- 5 JUN

Our newsletter is extra fat this month. As promised, Fitch has produced a whopper, and it looks like good reading. Bob says there is more to follow!

Napper has submitted a short abstract of his interests, but he will amplify on these with substantial contributions in the next few issues.

Vanderhoff has contributed titles of interest from recent Chem. Abstracts, plus abstracts from his latest two papers with Bradford. Full-length versions of the latter may be obtained by writing to John.

Stannett has failed to respond to calls for a contribution. I will ask him to distribute his before mid-June.

Our Micro-Symposium is to begin Friday, June 16 at 9:00 am in John Vanderhoff's office. I expect it will run until Saturday afternoon. A tentative program is attached. The social highlight of the meeting will be a group dinner (banquet?) Friday evening. Vanderhoff and/or Poehlein will make the arrangements. Remember to bring your graduate students plus others who might be interested and who are prepared to contribute.

I look forward to seeing you on the 16th.

May 1972

Polymer Colloid Group

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Polymer Colloid Group

Schedule for

Micro-Symposium

June 16-17, 1972

Lehigh University

(a)   Formation of Polymer Colloids

   D.J. Williams, chairman

This session will stress the fundamentals of particle growth and nucleation.

   (1) Nucleation - R. Fitch

   (2) Particle Growth - D. Williams

   (3) Continuous Reactors - G. Poehlein

   (4) Vinyl Chloride Pen - Ugelstad

(b)   Characterization of Polymer Latices

   R.H. Ottewill, chairman

   (1) R.H. Ottewill.   Introduction

   (2) J.W. Goodwin (University of Bristol).   Results obtained in the characterization of latices formed by emulsifier free polymerization, including molecular weight distributions, conductometric determinations, potentiometric determinations, dye methods of estimating end groups, etc.

   (3) E.L. Zichy (I.C.I. Limited).   Characterization of P.V.C. latices.

   (4) Possibly Dr. D.R. Bassett (Union Carbide), but this has not yet been confirmed.

(c)   Colloid Properties

   I.M. Krieger, chairman

   (1) Rheological Properties - I.M. Krieger

   (2) Light Scattering - T.P. Wallace

   (3) Ordered Dispersions - I.M. Krieger

   (4) Other Properties*

*Since many of the "other properties" are used in characterizing polymer colloids, the scope and duration of this section will depend on what is covered in Professor Ottewill's session (b).

(d)   Applications of Polymer Colloids

   John Vanderhoff, chairman

Polymer Colloid Group Newsletter - May 1972

A. S. Dunn
(UMIST, Manchester, England)

A last-minute change in my teaching duties left me with much less time for paper writing during the Lent Term than I had expected so that there has been little progress in preparing the papers foreshadowed in the February Newsletter.

Success continues to elude our attempts to prepare azo-sulphonate initiators although more sodium sulphate has been successfully isolated! The work to check the supposed stereoregulating properties of interfacial redox initiating/emulsifying systems has yielded a more positive result - it appears that there is no such effect!

Medvedev's Plenary Lecture on 'Some Problems of Emulsion Polymerisation' which was given (in Russian) to the 1969 IUPAC Symposium on Macromolecular Chemistry on 'Kinetics and Mechanism of Polyreactions' in Budapest has recently been published in English. The reference is 'Kinetics and Mechanism of Polyreactions - IUPAC International Symposium on Macromolecular Chemistry - Plenary and Main Lectures', Akademiai Kiado, Budapest (1971) pp 39 - 63. This provides a new kinetic treatment for his theory of emulsion polymerisation concentrating on the case of oil-soluble initiators and introducing the Langmuir adsorption isotherm to account for the supposed adsorption of the initiator at the surface of the latex particles similar to the treatment given by L.G.Melkonyan (Arm. Khim. Zh. $\underline{21}$ (1968) 187) although no reference is made to this work. Incidently an English Translation of this paper is now available from the National Lending Library, Boston Spa, Yorkshire LS23 7BQ as RTS 5498 at £1.63. Medvedev repeats the table taken from Chernikhov and Medvedev (Doklady Phys. Chem. $\underline{182}$ (1968) 1369 (Russian) or 795 (English)) which is printed as Table III in my lecture 'The role of the emulsifier in emulsion polymerisation', but adds 'the existence of a chemical bond between the active centre and the emulsifier chain represents an additional condition for the realization of the stereospecific polymerization'. Although I am not yet very clear as to what this means, I don't think it affects our conclusion that there is no effect.

Very little attention has been given to the effect of the nature of the emulsifier in emulsion polymerisation. The only extensive study is that of Hopff & Falka (Makromol. Chem. $\underline{88}$ (1965) 54: results reprinted Br. Polym. J. $\underline{2}$ (1970) 40) in which the effect of 85 different pure and technical emulsifiers on the rate and molecular weight obtained in the emulsion polymerisation of vinyl chloride was studied at a constant emulsifier concentration of 8 g dm^{-3}. Unfortunately because the molecular weights of the emulsifiers vary by a factor of 3 or more, the molar concentration of emulsifier is by no means constant. Within a given series of emulsifiers (carboxylates, sulphates, sulphonates etc.) rates of polymerisation went through a maximum within the range of alkyl chain lengths investigated $C_{10} - C_{18}$. There were variations in rate between series by a factor of at least 5 although there is some doubt about the possible effect traces of metallic ion impurities may have had on the persulphate/bisulphite initiator used in some cases. No determinations were made of the number of latex particles formed and the adsorption isotherms of the emulsifiers on the polymer have not been determined. It appears that it might be useful to extend investigations of this type to other emulsion polymerisation systems since most investigators have confined themselves to the use of one or two emulsifiers only particularly if a study of the properties of the latices produced were included in the investigation.

POLYMER COLLOID GROUP

Progress report by R. M. Fitch

Yashavanth Kamath has recently completed experimental work towards a Ph.D. and is now writing up. He has been concerned with organic latex polymerization, kinetics and particle formation. The system used throughout has been MMA in n-heptane at 30°C. Various aspects of this work are described below, along with a very brief summary of experimental results. We are still actively discussing interpretation of many of the results and would welcome your comments.

Dilatometer

A continuously recording dilatometer was designed and built in which a Pt wire extends the length of the capillary which is filled with Hg. As the volume contracts more wire is exposed, the length of which is measured by its electrical resistance. This principle was earlier used by Hummel, Ley and Schneider. The Hg column is in direct contact with the reaction mixture and, by turning a stopcock, with a leveling bulb. This allows us to remove samples (hypodermically) periodically and to refill the capillary. We thus have the unique advantage of continuously recording the rate, whilst taking samples from the same reaction mixture. The dilatometer is so designed that various reagents may be added sequentially and outgassed directly on the vacuum line by freezing and thawing.

DSC

Differential Scanning Calorimetry is a marvelous technique for obtaining kinetic data rapidly. Obviously one can't take

6/

samples or make other observations during a run. It is now possible to hermetically seal the sample pans under inert gas, after oxygen removal. The seals will withstand several atm pressure.

Particle-size Determination

We have used electron microscopy almost exclusively: carbon supports and Pt-C shadowing. This gives us the lowest noise background without causing decomposition of the polymer. Quantitative measurement of particle sizes below ca. 7 nm are almost impossible because of the low density of the polymer. We are currently looking for good staining procedure for PMMA.

