean E. Ley, Director of Corporate Research at the B.F. Goodrich Company Research and Development Center, 9921 Brecksville Road, Brecksville, Ohio 44141 will try to help with any unfinished business which members of the Group may have had with Dr Paxton.

Although some members did send their contributions in good time for this issue, others evidently failed to repeat to themselves 'I must write my Newsletter contribution as soon as I get back' all the way home from the Gordon Conference so that I still have not heard from them. Dr Nomura excused himself from this year's issue having been on study leave with Morton Litt at Case, and the management at ICI Paints have stamped on Dr Osmond's intended contribution for reasons of commercial security. The deadline for the Spring issue will be Monday 24th April 1978 in Manchester so make a note now to get your news into the post at least a week before that date.

The Chemical Society Macromolecular Group meeting in London last week attracted 150 participants. John Ugelstad had to withdraw at the last minute but Finn Hansen, David Blackley, Ron Ottewill, and myself gave papers and Alan Robertson was also able to be there.

I am hoping that the Faraday Division of the Chemical Society will agree to hold a General Discussion on emulsion polymerisation in the spring or autumn of 1980 or 1981 with which the Annual Meeting for that year might be held in conjunction. These general discussions are the most prestigious of any physical chemistry symposia which should assist applications for travel funds. I expect that most members of the Group would be able to offer suitable papers and would be eager to contribute to the discussion which is normally extensive and animated at these events. Some funds would be available to help with travel though probably only to the extent of a Gatwick-New York ticket on 'Skytrain'. (Because of the depreciation of the pound since this service was first proposed the New York-London fare is more expensive!). We should know whether this is likely to be on or off by mid October.

The PRI International Polymer Latex Conference is now scheduled for 31 October and 1 and 2 November 1978 in London. Enquiries to Mr R.H. Craven at the Plastics and Rubber Institute, 11 Hobart Place SW1W 0HL or to David Blackley.

Other items on future meetings likely to be of interest to members appear in the Minutes of this year's Annual Meeting.

Irv Krieger arrived in Bristol in mid-September where he is putting in five months as Visiting Professor.

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England.

28 SEP 1977

The Polymer Colloids Group had its Annual Meeting at Holderness School, New Hampshire on August 22, 1977. 20 people attended (an attendance list is enclosed).

Among the items of business discussed were the following:

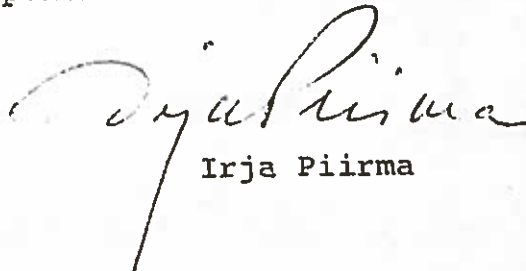
1. Voted unanimously to request a second Gordon Conference for Summer 1979.
2. Decided to have the next meeting of the Polymer Colloids Group in Miami, Florida, September 1978 during the American Chemical Society National Meeting. The meeting was to be preferably a dinner meeting.
3. Learned that the deadline for submission of Abstracts of papers for the Polymer Colloids Symposium in the ACS Division of Colloid and Surface Chemistry chaired by R. M. Fitch is April 1978.
4. Proposed to tie-in the NSF sponsored Japan-US Polymer Colloids Seminar with the ACS-Japan Chemical Society joint meeting in Hawaii. Dr. Fitch was to explore this further.
5. Proposed on the question of new members for the Polymer Colloids Group
 - a) not to get too much larger.
 - b) accept nominations occasionally and consider them singly.
6. Nominated two scientists for consideration as new members:

PROFESSOR ROBERT ROWELL - University of Massachusetts, Department of Chemistry, Amherst, Massachusetts 01003

PROFESSOR CHEN-CHONG LIN- National Taiwan University, Department of Chemical Engineering, Taipei, Taiwan

(Both received an unanimous "yes" vote).
7. Decided to ask Dr. Dunn to suggest guidelines for Newsletter concerning
 - a) length of contributions.
 - b) mode of distribution to cut increasing cost

(Dr. Gardon volunteered permanent U. S. distribution).
8. Decided to keep Newsletter confidential i.e., no circulation outside the immediate membership.
9. Learned from Dr. Gardon that an Organic Coatings Workshop is planned (2/3 industrial, 1/3 academic) in Cleveland ca. June 1978 jointly sponsored by the NSF and the Coating industry.
10. Decided to ask for postponement of the Emulsion Polymerization Symposium (planned by the ACS for Fall 1979) to Fall 1980. Dr. Gardon volunteered to handle the postponement.


Irja Piirma

FURTHER DEVELOPMENTS IN THE THEORY OF COMPARTMENTALISED FREE-RADICAL
POLYMERISATION REACTIONS

D. C. Blackley, National College of Rubber Technology, The Polytechnic
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The story summarised in our contribution to the previous number of the Polymer Colloid Group Newsletter has had a happy ending in that a full paper on our solution to the "Gilbert-Napper" problem has been accepted for publication in Faraday Transactions I, and should be appearing shortly. I imagine that our paper was accepted for publication, notwithstanding anticipation of our principal result by Weiss and Dishon, principally because we have given a fairly full discussion of the implications of the result, and also reasonable details of the method by which we obtained the result. We have also given a clear statement of the type of polymerising system to which the theory could be expected to apply; this is important in view of the serious restrictions which the theory places upon the reaction system.

We have now found that it is possible to generalise our result in such a way as to remove some at least of these restrictions. Our generalisation extends the result to cases for which the parameters σ and k are functions of time; it will be recalled that these parameters characterise respectively the rate of entry of radicals into, and the rate of exit of radicals from, the reaction loci. The generalised analysis still neglects radical-loss mechanisms which are other than first order in radical concentration at the reaction locus. In general, the important assumption is still made that radicals which are lost from the reaction loci by diffusion into the external phase are not available for re-initiation of polymerisation. However, it is possible to take into account re-initiation by radicals which have diffused out of reaction loci if the time-dependence of σ is such as to include a contribution due to radicals which have become available for re-initiation by this mechanism.

We have found that the characteristics of the generalised reaction system are governed by a function, $\theta(t)$, of time which can be obtained by solving the ordinary differential equation

$$\frac{d\theta(t)}{dt} = \sigma(t) - k(t) \cdot \theta(t) \dots\dots\dots (1)$$

and inserting the initial condition $\theta(0) = 0$. (In this differential equation, the parameters σ and k are written as $\sigma(t)$ and $k(t)$ in order to emphasise their possible time-dependence.) Having obtained the function $\theta(t)$ for any particular case, it appears that it is then possible immediately to write down expressions for the locus-population generating function, $\Psi(\xi, t)$, the locus populations themselves, $n_r(t)$, the average number of radicals per locus, $\bar{i}(t)$, and the total number of radicals in all the reaction loci at time t , $\sum_{i=1}^{\infty} i n_i(t)$. The results are

$$\Psi(\xi, t) = N e^{(\xi - 1)\theta(t)} \dots\dots\dots(2)$$

$$n_r(t) = N \frac{\{\theta(t)\}^r}{r!} e^{-\theta(t)} \dots\dots\dots(3)$$

$$\bar{i}(t) = \theta(t) \dots\dots\dots(4)$$

and $\sum_{i=1}^{\infty} i n_i(t) = N \theta(t) \dots\dots\dots(5)$

where N is the total number of reaction loci in the system. It thus appears that the problem of predicting theoretically the characteristics of any particular reaction system of the class to which the theory applies can be reduced to that of solving a first-order ordinary differential equation involving t as the independent variable, rather than the more difficult task of solving a first-order partial differential equation with ξ and t as independent variables. An interesting conclusion which emerges from the new theory is that, whatever the nature of the time-dependence of σ and k , the n_r are predicted always to form a Poisson distribution with respect to the r , the function $\theta(t)$ being always the parameter of the distribution at any instant. These conclusions follow immediately from the observation that the expression for $\Psi(\xi, t)/N$ given by equation (2) is in fact the frequency-generating function for a Poisson distribution of parameter $\theta(t)$.