Note: We have embarked upon using exclusion chromatography for measuring particle size distributions, with some encouragement from Hamish Small at Dow. We've obtained some peaks on a DuPont liquid chromatograph. Nothing quantitative yet. This has been in aqueous systems solely, to date.

Stabilizer Systems

Three different polymeric stabilizers have been used:

1. Melamine-formaldehyde/alkyd: superb for HO-containing polymers polymerized at elevated temperatures; no good at 30°C.

2. Laurly methacrylate/MMA "feather"-type graft copolymer à la Osmond at ICI: extremely inefficient and possessing very broad molecular weight and compositional distribution. We found that as much as 90% of this "stabilizer" composition was not adsorbed onto the polymer/heptane interface.

3. Poly (hydroxystearic acid)/PMMA "comb"-type graft copolymer à la Osmond: forms very stable colloids at 30° with very high efficiency of adsorption. Probably some grafting to the polymer latex particles also takes place.

Solutions of these stabilizers were not perfectly clear
in heptane, i.e. we saw a Tyndall effect when an intense light
beam was used. Therefore we cannot be absolutely sure that
homogeneous nucleation of polymer particles occurs (vide infra).

As prepared, the stabilizers (2. + 3. above) had no trace
of contaminants which would affect the rate of MMA polymeriza-
tion. This was checked by solution polymerization with and
without stabilizer present.

Initiator Systems

Because we worked at 30°, it was convenient to use redox
systems, rather than thermally unstable compounds, even though
the latter have simpler kinetics. Two systems were used:

1. Cumene hydroperoxide/dodecyl mercaptan: The kinetics
of this system are extremely sensitive to traces of O_2; thorough
degassing is mandatory. We have found that the rate of effective
radical formation in MMA polymerization at 30°C is:

$$R_i = 5.2 \times 10^{-5} [CHP]^{0.70} [DDM]^{0.28} \text{ m}\ell^{-1} \text{ sec}^{-1}.$$

2. Benzoyl peroxide/dimethyl aniline: We have applied
the results of Tobolsky and Metzner, taken in styrene at 30°,
to our system

$$R_i = K[BP]^{0.80} [DMA]^{0.80} \text{ m}\ell^{-1} \text{ sec}^{-1}.$$
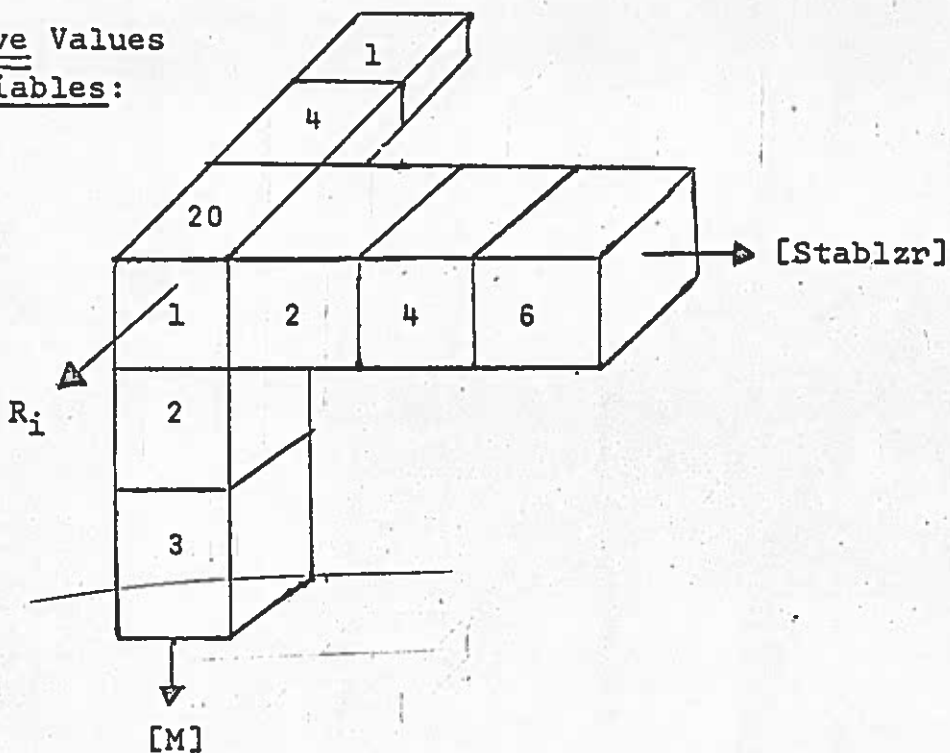
Experimental

A series of experiments were made in which the effects of
three variables were explored, rate of initiation (R_i), concentration
of (comb-type) stabilizer and monomer concentration.

Experiment Numbers
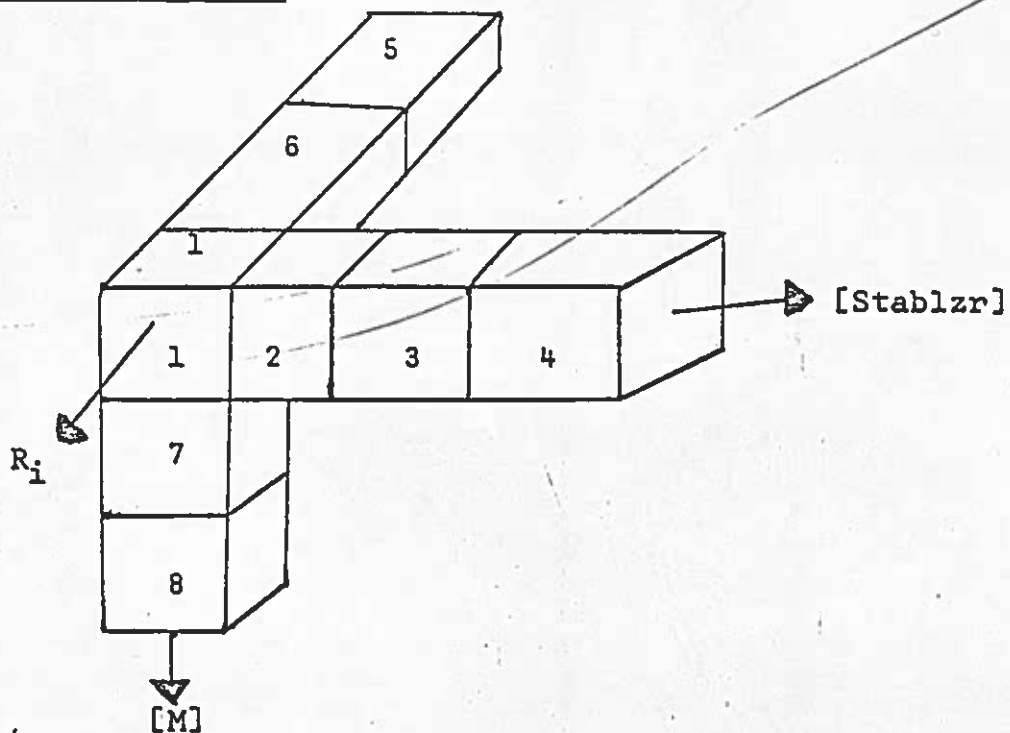
Relative Values
of Variables:

For experiment number 1 the actual values were:
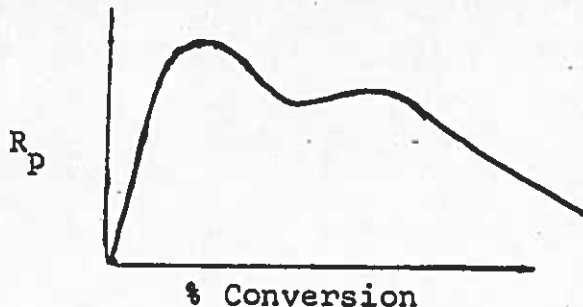
$$R_i = 1.07 \times 10^{14} \text{ molecules/l./sec.}$$

$$[M]_o = 0.915 \text{ molar}$$

$$[Stablzr] = 9.52 \text{ g/l.}$$

Rate of Polymerization

The rate behavior was in many ways very similar to analogous systems in aqueous media. A typical plot would look like this:


The dip in the curve is very real, and corresponds to the conversion at which the maximum rate of flocculation is observed. This flocculation is evidenced by a very rapid decrease in the average number of particles and the appearance of multiplets in the electron micrographs. A typical plot looks like this (where N is particle concentration):
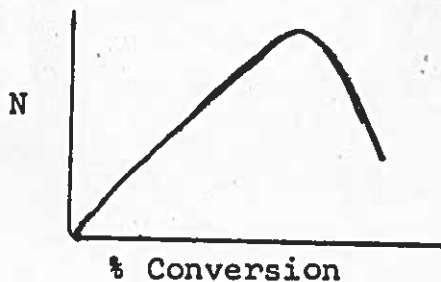
The conversion at which the dip in the rate curve appears is a function of the stabilizer concentration:

Exp. No.	[Stablzr]	% Conv. at dip	% Conversion for rapid flocc'n
1	9.5 g/ℓ	8	7
2	19.0	16	13
3	39.4	30	19
4	57.1	not detected	—

The dip in the rate curve is very reminiscent of results an earlier student of mine, T. J. Chen, obtained for MMA aqueous latex polymerization under conditions leading to limited floccu-lation (not yet published). Except for this dip, the rate of polymerization (overall) appears to be blithely independent of the particle concentration:

————Exp. #4
— — — -Exp. #2
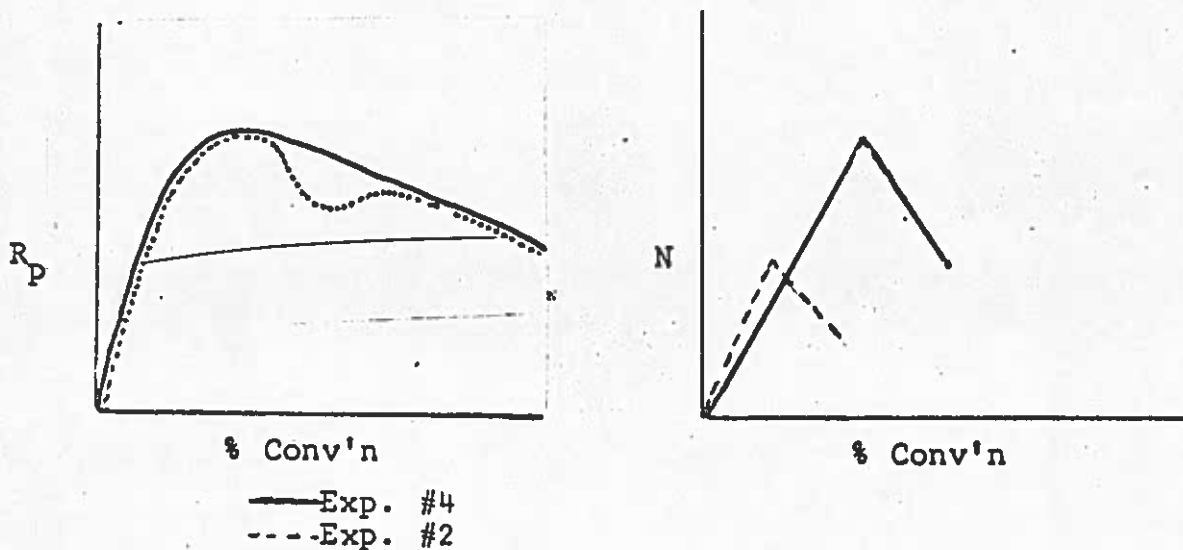
Chen also found the rate to be independent of the final value of N. Apparently the pseudo steady state is upset by rapid flocculation, but only temporarily. The rate returns to the value it would have had in the absence of flocculation. (We can go on measuring rates far beyond the time that flocculation makes it impossible to get good particle size data).

We believe that under these experimental conditions, we are seeing modified Smith-Ewart Case III type behavior. We should be well into the gel effect right from the start. There is even evidence that propagation is diffusion controlled from the very beginning. For instance, the overall rate is nicely

proportional to the radius of the particles, at the two higher values of R_i. The diffusion coefficient of monomer into the glassy particles at 30° is on the order of 10^{-11} cm^2 sec^{-1}, according to our calculations. This means that monomer polymerizes faster within the particle than it can be replenished and polymerization then only occurs in a surface zone at these monomer concentrations. Nevertheless, the number of radicals per particle is probably relatively large (Case III), so that mutual termination governs the steady state radical concentration. Chain transfer with subsequent exodiffusion and re-entry of small radicals must also be taken into account (see Hummel, Ley and Schneider). John Ugelstad has just developed the equations (modified from Stockmayer's method) to account for this last effect.

Particle Concentration Changes

We believe that particle formation occurs by way of homogeneous self-nucleation of growing oligomeric radicals in solution in these organosols, in a manner exactly analogous to that we have proposed for aqueous systems. The kinetics of particle formation are then controlled by three competing rate processes: the generation of new radicals, R_i, the capture of radicals still in solution by already formed polymer particles, R_c; and flocculation, R_f:

$$\frac{dN}{dt} = R_i - R_c - R_f.$$

Such a system is apparently capable of oscillation, such that N rises and falls. In our systems, aqueous and organic, this

this occurs with pronounced "damping":

N

t
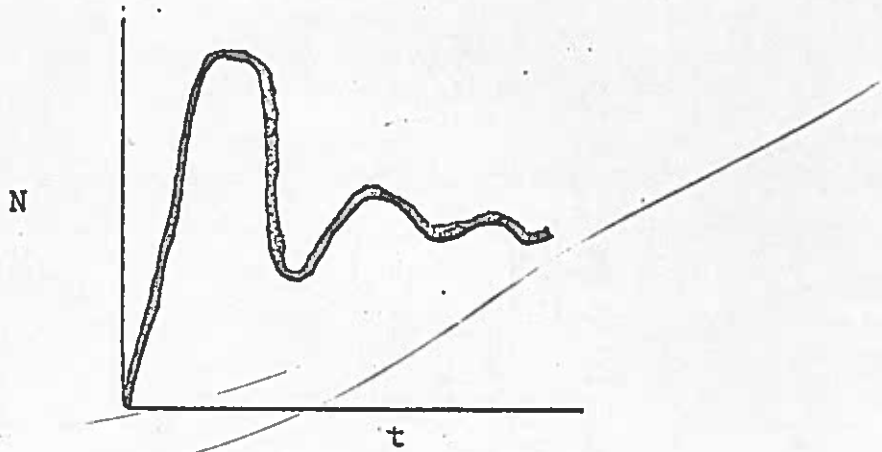
A recent conversation with John Bdzil at SUNY, Albany confirms that this is theoretically possible. Bob Rowell at UMass has observed the same effect in following the kinetics of particle formation of LaMer sulfur sols by light scattering.