A note on the new result is due to be published shortly in Chemical Communications, and a full paper is also being prepared for publication. The latter will give details of the derivations, together with applications of the method to a few cases of potential interest. Foremost amongst these is the case where k is constant and σ is an exponentially-decaying function of time say, $\sigma = \sigma_0 e^{-\alpha t}$; this case is of particular interest because it enables prediction to be made of

the effect of initiator depletion when the rate of generation of radicals is first-order in the concentration of initiator in the external phase. So long as $\alpha \neq k$, the result for $\theta(t)$ is

$$\theta(t) = \frac{\sigma_0 e^{-\alpha t}}{k-\alpha} (1 - e^{-(k-\alpha)t}) \dots\dots\dots (6)$$

from which expression for $\Psi(\xi, t)$, $n_r(t)$, $\bar{i}(t)$ and $\sum_{i=1}^{\infty} i n_i(t)$ can immediately be written down using equations (2), (3), (4) and (5) respectively. The result for $\theta(t)$ requires modification for the special (and extremely improbable) case where $\alpha = k$. The result is now

$$\theta(t) = \sigma_0 t e^{-kt} \dots\dots\dots (7)$$

Knowing the prediction for $\bar{i}(t)$, it is a simple matter to write down an expression for dM/dt , the rate of conversion of monomer to polymer in the reaction system as a whole. Integration of this expression gives the prediction for the conversion-time relationship. For the case where k is constant and σ decays exponentially with time, and $\alpha \neq k$, the result is

$$M(t) = k_p [M] N \frac{\sigma_0}{k-\alpha} \left\{ \frac{e^{-kt} - 1}{k} - \frac{e^{-\alpha t} - 1}{\alpha} \right\} \dots\dots (8)$$

where $M(t)$ is the amount of monomer converted to polymer in time t , $[M]$ is the concentration of monomer at the reaction locus (assumed to be constant), and k_p is the rate coefficient for the propagation reaction (also assumed to be constant). For the special case where $\alpha = k$, the expression for $M(t)$ modifies to

$$M(t) = k_p [M] N \frac{\sigma_0}{k^2} \left\{ 1 - (kt + 1)e^{-kt} \right\} \dots\dots\dots (9)$$

Working on the idea that small differences in the procedures used by different manufacturers may affect the blockiness of different samples and that this would affect the adsorption of the polymer by latex particles and thus the course of the polymerisation, we have prepared from the same polyvinyl acetate samples of polyvinyl alcohol with similar residual acetyl contents either by saponification in aqueous alkali which is known to give a product with an average block length $n = 40$ and by methanolysis with an alkaline catalysts (the usual commercial process) which gives a short block length, $\bar{n} = 5$, which is still, however, much larger than would be obtained by random acetylation to 12 mole % acetyl. However the particle sizes of the latex produced in the presence of these products from either 2 % solutions or a 40% emulsion is similar when persulphate initiation is used although there is evidence in the literature that blockier polyvinyl alcohols do give smaller particle sizes when hydrogen peroxide initiation is used. Hydrogen peroxide, however, produces much larger particles which are not stable in the absence of polyvinyl alcohol. It seems, therefore, that partial electrostatic stabilisation by the sulphate end-groups masks any effect the blockiness of the polyvinyl alcohol may have.

Installation by the S.R.C. of a ^{13}C n.m.r. spectrometer in the Manchester University Chemistry Department gave us the opportunity of seeing whether this technique could be used to determine sequence distribution in polyvinyl alcohol acetates. Although it appeared that it could, our conclusion was that determination of the crystalline melting point by D.T.A. was simpler and more convenient. However Moritani & Fujiwara of the Kuraray Co. (*Macromolecules* 10 (1977) 532) have had the same idea and have worked out the n.m.r. determination of blockiness in polyvinyl alcohol-acetates completely. However we noticed that the splitting pattern in the main CH and CH_2 resonances (which arise from completely hydrolysed sequences) differ according to the method of preparation. The splitting arises from sequences of different tacticity (cf. e.g. Wu & Cvenall, *Macromolecules* 6 (1973) 582) and the tacticity of the sample could not be changed by hydrolysis except perhaps because of the removal of hydrolysable long-chain branches which had, however, previously been shown not to be present in the polyvinyl acetate used. It is also possible to deduce the acetyl content from the n.m.r. spectrum: for the saponified samples this was much lower than that determined chemically. The explanation seems to be that water is a selective solvent for the blocky sample and the unhydrolysed blocks, being in suspension rather than solution, do not give a high resolution n.m.r. signal. There must be a steric effect on the rate of the saponification reaction since the tacticity of the saponified sequences differs from the tacticity of the entire polymer. This may be an additional factor accounting for the differences in behaviour of nominally similar polyvinyl alcohols. Another factor is certainly the extent of oxidation and dehydration indicated by the ultraviolet absorption of the samples. However although the intensity of u.v. absorption does correlate with the effect of polyvinyl alcohols in reducing the rate of polymerisation of vinyl acetate solutions, the coefficient of correlation (on the assumption, adopted for simplicity and not for any theoretical reason, that a linear regression is appropriate) is only 0.7 indicating that some other factor, perhaps that described above, is also relevant. (S. R. Naravane)

W. Al-Shahib has just completed his Ph.D. thesis and will be returning to Iraq shortly. We have been trying to find an explanation for our observations that equal numbers of particles are finally formed and that equal Interval II rates are observed when equal micellar concentrations of emulsifiers are used. We think that the determining factor is the total surface area of the original micelles. No information on the size of monomer swollen micelles is available and agreement between determinations of micelle size by different techniques is poor. (cf. However, following Tartar (*J. Phys. Chem.* 59 (1955) 1195, *J. Coll. Sci.* 14 (1959) 115) it is possible to calculate the volume and surface area of micelles on the basis of experimental aggregation numbers. Aggregation numbers increase with alkyl chain length so, when the total concentration of micellar surfactant is the same, the number of micelles must decrease. For the alkyl sulphates and alkyl sulphonates, the total surface area remains

constant suggesting that it is this factor which determines the ultimate formation of the same number of latex particles. For the alkyl carboxylates the total surface area decreases with increasing chain length: we are inclined to doubt the only available aggregation numbers for these materials (Ryabova, Beresnev, & Smirnov, J. Appl. Chem. USSR 45 (1972) 149 but we are hoping that it will be possible to check these in the near future.

The value of A_s , the area occupied by a surfactant molecule in a saturated monolayer on the surface of a latex particle appears to depend not only on the nature of the polymer but also on the procedure used to prepare the latex (i.e. on the surface charge density due to initiator residues). The soap titration procedure was used to determine A_s for the actual latices under investigation in some cases but the method was found to be inapplicable to the latex prepared at an equal micellar concentration of potassium octanoate because the surfactant concentration in the final latex was still above the critical micelle concentration. With the alkyl carboxylates the duration of Interval I increases as the alkyl chain length decreases but the same rate is nevertheless observed during Interval II and the same number of latex particles are ultimately formed. The total soap concentration is high since this soap has a very high c.m.c. Evidently ample soap is present to stabilise all the latex particles formed without reducing the concentration of soap in the aqueous phase below the c.m.c. In discussion at the London symposium, Finn Hansen suggested that potassium octanoate may not solubilise styrene effectively so that the presence of micelles could be irrelevant in this case, particle formation proceeding by oligomeric precipitation. This is a possibility which we should clearly check.

The solubility in water of sparingly soluble monomers is clearly a vital factor in emulsion polymerisation (cf. Osmond's contribution to the last Newsletter and Piirma's contribution to this one). What is the solubility of butadiene? This monomer does not appear to polymerise at all below the c.m.c. of the surfactant and Duck has suggested that the role of mercaptans in promoting diene polymerisations is to increase the rate of radical entry into charged micelles by forming an uncharged radical after hydrogen abstraction by a charged initiator radical. There is good evidence from flash photolysis experiments to show that the supposed reaction of sulphate radicals with water to give hydroxyl radicals does not occur. Hydroxyl end-groups may all result from hydrolysis of sulphate end-groups. On the other hand, how is oxygen produced from persulphate in water in absence of any other substrate? I have had in mind for the last two years that an experiment in heavy water should discriminate and the Fronaeus-Ostman mechanism

$$S_2O_8^{2-} + H_2O = SO_4^{\cdot-} + HO\cdot + HSO_4^-$$
which offers a resolution of this dilemma. I haven't succeeded in persuading anyone to try the experiment so far, however.

Z. Said is completing a M.Sc. Dissertation extending the work Al-Naama did last year on the adsorption of alkyl sulphates on surfactant-free polystyrene latex to higher concentration. We thought Al-Naama's results indicated that a 'gaseous' monolayer with the alkyl chains lying flat on the polystyrene surface might be formed at low concentrations but it looks as though his results were actually due to not using large enough concentrations of the Methylene Blue reagent! M.A.Momen (Postgraduate Diploma) determined the effect of polyvinyl alcohol on the solubility of vinyl acetate at 60°C and F.K.Boakye (2nd Yr. undergrad.) the effect of ethanol on the solubility of vinyl acetate at room temperature. Both alcohols increase the solubility but to a much smaller extent than Enfiadzhyan et al. claim. I think the refractive index method which they used to determine concentrations may have been subject to a systematic error. We used the synthetic method.

3 OCT 1977

UConn News

The past summer was a time for writing. The following manuscripts have either been accepted (*), submitted for publication (**), or are in final stages of preparation:

*1. Preparation and surface chemistry of polystyrene colloids stabilized by sulfonate surface groups, by McCarvill & Fitch (J. Colloid Interface Sci.).

**2. Surface chemistry of polystyrene colloids prepared by mixed initiator/surfactant systems, by Fitch & McCarvill.

**3. Surface chemistry of polystyrene latexes initiated by the persulfate/bisulfite/iron system, by McCarvill and Fitch.

4. Coagulation kinetics in polymer colloids determined by light scattering, by Fitch and Watson.

5. Heterogeneous acid catalysis of ester hydrolysis by polystyrene colloids, by McCarvill & Fitch.

We shall be happy to send copies to anyone requesting them.

News from the group:

A.R.M. Azad. Latex particle formation in suspension polymerization of methacrylate monomers is being investigated. We believe latex particles are formed, in addition to the expected particle nucleation mechanism, by monomer dissolution from the smaller sized beads, especially in the case of water soluble monomers. Radical desorption from beads is also being studied in order to distinguish between the two possible routes of "latex" particle formation, and to study the effect of water solubility of the oil-soluble initiator.

T. H. Palmgren. This work is on the kinetics of the earliest stage of emulsion polymerizations using aqueous biacetyl photo-initiated MMA-systems. Attempts to use light scattering and/or interferometry as a means of detecting the oligomeric growth after initiation are being pursued.

Prakash Kasargod is currently engaged in the synthesis of the water-soluble initiator, p-sulfo-methyl benzoyl peroxide.

Robert Miller is synthesizing a surface active monomer, ω -sulfodecyl styryl ether sodium salt and will study the surface chemistry of polystyrene latexes made from it.

Diane Sheldon has changed her project to undertake an extremely complex synthesis: a human child. The result of her labor is expected in about eight months!



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September 9, 1977

13 SEP 1977

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Dear Sandy:

Here is my contribution to the Newsletter:

"John Gardon (M&T Chemicals Inc.) published some papers and can furnish reprints on request.

- (1) "Emulsion Polymerization Theory", Encyclopedia of Polymer Science and Technology, Supplemental Volume 1, pp. 238-259 (1976), N. Bikales, Editor.- The same paper is also published in the book "Applied Polymer Science", Craver and Tess, Editors, Organic Coatings and Plastics Chemistry Division of the American Chemical Society, pp. 138-160 (1976).
- (2) "Interfacial, Colloidal and Kinetic Aspects of Emulsion Polymerization" in the book "Interfacial Synthesis", Millich and Carraher, Editors, Marcel Dekker Inc., New York, pp. 205-254 (1977).
- (3) "Emulsion Polymerization", for the new forthcoming edition of Schildknecht's "Vinyl and Related Polymers". This is in press now and is a rather long and detailed review with many tables and figures.

While these papers are reviews, they do contain original material in that some old data from the literature are recalculated showing that they are in good agreement with the current quantitative theories. Also, the concept is emphasized that the commonly used monomers yielding water-insoluble polymers can be classified into at least three categories:

- (a) Styrene-like (including acrylates, methacrylates, dienes, chlorophene) which have low chain transfer coefficients to the monomers and are good solvents for their polymers: these follow Smith-Ewart Case 2 or Case 3 kinetics and follow the classical particle nucleation mechanism in the presence of micellar anionic surfactants and water-soluble initiators

having long half-lives. For these monomers, the dominating termination step is within the particles.

- (b) Vinyl-chloride-like (including vinyl acetate and ethylene) which have high chain transfer coefficients to the monomers and follow Smith-Ewart Case 1 kinetics because the chain transfer to the monomers in water provide the dominating mechanism for chain termination in the particles. These monomers do not follow the classical particle nucleation concepts.
- (c) Acrylonitrile-like (including vinylidene chloride) which are non-solvents for their polymers so that the locus of polymerization is not within but on the surface of the particles. These two monomers nevertheless give results similar to styrene-like monomers in that, unlike vinylchloride-like monomers, they give high molecular weights and fast reactions.

The most important difference between styrene-like and vinyl-chloride-like monomers is that for the former the average number of radicals per particle is always equal and larger than half, while for the latter it is always much smaller than half. A complicating factor is that certain nonionic surfactants are good chain transfer agents and they can render even styrene-like monomers to behave according to Case 1.