This effect is further illustrated by the particle size distributions taken at various times during a single run. The example given on the following page is from Exp. No. 8. A second and third generation of small particles appear at approximately one and two hours, respectively. (Note change in abscissa scale).
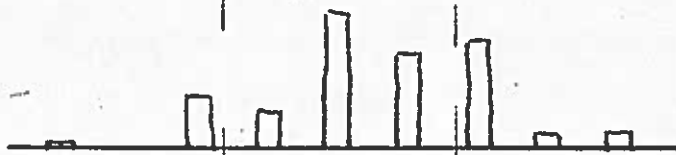
DSC Results

The principal advantage of this technique is that it gives rate as direct output. A typical dispersion run is shown below in which initial monomer concentration was 5.0 M and "comb" stabilizer was present in the amount of 25.5 g/ℓ.
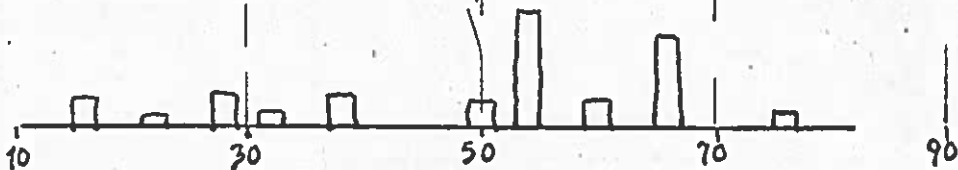
$\dfrac{dH}{dt}$

t
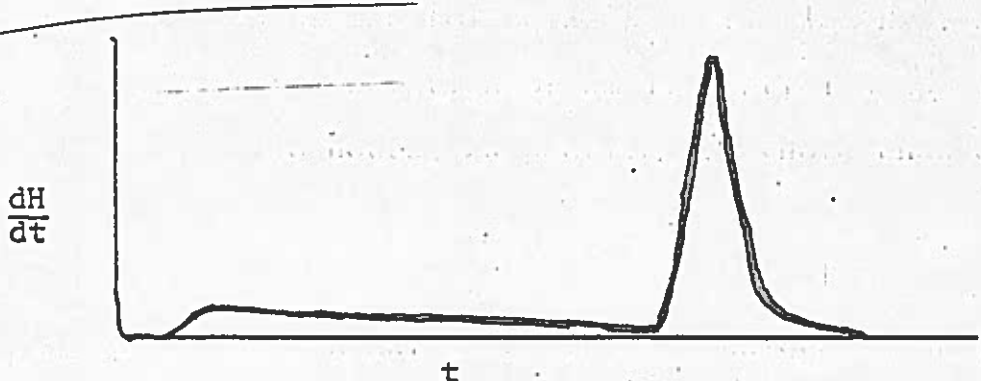
Reaction
time

4.0 hr

3.0 hr

2.0 hr

1.5 hr

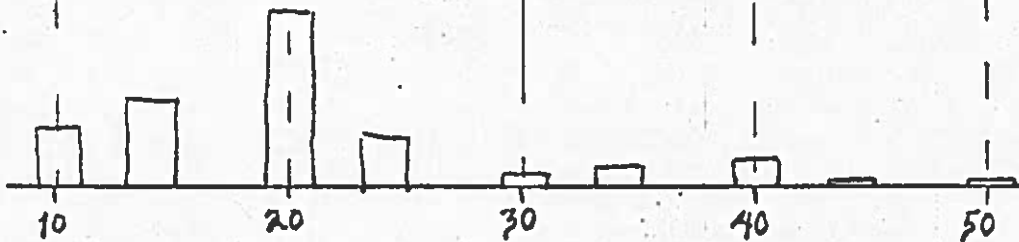1.0 hr

0.6hr

0.5 hr.

Diameter , nm

There is the initial, rather slow reaction, very slowly decreasing in rate with time, the very pronounced gel effect, rapidly dropping off at the end. Most of the area under the curve appears under the second peak. Detailed interpretation is currently being worked out. We do not believe that the interpretation of Barrett & Thomas may be applied here because of the probability of a monomer concentration gradient within the particles.

———————————— x ——————— x ————————— x ————————— x ——

Be sure to obtain your copy of the next quarterly Newsletter of the International Polymer Colloid Group to read the exciting sequel to our adventures in the mysterious world of polymer organosols!
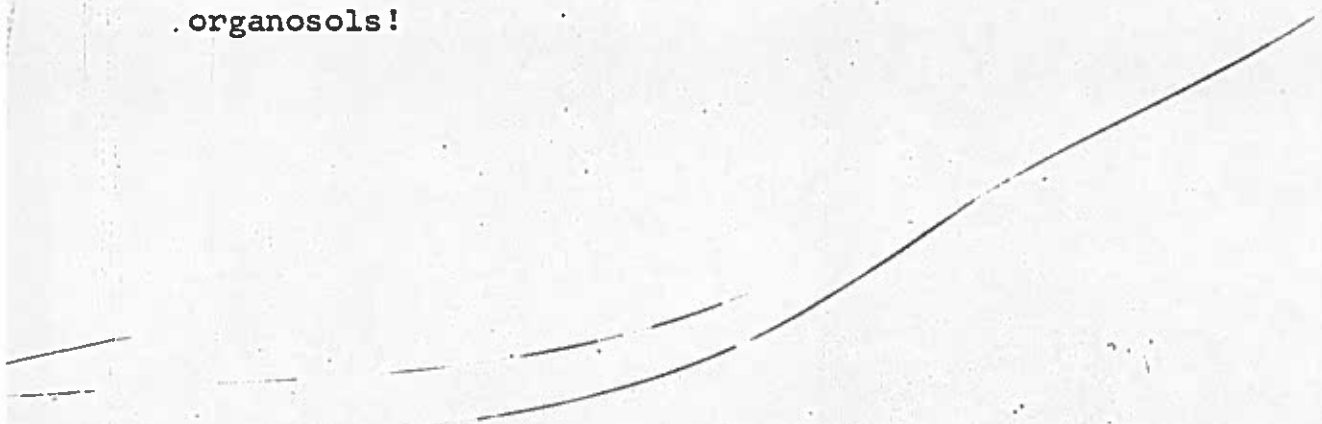
Continuing progress reports on current projects:

Emulsion Polymerization Studies (M. Juang)

Attempts to increase bound surface charge on polystryene latex by
incorporating a vinyl sulfo-ester comonomer appear to be successful.
Small amounts of sulfo-ester can replace ionic surfactant in our standard
recipe (J. Paint Tech. 40, 541 (1968)), without change in particle diameter
or in monodispersity. With heavier comonomer charges, smaller particle
size results unless the nonionic surfactant concentration is augmented.
Charge densities up to 13 charges per 1000 A^2 have been achieved; considering
the immobility of chemically bound surface groups, this is close to full
monolayer coverage. Dialysis removes up to 7% of the charge, probably indi-
cating that this portion was adsorbed, while the other 93% is chemically
bound. Seeding operations using the sulfo-ester latex as seed have yielded
monodisperse latexes of larger diameter. An occasional anomaly has been
observed in latexes of the same size and concentration having different
surface charges. In some instances the latex of higher charge shows a lower
viscosity, even after deionization. This may be due to presence of residual
electrolyte. We plan radio-tracer studies of the effectiveness of our
deionization procedure.