These concepts were also explained in Gardon's presentation at the recent Gordon Research Conference.

Gardon also published a paper which does not deal with polymeric colloids but could be of interest to the group since it deals with intermolecular interactions. The title is "Critical Review of Concepts Common to Cohesive Energy Density, Surface Tension, Tensile Strength, Heat of Mixing, Interfacial Tension and Butt Joint Strength". It is published in the J. Colloid Interface Science 59 582 (1977) and in the Progress of Organic Coatings 5 1 (1977)."

Sincerely,



J. L. Gardon, Director
Research & Development

JLG/ht



McGill
University

Department of Chemistry
Pulp and Paper Building

15 SEP 1977

S.G. Mason and A.A. Robertson

Contribution to the Polymer Colloid Group Newsletter

September 1977

The series of investigations under the general title "Interactions of Colloidal Particles in Shear Flow" has been continuing and an account of some of the work was presented by K. Takamura at the recent Gordon Conference on Polymer Colloids.

The studies of the rotation of doublets of latex spheres and the application of the theory applicable to such systems has permitted several conclusions to be reached.

Perturbation of the period of rotation of the doublet caused by rotary Brownian diffusion is significant under the conditions prevailing in the experiments. Hence, it was necessary to measure at least 60 rotations of a doublet to obtain statistically significant values of the average period of rotation, and hence the equivalent ellipsoidal axis ratio r_e .

The distribution in r_e for doublets at 10^{-2} M KCl, appears to indicate the existence of both primary and secondary doublets, having $r_e \approx 2.3$ and $r_e \approx 2.5$, respectively. The separation gap, h , between sphere surfaces calculated from the mean r_e using the hydrodynamic theory developed by van de Ven and Mason, was found to lie between 15 and 20 nm for doublets at the secondary minimum. From the DLVO theory of colloid stability, it can be shown that a gap width of 18 nm would correspond to a Hamaker constant $A = 10^{-20}$ J, which is a reasonable value. It has been found that h for doublets at the secondary minimum decreases with increasing electrolyte concentration at 3×10^{-2} M KCl with h lying between 5 and 10 nm. Here, the DLVO theory using the above value of A gives $h = 8$ nm.

At the lowest electrolyte concentration of 10^{-3} M KCl only primary-minimum doublets were observed. Here, it is presumed that the secondary minimum is so shallow that the hydrodynamic forces were sufficiently strong to separate the spheres and only primary doublets formed during the storage of the latex suspension survived the shear motion.

The effect of adding a cationic polyelectrolyte was investigated. The initial zeta-potential of -17.4 mv was reduced by the addition of Cat-floc (Calgon Corp.) to the latex suspension and a reversal of charge occurred at a polymer concentration $> 10^{-5}$ g/100 ml. Measurements of the period of rotation were made under the following conditions: (i) where

there was < 1.0% coverage of the surface and (ii) at almost full coverage of the latex sphere surface corresponding to polymer concentrations of 3×10^{-6} and 10^{-4} g/100 ml, respectively.

Distributions of r_e reveal significant changes as a result of polymer adsorption in the suspensions. Thus, at full surface coverage, almost 80% of doublets are touching and have $r_e = 1.95$ to 2.05 . Polymer-bridge formation between sphere surfaces appears to be the most reasonable explanation for the existence of such doublets at the polymer concentrations employed.

At the lower polymer concentration, however, there was a broad distribution in r_e , from 1.95 to 2.40 . A possible explanation for this result may lie in an increased surface heterogeneity of the spheres due to only partial coverage by polymer that could lead to a mosaic pattern of surface charge, with some parts positive and some negative.

The alignment of positive and negative charge domains on adjacent spheres would then result in an inhibition of relative rotational motion and the consequent decrease in r_e from the value expected at the secondary minimum.

The studies are continuing with the examination of systems involving non-ionic polymers and steric stabilization.

Polymer Colloid Newsletter Contribution
from
Case Western Reserve University
September 1, 1977

SEP 1977

All of you should have received a preprint of an article by L. J. Liu and I. M. Krieger on the control of surface charge. This summarizes our most recent work on preparation of polymer colloids, and outlines two promising routes to achieve a latex whose only ionizable surface groups are sulfonic acid residues. In the first method, persulfate is replaced by one of several sulfonated azo-initiators, which are water-soluble and which decompose into two identical ion-radicals, at a rate similar to that of persulfate. These initiators can be used in combination with styrene-sulfonic acid, in recipes similar to those published by Juang and Krieger. The second method utilizes vinylbenzyl chloride as a monomer, and replaces surface chlorides by treatment with sodium sulfite. This method has the advantage that surface charge can be varied at constant particle size, depending upon the extent of sulfonation. The principle disadvantage is that the reactions must be conducted at lower temperatures, to avoid hydrolysis of the vinylbenzyl chloride. This necessitates the use of redox initiators and, if uniform particle size is desired, mixed ionic and non-ionic surfactants.

We are currently investigating some of the implications of our observations on the second electroviscous effect. In particular, the fact that this effect is virtually independent of the nature of the added electrolyte implies that most of the added counterions go into the Stern layer. We are starting to make measurements of conductance, pH, mobility, in order to see if this is true. Mobility measurements will be made by mass transfer, in

order to permit studies of concentrated dispersions. Some of you have mastered the problems of this technique, and we would appreciate your suggestions.

Computer programs have been written which should enable us to carry out some calculations of radial distribution functions in systems of interacting particles.

POLYMER COLLOIDS AT THE UNIVERSITY OF SYDNEY

REPORTER : D.H.NAPPER

13 SEP 1977

STERIC STABILIZATION IN WORSE THAN θ -SOLVENTS

The existence of a strong correlation between the point of incipient instability of many sterically stabilized dispersions and the θ -point for the stabilizing moieties is now well-established. Yet there unquestionably exist systems that are stable in dispersion media that are significantly worse solvents than θ -solvents. We first encountered this in stabilizing polystyrene latex particles, which contained a high surface density of carboxylic acid groups, using polyoxyethylene chains.

The primary requirement for stability in worse than θ -solvents, which we have termed 'enhanced steric stabilization', is for the stabilizing moieties to interact strongly with the interface. Consequently, the chains adopt a loopy type of conformation, in which the segment density decays exponentially as a function of the distance from the surface. This results in the segment density in the peripheral regions of the steric barrier being significantly reduced, compared with that for a tail, for example.

Flocculation near to the θ -point in sterically stabilized systems is a consequence of penetration into the worse than θ -solvent domain. We have shown theoretically that a penetration of less than, say, 1 K is all that is required to induce flocculation in systems stabilized by loops. However, for an exponential distribution we have found theoretically that an order of magnitude greater penetration is needed (say, 10-30 K) to compensate for the small segment densities. This is in line with the experimental observations. Non-aqueous dispersions are predicted to display much greater enhancement than aqueous dispersions because of the larger molar volumes of the dispersion media.