Electroviscous Effect (M. Eguiluz)

Despite their adequacy for ordinary non-Newtonian fluids such as aqueous
carboxymethylcellulose solutions, our Ferranti-Shirley rotational rheometer
and our falling-head capillary viscometer have not given consistent measure-
ments on concentrated deionized latexes. Apparently these latter fluids show
a yield point at stresses around 100 dyne-cm^{-2}, and a high-shear limiting
viscosity which is as low as that of an uncharged dispersion. The available
stresses and strain rates on the Ferranti-Shirley viscometer are not low
enough to characterize this behavior. Preliminary measurements using the
Weissenberg Rheogoniometer in parallel disk mode have given encouraging
results; we will use this instrument in preference to the Ferranti-Shirley.
In filling the capillary instrument, the liquid entraps bubbles, which are
difficult to remove because of the apparent gelation of the latex when at
rest. A filling technique has been worked out which avoids bubble entrap-
ment, so that this instrument may provide usable data.

Order-Disorder Transition (S. Gottschalk)

This project, stalled pending delivery of new quartz optical cells,
has been further delayed while Mr. Gottschalk, an undergraduate Physics major,
completes his final exams and gets married. He will work full time this
summer, when we expect to complete measurements defining the heat of transition
and to inaugurate further studies. Mr. Niu, in preparing a concentrated
redispersion of cross-linked polystyrene in m-cresol, has encountered a

rheo-optical phenomenon which we have been anticipating. The iridescence of the sample is momentarily lost when the containing flask is rotated from rest, reappearing in a small fraction of a second. Studies of iridescence vs. shear rate should cast light (in both senses) on the kinetics of the transition.

Time-Dependent Rheology (T.-F. Niu)

As mentioned in the preceding paragraph, Mr. Niu has prepared a re-dispersion of cross-linked polystyrene in m-cresol, by a sequence of steps: (1) dialysis of the deionized aqueous latex against methanol; (2) addition of m-cresol; (3) evaporation of the methanol in a rotary evaporator; and (4) further evaporation of m-cresol at higher temperature (105°C) and reduced pressure. The resultant redispersion at ca. 40% solids is iridescent and very viscous, and shows the new rheo-optical effect described above.

The computer-rheometer coupling described in the previous report has been completed, and extensive calibration runs have been made with Newtonian oils in oscillatory shear. Both strain rate and stress show negligible harmonic content; the amplitude ratios and phase angles agree well with those predicted from Markovitz's analysis of oscillatory Couette shear of a Newtonian fluid. The next step is study of non-linear viscous fluids in oscillatory shear, using the new instrumentation to apply Dodge's technique (Trans. Soc. Rheology 15, 589 (1971)).

POLYMER COLLOIDS RESEARCH AT THE UNIVERSITY OF SYDNEY

D.H.Napper, Department of Physical Chemistry,
University of Sydney, N.S.W., 2006.

———————

Our interests in the polymer colloids field fall
into two general categories, one kinetic and the other
thermodynamic.   The kinetic interests are exemplified
by recent studies of the role that nonionic surfactants
play in the seeded heterogeneous polymerization of vinyl
acetate.   (Reprints are available).   Other monomers
(e.g., styrene, methyl methacrylate) are currently being
examined.   These studies provide additional information
on the locus of heterogeneous polymerizations and on
the general polymerization mechanisms.

Our second area of investigation lies in the
realm of steric stabilization.   We are trying to
understand how it is that macromolecules are able to
impart colloid stability, especially to polymer latices.
We have catalogued some of the phenomenology of steric
stabilization and developed a first order theory based
upon the somewhat old-fashioned Flory-Huggins theory.

Newsletter RHO/3

Forces between Latex Particles   R. H. Ottewill

    Experiments are continuing to measure directly the forces
between polymer latex particles. The apparatus used is illustrated
in Figure 1. A known volume of dilute latex is enclosed between
the rubber membrane and a millipore filter and pressure applied to
the dispersion by the hydraulic system. At a particular pressure
the system comes to equilibrium and the volume of liquid expelled
can be obtained from the measured rise in the capillary, h.
Hence, the volume fraction of the latex remaining in the cell can
be determined.

    A typical set of curves of pressure against volume fraction
are shown in Figure 2. These show a dependence on electrolyte
concentration in the order expected and a comparison of these
experimental curves is now being made with theoretical curves
calculated from the DLVO theory.

    A systematic experimental investigation of the effect of particle
radius has also been made. At an electrolyte concentration of 10^{-4} M
with small particle size latices (less than ca. 8000 $\overset{o}{A}$ diameter)
ordered parking of the particles occurs to give essentially a
hexagonally close packed system. With larger particles, ca 1μ in
diameter, the ordered packing is lost and the arrangement of particles
appears to approach random packing. We regard this as evidence
for the onset of secondary minimum association.
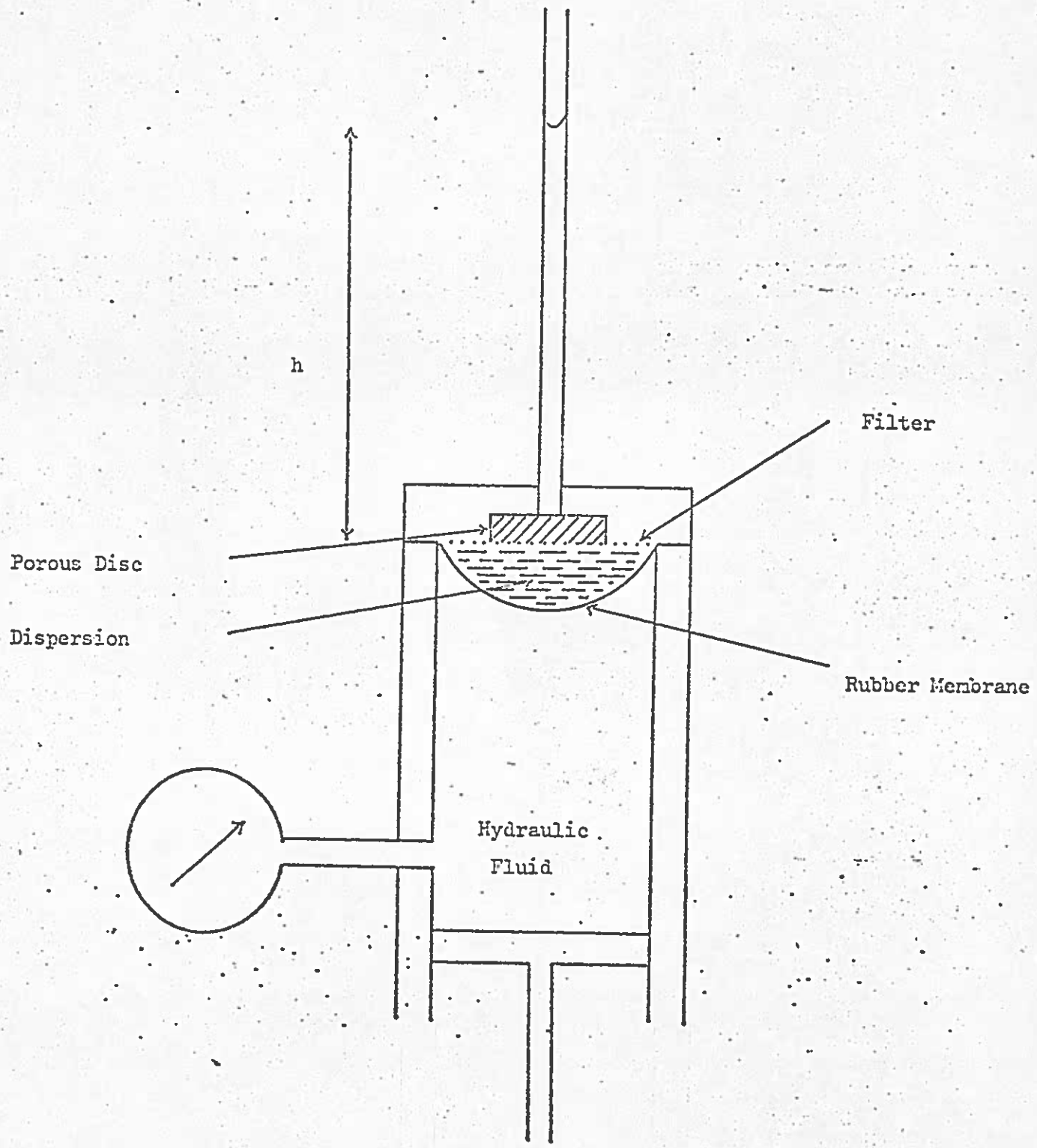
Filter