A second effect of loopy adsorption is the change in the thermodynamic parameters of the stabilizing chains, compared with the values in free solution. The 'folded' chains behave much more like Bragg-Williams chains than Flory-Huggins chains. Qualitatively, this will mean that the effective θ -point corresponds to greater than $\chi_1 = 1/2$ (appropriate for a Flory-Huggins chain) but less than $\chi_1 = 2$ (a Bragg-Williams molecule). Thus, changes in the thermodynamic parameters promote enhancement as well. To get at these effects quantitatively seems a formidable problem at present.

Polymer Colloids Newsletter Contribution

April 1977

T. R. Paxton

The BFGoodrich Company, Corporate Research

Research & Development Center, Brecksville, Ohio

Recent studies show that potassium laurate and myristate soaps have the same squatting area per adsorbed soap ion in PVC latexes. We also find about the same area for the laurate ion on polystyrene as on PVC.

We have made some additional measurements of soap adsorption in polymer latexes: potassium laurate on poly(vinyl chloride) (PVC), and on polystyrene (PS), and potassium myristate on PVC. The titration of latex with soap and the treatment of the resulting data was essentially the same as described in our previous report on emulsifier adsorption (1). The latex samples were all titrated at $\text{pH} = 10 \pm 0.5$. In the case of potassium myristate adsorption on PVC with no added salt, the results have been obtained from titration of sixteen different latexes, varying in particle size from 0.093 to 0.906 μm diameter. In the other cases, we titrated a single latex at several polymer concentrations.

Latex particle sizes were determined by electron microscopy. We measured about a thousand particles and found the size distribution to be fairly narrow - dw/dn between 1.02 and 1.08. Since PVC particles shrink in the electron beam, we have corrected electron micrograph diameters by multiplying them by the factor 1.25 (see Ref. 2). In our experience this correction is justified since we find the shrinkage to be fairly reproducible. In the case of large-particle latexes, we also checked particle sizes by the higher-order Tyndall spectrum method described by Maron (3).

The table shows the resulting adsorption parameters for each soap, polymer, and salt system. C_m is the free soap concentration at the titration end-point (CMC). A_m is the surface area available to the soap at this point, in $\text{\AA}^2/\text{molecule}$. The adsorption data were also fitted to a Langmuir isotherm,

$$\frac{\Gamma}{\Gamma_0} = \frac{A_0}{A} = \frac{KC}{1 + KC},$$

which leads to values for the limiting adsorption area, A_0 , and the adsorption equilibrium constant, K .

The values for A_0 are all about the same and are close to the value expected for a fatty acid film in the liquid condensed state.

Soap Adsorption Parameters

<u>Soap</u>	<u>Polymer</u>	<u>Salt</u> mmol/L	$\frac{C_m}{\text{mmol/L}}$	$\frac{A_m}{\text{\AA}^2}$	$\frac{A_0}{\text{\AA}^2}$	$\frac{K}{\text{L/mmol}}$
K Laurate	PVC	.027 KCl*	21	51	26.5	0.052
K Laurate	PS	.020 KCl*	22	51.5	25	.045
K Myristate	PVC	- †	6.8	52.9	24.4	.125
K Myristate	PVC	.017 K ₂ HPO ₄ †	4.1	47	25	.277
K Myristate	PVC	.057 K ₂ HPO ₄ †	2.0	40	25	.805

*Plus 3.7 m.e./L KOH and K₂S₂O₈.

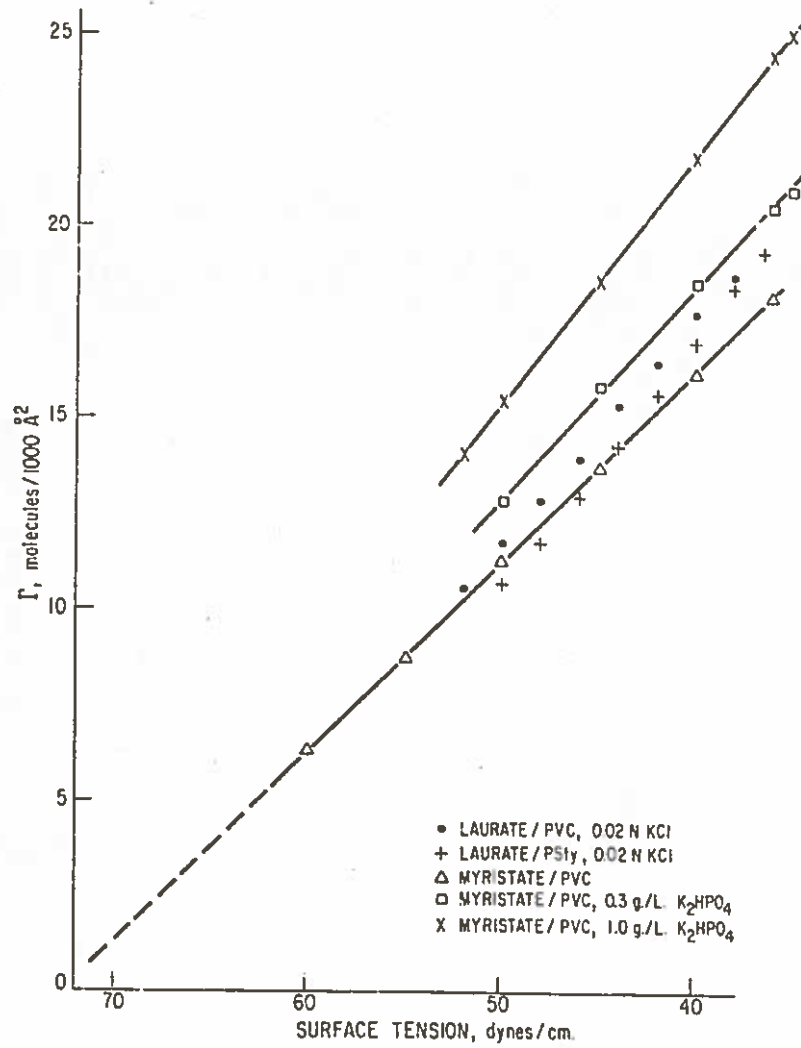
†Plus 3.5 m.e./L KOH and EDTA-Fe complex.

The adsorption equilibrium constants increase with electrolyte concentration and are higher for myristate than for laurate, as expected, corresponding to the variations in C_m . The values for A_m also decrease somewhat with increasing electrolyte concentration; we have noted this earlier (1). The values for A_m in PVC are approximately the same for laurate and myristate soaps. And the values of A_m for laurate soap on PVC and on PS are about the same. This last is surprising, since I would have expected A_m to be higher on PVC because of the polar nature of the polymer.

A useful empirical relationship is shown in the figure, where we have plotted $\Gamma = \frac{1000}{A}$ as a function of the latex surface tension at that degree of soap coverage. This is useful for the rapid estimation of relative soap coverage, provided there is only one surface-active agent present.

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STUDY OF NUCLEATION OF ACENAPHTHYLENE IN AQUEOUS
EMULSION: A PRECURSORY HOMOGENEOUS APPROACH

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Introduction

In emulsion polymerization the nucleation phenomenon is a combined chemical and physical process which yields a vast number of oligomeric or polymeric particles. These particles provide sites for further polymerization. Nucleation of polymer particles has, therefore, received considerable attention from numerous investigators. Basically two schools of thought have been advanced. Harkins¹ is credited with the micellar nucleation theory, and Roe,² Fitch et al.³⁻⁵ consider the true aqueous phase to be the nucleation site. Experimental evidence for both theories have been published.¹⁻⁷ Peppard⁸ has proposed that both micellar and aqueous phase nucleation mechanism coexist in emulsion polymerization systems.