Porous Disc

Dispersion

Rubber Membrane

h

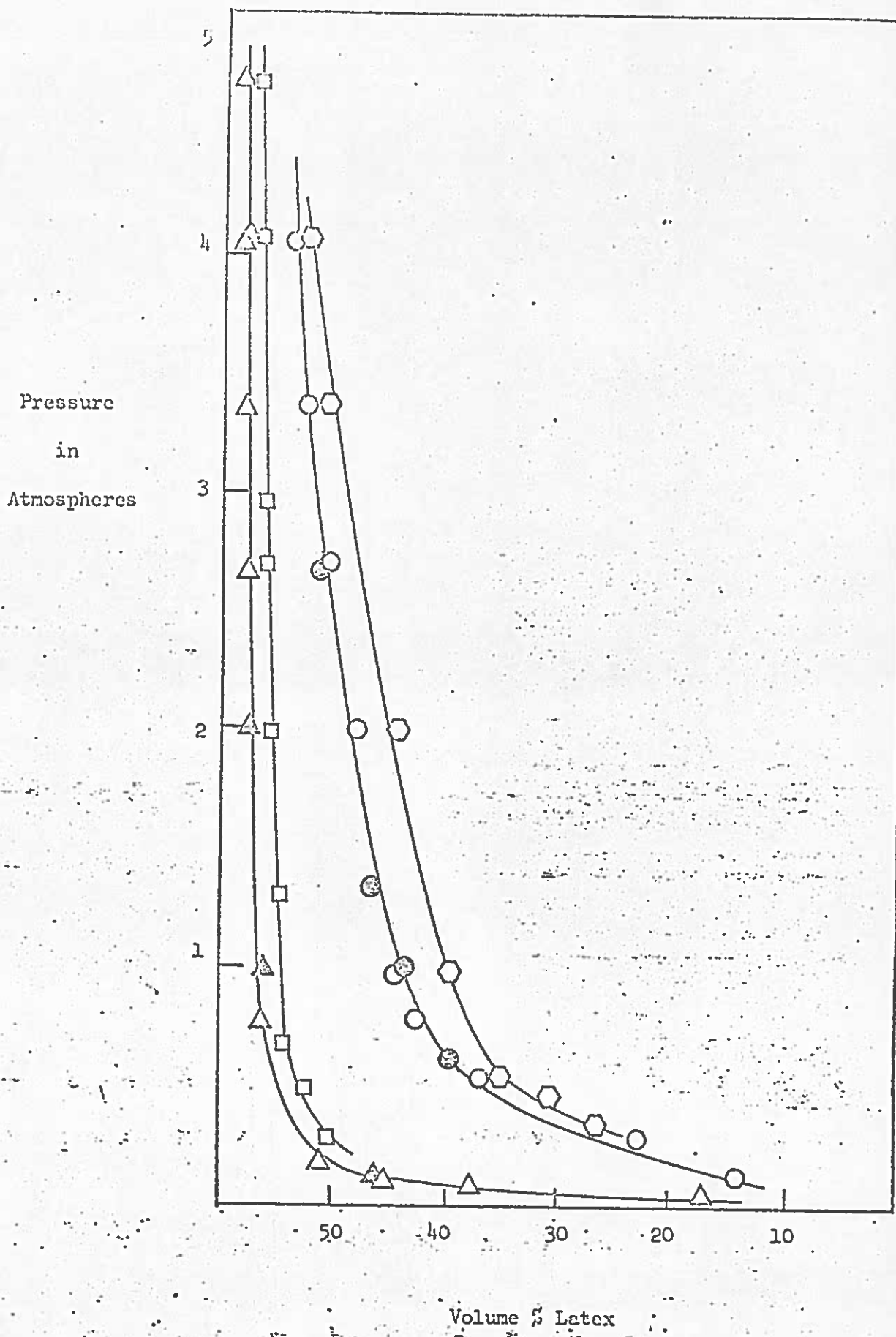Hydraulic
Fluid

P_{Ap}

Figure 2   Pressure against volume concentration for a polystyrene

latex dispersion in sodium chloride solutions at pH 5.0 and

25°C.   Particle radius = 3520 Å.

G. W. POEHLEIN - - POLYMER COLLOID NEWSLETTER

Progress during the past quarter has been minimal. I have only one student working in the emulsion polymer area and he is having problems getting our continuous reactor to run at a steady state with MMA. We suspect problems with trace inhibitors and a poor reproducibility in the initiation rate due to variations in iron concentration.

In my last newsletter contribution I reported that Gerrens' (1) data for MA did not follow the continuous reactor model based on S-E Case 2 kinetics. Deviations in rate were explained, at least qualitively, on the basis of $\bar{n} < 1/2$ due to transfer of free radicals out of active particles. Our future work in the model development will include consideration of this phenomena. The relationships presented by Uglestad et al (2) will be employed if possible. This work represents an improvement in the original theories of Stockmayer (3) and O'Toole (4). Uglestad and coworkers have included the free radicals coming out of particles in the equations as a radical generation mechanism. Stockmayer & O'Toole did not account for the future potential of these radicals.

1. British Polymer Journal, Vol. 2, Jan. 1970.

2. Journal of Polymer Science: Part A-1, Vol. 5, 1967.

3. Journal of Polymer Science, Vol. 24, 1957.

4. Journal of Polymer Science, Vol. 9, 1965.

14 April 1972

CONTRIBUTION TO POLYMER COLLOID GROUP QUARTERLY NEWSLETTER

May 1972

A.A. Robertson, Department of Chemistry, McGill University

A thesis entitled FILM FORMATION FROM LATEXES by M.S. El Aasser has been accepted as a partial requirement for the Ph.D. degree. The following is an abstract and a list of claims to original research.