In order to understand the mechanism of nucleation, it is imperative to study the emulsion polymerization reaction in its very early stages. In this investigation the oligomerization kinetics of acenaphthylene in aqueous phase was studied in the absence and presence of an emulsifier. Presumably the homogeneous system offers simplicity and the kinetics can be followed with relative ease.

Experimental

Materials: Acenaphthylene (AcN)-Technical grade, purified by sublimation under vacuum and recrystallization from pentane. Purity = 98.6%. M. P. 88-90°C. Sodium Oleate-Purified oleic acid (U. S. P. grade) was neutralized by sodium hydroxide in methanol. The solvent was removed under low pressure at 50°C, and the emulsifier was stored at 5°C before use. Water-Doubly distilled, boiled and cooled to room temperature by nitrogen purging. Potassium Persulfate and Sodium Lauryl Sulfate-Commercial, reagent grade, used as received.

Procedures: A. Preparation of Aqueous Acenaphthylene Stock Solution-About 3 g. of acenaphthylene crystals were mixed with one liter of water. The mixture was shaken manually, then let stand in a thermostated water bath at 50°C for 12 hours. The excess AcN crystals were removed by filtration. 0.3055 g. of K₂S₂O₈ were added to the filtered aqueous AcN solution to make a stock solution. B. Oligomerization of Acenaphthylene-For each kinetic experiment, 100 g. of the stock solution were charged into an 8 ounce narrow-mouthed glass bottle with perforated metal screw cap lined with self-sealing butyl rubber gaskets. At this point a desired amount of emulsifier was added, if used. The bottle was capped and purged with nitrogen before it was clamped on the rotating (40 rpm) shaft in a water

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bath at 50°C. At specific intervals, samples were withdrawn from the bottle with a hypodermic syringe. The lost volume was made up by nitrogen gas. The withdrawn solution was discharged into an ice-cooled bottle. After the sampled solution reached room temperature (20°C), an aliquot of the sample was diluted with methanol for ultraviolet visible spectroscopic analysis.

C. Determination of Acenaphthylene Concentration in Solution-
A Perkin-Elmer 450 UV-VIS-NIR Spectrophotometer was used for the quantitative measurement. A calibration curve of known AcN concentration in methanol was established for all the quantitative work.

Results and Discussion

1. Aqueous Phase Initiation and Oligomerization of AcN-The solubility of the AcN in water was established to be 5.05×10^{-5} M at 25°C.⁹ In the present study a saturated solution of monomer at 50°C was used, which would have an AcN concentration slightly higher than the above mentioned value. The oligomerization of AcN initiated by thermally decomposed $K_2S_2O_8$ in aqueous phase was determined by monitoring the absorption maximum of AcN at 319 m μ . Figure 1 shows the disappearance of the AcN monomer and the appearance of the oligomeric AcN on this uv spectra as a function of time. The absorption maxima for the oligomeric AcN can be found at 283 m μ and 274 m μ . The conversion vs. time plot in Figure 2 shows nonlinearity; the corresponding data can be found listed in Table I.

A second-order plot in Figure 3 shows a linear relationship indicating that the monomer plays an important role in the initiation stage. The formation of the secondary radical $-SO_4^-AcN\cdot$ could be considered to be the rate determining step. The initiator concentration in this system was not minute, i.e. in catalytic amount, but in excess instead. This excess initiator concentration enables us to treat the kinetics in a normal second-order fashion. A similar study with styrene monomer was carried out by Bovey and Kolthoff.¹⁰ The $K_2S_2O_8$ concentration was also in excess of the styrene concentration, and they found a square-root dependence of the rate on persulfate. The half-order dependence in a homogeneous free radical polymerization implies that the oligomeric radicals terminate by coupling.¹⁰ If one assumes coupling termination in the AcN homogeneous oligomerization, the following expression applies

$$d[AcN]/dt = -K[AcN]^2 [K_2S_2O_8]^{1/2}$$

2. Effect of Emulsifier on Rate of Oligomerization-The effect of the sodium dodecyl sulfate and the sodium oleate emulsifiers on the rate of oligomerization can be seen in Figures 3 and 4. These second-order rate curves show clearly that the presence of emulsifier micelles has decreased the reaction rate. Assuming no change in the decomposition rate of persulfate, this decrease in the rate of monomer conversion can be rationalized as being due to a combination of the following reasons: a) In the presence of emulsifier micelles, the AcN monomer most probably distributes between the aqueous phase and the micellar phase thus reducing the chance of being initiated in the aqueous phase to form $-SO_4^-AcN\cdot$; b) Initiation inside the micelles is less likely due to the electrostatic repulsion between the

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polar heads of the anionic emulsifier molecules and the $\text{SO}_4^{\cdot-}$ or $^-\text{SO}_4\text{-AcN}$ i.e. the primary or secondary radical ions; c) The micellarly solubilized monomer can become available only through its diffusion out of the micelles or the oligomeric radical penetration into the micelles.

Reactions carried out in the presence of excess acenaphthylene crystals show that the concentration of the oligomer keeps increasing (Figure 5), while the monomer concentration in the aqueous phase remains constant.

Conclusion

The homogeneous oligomerization of acenaphthylene with the potassium persulfate as the primary free radical generator in the pure aqueous phase is a second-order kinetic process. The formation of the secondary free radicals ($^-\text{SO}_4\text{-AcN}$) is proposed to be a rate-determining step. Anionic emulsifiers in micellar concentrations such as sodium dodecyl sulfate and sodium oleate were found to slow down the oligomerization rate. This is attributed to the reduced aqueous phase initiation and the solubilization of the acenaphthylene monomer inside the emulsifier micelles.

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TABLE I

Kinetic Data of Oligomerization of Acenaphthylene in Aqueous Phase

Time (min.)	[AcN] ($\times 10^5$ mol/l.)	[AcN] ₀ - [AcN] ($\times 10^5$ mol/l.)	Conv. (%)	$\frac{[\text{AcN}]_0 - [\text{AcN}]}{[\text{AcN}]_0[\text{AcN}]}$ ($\times 10^{-2}$ l./mol)
0	4.96	0	0	0
5	4.84	0.12	2.4	4.50
15	4.44	0.52	10.5	23.6
25	4.02	0.94	19.0	47.1
40	3.74	1.22	24.6	65.8
60	3.28	1.68	33.9	103.
80	2.96	2.00	40.3	136.
100	2.70	2.26	45.6	168.
110	2.64	2.32	46.8	177.

$[\text{K}_2\text{S}_2\text{O}_8] = 1.130 \times 10^{-3}$ mol/l. Temp. = 50°C.

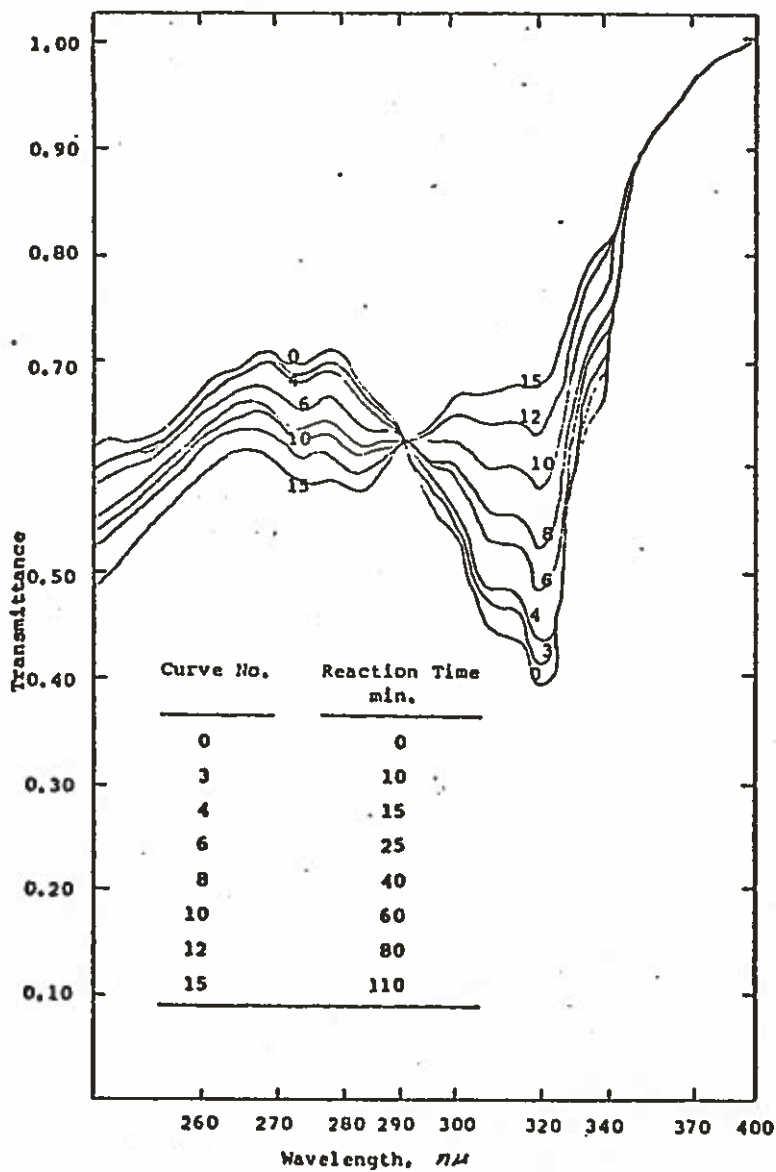
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TABLE II

Second-order Kinetic Data of Oligomerization of Acenaphthylene at 50°C

Emulsifier Conc. ($\times 10^2$ mol/l.)	$K_2S_2O_8$ Conc. ($\times 10^3$ mol/l.)	$[AcN]_0$	Second-order Rate Constant k_p , ($l. mol^{-1} min^{-1}$)	Second-order Rate ($mol l.^{-1} sec^{-1}$)
0	1.13	4.96×10^{-3}	5.23×10^3	7.2×10^{-9}
0.516 (S.L.S.)	1.13	5.22×10^{-3}	2.23×10^3	3.4×10^{-9}
10.4 (S.L.S.)	1.13	4.94×10^{-3}	1.16×10^3	1.6×10^{-9}
7.28 (Na-oleate)	1.06	5.67×10^{-3}	2.23×10^2	3.9×10^{-6}
29.1 (Na-oleate)	1.05	2.04×10^{-2}	15.4	3.5×10^{-6}

Figure 1. UV Spectra of Acenaphthylene as a Function of Reaction Time.



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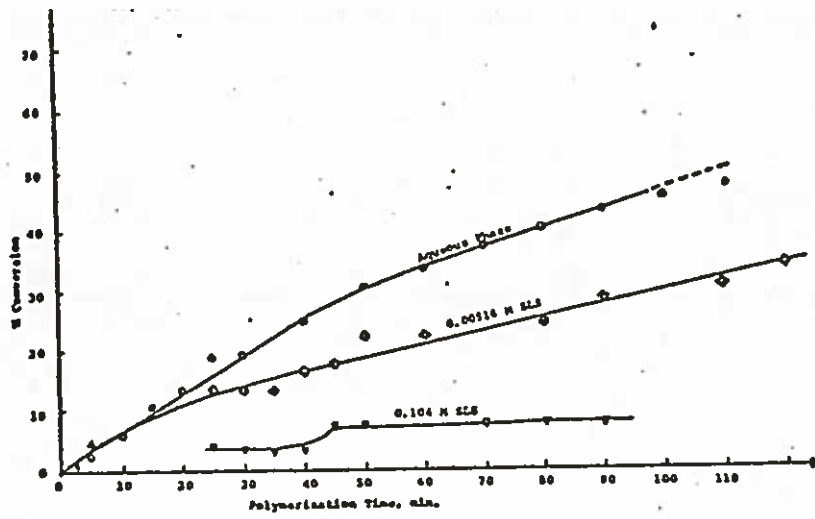


Figure 3 Second-Order Kinetic Curve of Acenaphthylene Oligomerization.

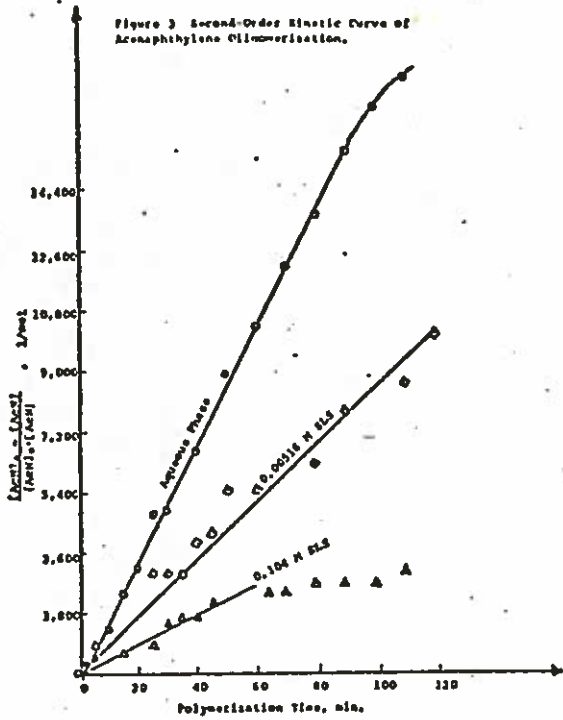


Figure 4 Effect of Na-Oxalate Multiplier on Second-Order Rate of Oligomerization of Acenaphthylene.