ABSTRACT

The use of the ultracentrifuge to determine the minimum pressure required for coalescence of latex particles is described. The extent of coalescence is found to reach an equilibrium value after a short centrifugation time and this equilibrium provides the basis for calculating the required pressure. Displacements of the emulsifier from the coalescing latex particles affect the equilibrium but can be taken into account.

The centrifugation method provides a measure of the forces opposing coalescence of the latex particles and can be used to follow the influence of pH, emulsifier content and electrolyte on the stability of the latex system. The results are accounted for by the DLVO theory for colloidal stability. The stability of this latex system is primarily determined by electrostatic repulsion.

Examination of the films produced by centrifugation, and following the aging of these films in air and in water, confirmed that the coalescence is initiated under the influence of the centrifugation force, and that the filming process is then slowly completed under the influence of the surface tension of the polymer.

CLAIMS TO ORIGINAL RESEARCH

The work reported in this thesis was primarily designed to measure the force required to initiate coalescence

of latex particles under various conditions. This has been achieved together with several original accomplishments and findings.

(1) Preparation and characterization of the mono-disperse styrene-butadiene (60:40) latex system required for this work.

(2) It has been shown that the consolidation or "further gradual coalescence" of films after inter-particle contact is independent of the presence of a polymer-air inter-face.

(3) It has been demonstrated that the surface coverage of the latex particles by stabilizer is not greatly changed by dilution down to 0.5% solid contents.

(4) It has been demonstrated that the centrifugation of the latex system, when coalescence is involved, results in the displacement of about 50% of the emulsifier originally covering the coalesced particles.

(5) Development of an equilibrium technique, which involves the use of the ultracentrifuge and the dispersion of the latex particles in sucrose solution, for the determination of the minimum pressure required for the initiation of particle coalescence.

(6) It has been proved that equilibrium is reached within a very short centrifugation time. The study of this equilibrium is in contrast to the study of rate of coalescence of oil emulsions during centrifugation in Vold's work (1).

(7) It has been proved that the minimum pressures required for coalescence measured by the ultracentrifugation technique are two orders of magnitude lower than the maximum available from capillary forces during filming. (2)

(8) It has been proved that coalescence of the latex particles occurs if the applied centrifugal force exceeds a certain minimum.

(9) It has been demonstrated that the minimum pressure required for initiation of particle coalescence provides a measure of the force barrier in the force-interparticle distance curve, which corresponds to the maximum slope of the potential energy curve, and so, is related to latex stability.

(10) The pH sensitivity of latex stability has been shown to be controlled by the changes in the ratio of the ionized

to the non-ionized emulsifier content of the system. The sen-
sitivity of the latex stability to CO_2 absorption is explained
on this basis.

(11) It has been shown that the ion-exchanged "clean"
latex has a very low barrier for the initiation of coalescence
and this is independent of the pH value.

(12) Increasing the surface coverage of the latex
particles with ionized emulsifier molecules has been shown to
result in increasing the stability of the latex system.

(13) Increasing the electrolyte concentration of the
latex system, at a given stabilizer coverage of the particles,
has been shown to increase the force required for coalescence at
low electrolyte concentrations. This trend is reversed at higher
concentrations and the required force decreases with electrolyte
concentrations.

(14) It has been demonstrated that the stability data
of the ultracentrifugation technique correlate qualitatively
with the DLVO theory, and that the stability of this specific
latex system is dominated by electrostatic factors.

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Mr. A. Homola has been employing the method of Kotera, Furusawa
and Takeda to produce monodisperse polystyrene latexes in the ab-
sence of surface active agents. This appears to be a simple, re-
liable procedure with reasonable control of particle size at least
between 0.4 and 1.5 microns.

Dr. B. Alince has been supervising some work on the
stabilization, coagulation and/or flocculation of microcrystalline
cellulose (Avicell) particles by polyelectrolytes. The roles of
bridging, electrostatic stabilization and steric stabilization ap-
pear to be distinguishable. A report is currently being written.
Does a dispersion of cellulose particles qualify as a "polymer
colloid" within the intention of the group?

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ADDITIONAL STUDIES OF THE MORPHOLOGICAL CHANGES IN LATEX FILMS

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ABSTRACT

It was shown earlier that a further, gradual coalescence and concurrent exudation of incompatible emulsifiers occurs upon ageing in the surface of dry, transparent, and continuous films of styrene-butadiene copolymers. These processes are now shown to occur at about the same rate in the film-substrate interface and the interior of the film. The rate at which the emulsifier exudations appear is correlated with the rate of the coalescence. The further, gradual coalescence is accelerated in oxygen and slowed in nitrogen; probably it involves oxidative softening of the styrene-butadiene copolymer. Other latex types which show further, gradual coalescence are ethyl acrylate-methyl methacrylate and vinylidene chloride-vinyl chloride-ethyl acrylate copolymers, as well as natural rubber. Polyvinyl acetate latexes do not undergo further, gradual coalescence, probably because of a polyvinyl alcohol layer formed by surface hydrolysis of the particles.

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The Simulation of Binder Migration in Latex-Clay Coatings
Using a Model System

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Abstract

A hypothesis is advanced to explain binder migration in latex-clay coatings:

during drying, the clay platelets become immobilized at a stage where some

latex particles are still free to move about; rigorous drying at this stage

generates surface tension-driven convection currents, which carry the latex

particles through the interstices between the clay platelets to the surface,

where they are left by evaporation of the water. A model system was devised

to test this hypothesis: the latex-clay coating composition is simulated by a

mixture of two monodisperse polystyrene latexes, 10990Å-diameter spheres

representing the clay platelets and 910, 1090, 1380, 1760, or 2340Å-diameter

spheres the latex particles. Upon drying, the large spheres form hexagonally-

packed arrays, with or without the small spheres; the minimum size of the

"hole" between the packed large spheres is 1700Å. The latex mixtures were

dried under various conditions, the film surfaces were replicated and the

replicas examined in the electron microscope, and the relative numbers of

small and large spheres in the surface were determined. With this model

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system, binder migration was simulated in the laboratory: for mixtures containing the 910 or 1090Å-diameter spheres, moderate drying rates left the small spheres inside the film, while rigorous drying rates brought them to the surface in profusion. For mixtures containing the 1380, 1760, or 2340Å-diameter spheres, some small spheres were always found on the surface, independent of particle number ratio and the conditions of drying; these small spheres cannot pass through the interstices between the large spheres. The results support the convection hypothesis. Arguments are presented against an alternate hypothesis based on capillarity.

SIZE DISTRIBUTION ANALYSIS OF POLYDISPERSED COLLOIDAL PARTICLES

T. P. Wallace

The size distribution analysis of polymer latex systems by use of angular light scattering measurements has been shown[1] to be very precise for fairly narrow size distributions. Unfortunately, there is no highly precise technique of size distribution analysis presently available for polydisperse colloidal particles. This is a preliminary report of what appears to be a successful size distribution analysis technique which combines ultracentrifugation and light scattering. The light scattering technique based on the extrema method has been recently published[2-4] and the details are given in the attached reprint. The method uses the observed angular position of the minima to determine the modal optical size whereas the ratio of the corrected output signal at the maximum and the minimum is used to evaluate the distribution of particle sizes.