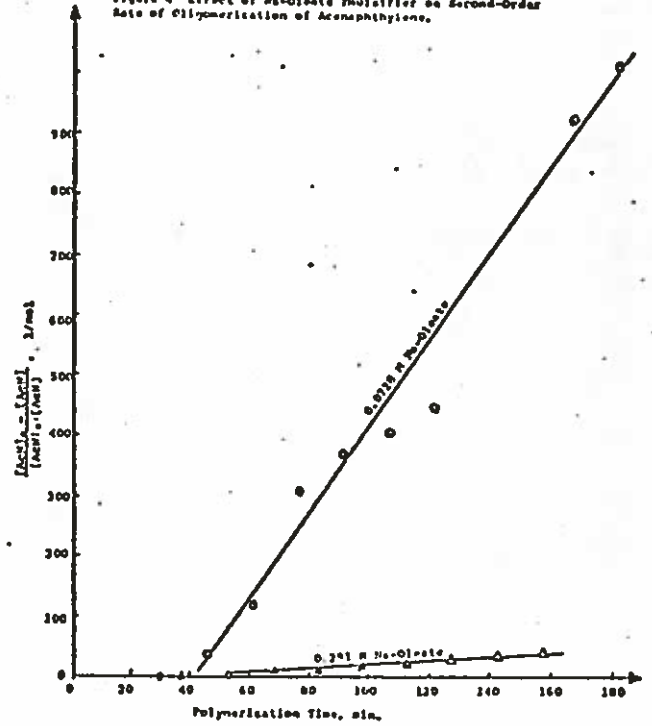
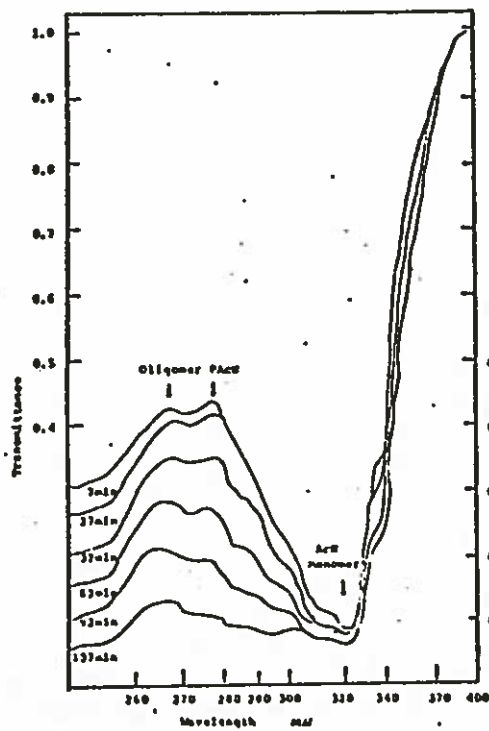


Figure 5 Aqueous Polymerization with Excess Acenaphthylene Crystals.



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The Effect of Angular Resolution on the Determination of Particle Size Distribution of Polymer Latexes by Light Scattering

20 SEP 1977

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The early history of the measurement of absolute angular intensities for Mie scatterers has been reviewed by Kratochvil and Smart (1) who explored the use of polarized incident radiation and the effect of solid angle subtended by the receiver aperture. They concluded that a planar angular spread of $\pm 1^\circ$ did not influence the results significantly. The angular spread was computed from the dimensions of an aperture inserted immediately in front of the photomultiplier in its housing.

Extension of the measurement of absolute angular intensities to polydisperse systems of Mie scatterers was carried out by Rowell, Wallace and Kratochvil (2) who also neglected the effect of receiver aperture.

In recent work on the depolarization of water by Farinato and Rowell (3) it was shown that acceptance angle of the receiver was very important. Accordingly, we decided to reinvestigate the effect of acceptance angle for Mie scatterers.

Typically, the simplest collimating system employs two slits separated by a distance d . In such a case it is not sufficient to characterize the angular resolution by a single constant. An improved characterization of photometer geometry involves acceptance angles ϕ and ψ and a simple slit function that has been given elsewhere (3).

The effect of finite acceptance angle is to integrate over the source functions used in the light scattering. Experimentally, acceptance angle integration gives the same kind of result as a finite polydispersity i.e. erosion of the maxima and filling-in of the minima.

In the present work we investigate the effect of acceptance angle and express the results in terms of an apparent polydispersity. It is shown that for small acceptance angles, the slit-width integration amounts to $2.14 \times 10^{-3} \sigma_0/\text{deg}$ where σ_0 is the zeroth-order log normal standard deviation and deg refers to the angle ψ as described elsewhere (3). The reported coefficient applies to α_M of 10 and a relative refractive index m of 1.2. In this domain, a 2° angular spread would give a σ_0 of 0.005 which is a large part of the apparent polydispersity of the latex.

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Polymer Colloids at the Department of Physical Chemistry
at Åbo Akademi, Åbo Finland

The research work has been centered on studies of EP without emulsifier.

(i) Basic studies of the mechanism of EP in water/methanol mixtures (Mr Juhani Laaksonen). The investigation of styrene polymerisation started by me at PPRIC following Robertson's and Homola's work on polymerisation in water/methanol mixtures has been continued in Åbo by detailed studies of the reaction kinetics in homogeneous solution before and after particle formation. It is evident that methanol interferes with the polymerisation as long as it takes place in solution, the order of reaction with respect to methanol being $\sim -3/2$. The increase in the rate of polymerisation with increasing concentration of methanol after particle formation correlates well with the increase in solubility of styrene when the methanol content is increased, at least up to 60% methanol. Analysis of the nature of the surface groups as a function of the methanol content is in progress. Preprints of a paper on this work will be available around Christmas.

(ii) EP of vinyl chloride (Mr J. Laaksonen). VC was polymerised without emulsifier in a glass autoclave using KPS as initiator and KCl to adjust the ionic strength (I). The following equation for the diameter was obtained from a simple 8-experiment factorial plan:

$$\frac{D}{nm} = 1679 + 2\left(\frac{[VC]}{W/W\%}\right) - 15\left(\frac{[KPS]}{mM}\right) - 8\left(\frac{I}{mM}\right) - 3\left(\frac{T}{K}\right)$$

The range investigated was $[VC] = 12-18\%$, $[KPS] = 5.5-8.5 \text{ mM}$
 $I = 25.5-30.5 \text{ mM}$, $T = 62-68^\circ\text{C}$.

In all cases, stable latexes were obtained with a standard deviation in D of $\sim 1.5\%$ and the reproducibility well within this standard deviation. Later investigations have shown that

if I is varied over a wider range (16.5-31.5 mM), D increases linearly with I. CaCl_2 gives much larger D values than the equivalent KCl concentration. It is also possible to polymerize VC in MeOH- H_2O mixtures without emulsifier; stable monodisperse latexes are formed. Research on polymerisation of VC in these mixtures is being continued.

(iii) EP of styrene-butadiene (Mr K. Nurmi). A 40-experiment factorial plan has been used to investigate the copolymerisation of styrene (S), butadiene (B), and acrylic acid (AA) in methanol/water mixtures with KPS as initiator as a function of the S/B ratio, MeOH concentration, T, I, $[\text{KPS}]$, $[\text{NaOH}]$, total monomer concentration ($[\text{M}]$), concentration of acrylic acid ($[\text{AA}]$) and reaction time t. The particle size and number, the conversion, the final pH and the remaining monomer concentration after the reaction had stopped were measured. The results are still being analysed but it is clear that in this case the latexes are not monodisperse. Increasing $[\text{AA}]$ increases the reaction velocity.

I am moving to Stockholm to become director of the Swedish Institute for Surface Chemistry. The research work on polymer colloids in Åbo will be continued, however, in close collaboration with the Swedish Institute.

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The good agreement between the theoretical values of $x_{\text{theor.}}$ and experimental results (see Table) indicates the validity of equation in the real case when $S_r/S_e < 1$.

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