Our approach to the size distribution analysis of a polydisperse system is to mechanically fractionate it into narrow size distributions which can be accommodated by the light scattering technique. The original size distribution is then reconstructed by combination of the analyses of the individual fractions. The fractionation procedure will be outlined and the results from analysis of two multi-modal systems will be reported.

The separation takes place within a B-15 rotor which is spun at a specified speed in the Beckman L2-65B Preparative Ultracentrifuge. Figure 1 shows a top view of the rotor. It has a capacity of 1665 ml which is divided among four sectional compartments each of which receives and expells liquids by means of ports shown by open circles in Figure 1. Using a special constant flow gradient pump, (Beckman Model 140), the rotor is loaded and a density gradient is established by pumping sucrose solution through the outer ports. The width of the density gradient can be adjusted for a particular system; all of which naturally give a lower density near the center of rotation. After the latex particles are distributed in the rotor according to size, the pump out procedure (Fig. 2) begins.

The media used for pump out has a higher density than used in initial loading of the rotor. This has the effect of pushing the medium out the center past with minimal mixing. During pump out the liquid passes through a Beckman DB-G in order to follow the turbidity with time and finally the liquid is deposited in a fraction collector. The recorded turbidity vs. fraction number trace gives an indication of whether separation has been accomplished.

A bimodal distribution having individual size parameters of $D_m = 627^{nm}$, $\sigma = 29$ nm, and $D_m = 439$nm, $\sigma = 32$nm was successfully separated. The size parameters were determined before and after mixing by the extrema light scattering technique and electronmicroscopy.

A mixture of five samples of narrow size distribution with diameters ranging from 0.25μ to 1μ have been separated and are presently undergoing final light scattering and electronmicroscopy analysis to determine if the separations were complete. Initial data indicate success.

NOTE: Information on possible sources of a polydisperse latex sample with a continuous distribution ranging from about $^-0.2$ μ to $^-2\mu$ would be appreciated.

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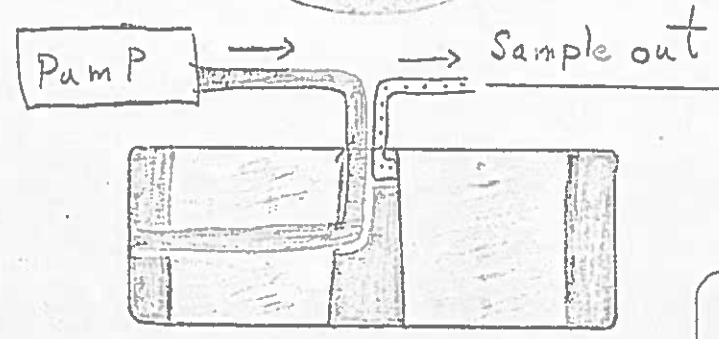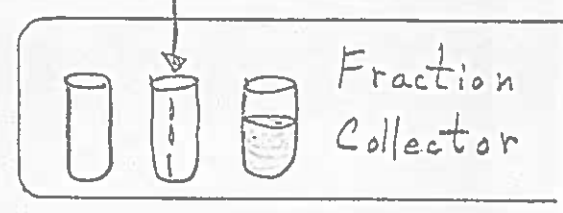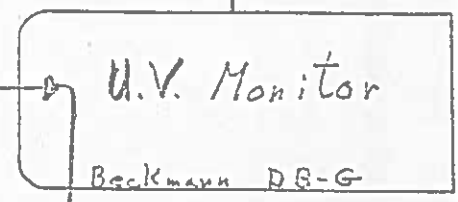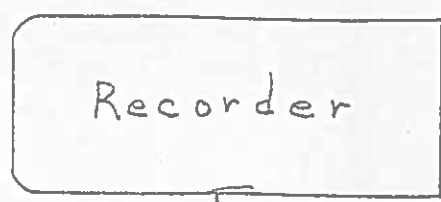Rochester, New York   14623

FIG. 1
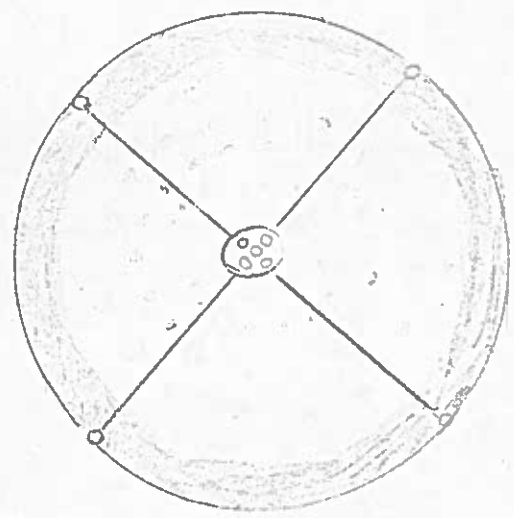
Dense
Displacing
Solution in

Pump → → Sample out

FIG. 2

Recorder

U.V. Monitor

Beckmann DB-G

Fraction
Collector

David J. Williams

The City College of New York

May 1972

My contribution is based on pages 19 to 22 in the preprint
recently distributed, "The Equilibrium Encapsulation of Poly-
styrene Latex Particles". On these pages, we present a heuristic
argument as a basis for further study of the factors controlling
the encapsulation phenomenon.

[The appellation "core-shell", which we have previously
introduced, ought not to be interpreted too literally, for it
implies true two-phase behavior. We have tried to avoid this
implication by adopting the terms "monomer-rich shell" and
"polymer-rich core". These terms imply a quasi two-phase behavior
where the polymer segment density distribution is modest within
the interior and near the periphery but steep at their interface.
The "core-shell model" was introduced to explain our kinetic
data. As the level of our understanding of the phenomenon
advances, we find that the term "core-shell" tends to be mis-
leading, and we now prefer to refer to the "ENCAPSULATION" model.]

In brief, we believe that saturation-encapsulation is
governed by the severe entropic restraints that would be imposed
on the polymer chains if the monomer and polymer were distributed
uniformly. I believe the key to understanding our viewpoint is
to recognize the importance of these conformational-entropic
restraints in the vicinity of the particle surface. If I recall
correctly, similar factors arise in discussing colloids stabilized
by adsorbed polymer.

The rationale presented on pages 19-22 suggest three experi-
ments which we are in the process of executing. (a) Clean a seed

latex to remove residual soap and initiator; add soap to
stabilize. Then add monomer with a trace of butadiene to
saturation; recommence polymerization with an <u>oil</u> <u>soluble</u>
initiator. This experiment would ascertain the importance that
end groups attached to the particle surface have in controlling
particle morphology. (b) Determine the effect of seed molecular
weight on the morphology. Latex seeds have been prepared with
$\bar{M}_v$ = 20,000; 40,000; 2,000,000; and 10,000,000. Saturation M/P
ratios range from 2/1 up to 3/1 from low to high values of $\bar{M}_v$.
Thus, molecular weight is a factor. These seeds will be over-
coated under conditions of saturation. If conformational restraints
are important in controlling particle morphology, then variations
in conformational size should manifest themselves. (c) Overcoat
a particle with monomer far below saturation, ca. 10%. If severe
entropic restraints are operating, monomer should distribute
itself as it is added in such a way as to relieve these restraints.
That is, at low levels of monomer addition, most of the added
monomer should locate in a thin shell surrounding the particle.