

Polymer Colloid Group
Quarterly Newsletter

Vol. 1, No. 2, February 1972
D.J. Williams, Editor

Our newsletter is somewhat later than intended, but I encountered difficulty in obtaining sufficient copy to compile it. Perhaps I was a bit late with my reminder and call for contributions. In any event, please be reminded that contributions for the next issue - May 1972 - are due in my office by April 17.

Our symposium entitled, "International Micro-Symposium on Polymer Colloids" is scheduled to be held at Lehigh on June 16 and 17. May I suggest that the session chairmen outline their plans for this meeting in the next issue? The sessions and the session chairmen are (a) Formation of Polymer Colloids, - Williams, (b) Characterization of Colloids - Otte~~l~~will, (c) Colloid Properties - Krieger, and (d) Applications of Polymer Colloids - Vanderhoff.

Fitch has not contributed to this issue, but he promised a whopper next time. Stannett has submitted a final report which he and E.P. Stahel prepared for the AEC on radiation induced emulsion polymerization. I have reproduced the abstract in this issue and he will prepare discussion material on various aspects of this report in subsequent issues. Copies of their 139-page report are available upon request.

On the basis of your responses to the nominations listed in my letter of January 12, 1972, I am extending an offer of membership to B.M.E. van der Hoff. The other nominees - Stahel and Formanck - received very limited support.

Morton has not responded in any form to my several calls for a contribution. My next letter will advise him of his precarious membership status.

Attached is an updated membership list.

Polymer Colloid Group

Membership List

Dr. Robert Fitch
U of Connecticut
Department of Chemistry
Storrs, Conn. 06268

Dr. Irvin Krieger
Olin Bldg.
Case Western Reserve U.
Cleveland, Ohio 44106

Dr. Ronald Ottewill
School of Chemistry
U of Bristol
Bristol, BS 8 ITS, England

Dr. Gary Poehlein
Ch.E. Dept.
Lehigh U
Bethlehem, Pa. 18105

Dr. John Vanderhoff
Center for Surface and
Coatings Research
Lehigh U
Bethlehem, Pa. 18105

Dr. David Williams
Ch.E. Dept.
The City College of New York
New York, N.Y. 10031

Dr. Maurice Morton
Institute of Polymer Science (?)
U of Akron
Akron, Ohio 44304

Dr. A.S. Dunn
Institute of Science & Technology
U of Manchester
Manchester M60 1QD, England

Dr. T.P. Wallace
Dept. of Chemistry
Rochester Institute of
Technology
Rochester, N.Y. 14623

Dr. A.A. Robertson
Pulp and Paper Bldg.
Department of Chemistry
McGill University
Montreal 2, P.Q., Canada

Dr. V.T. Stannett
Dept. of Chemical Engr.
Box 5035
North Carolina State Univ.
Raleigh, No. Carolina 27607

Dr. B.M.E. van der Hoff
Dept. of Chemical Engr.
U of Waterloo
Waterloo, Ontario
Canada.

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

My lecture, 'The role of the emulsifier in emulsion polymerisation' ultimately appeared in 'Chemistry & Industry' on 4th December ((1971) 1406 (No. 49)). The reprints are not yet to hand, however.

Tonge's Ph.D. Thesis was accepted and he graduated in December: he is now with Wallpamur Ltd., Darwen, Lancs. working on decorative paints. The summary of his thesis (Ph.D. Thesis, Manchester, 1971) is as follows:

"The kinetics of the aqueous polymerisation of vinyl acetate have been investigated with special regard to initiation and to the effect of added poly(vinyl alcohol).

"The thermal decomposition of potassium peroxydisulphate at high concentration (0.02 M) was found to be accelerated by the addition of poly(vinyl alcohol) and vinyl acetate. The decomposition was also followed at a concentration close to that used in the polymerisation studies ($2 \times 10^{-3}M$) by a spectrophotometric method utilising the free-radical scavenger 1,1'-diphenyl-2-picrylhydrazyl (DPPH). The rate constants and the activation energy were lower than those found by other methods. The difference was attributed to the use of 50% aqueous ethanol as the solvent instead of water. The rate constants were unaffected by the addition of poly(vinyl alcohol) or vinyl acetate. A sampling method was used in conjunction with the DPPH technique to follow the decomposition in the presence of a polymerising latex. The results did not indicate any acceleration of the decomposition in the presence of the latex.

"An attempt to prepare 2,2'-azobis(sodium 2-cyanobutyrosulphonate) was unsuccessful. The preparations of the isomers 4,4'-azobis(4-cyanopentanoic acid) and their sodium salts are described. The decomposition kinetics were followed both by the DPPH method and by the disappearance of the azo-group absorption from the ultra-violet spectrum. The difference between the results from the two techniques was explained on the basis of a 'solvent cage' effect. The use of the salts as the initiator for aqueous vinyl acetate polymerisations did not result in the formation of a stable latex unless surfactant was present.

"The effect of the concentration, acetyl content, and molecular weight of the poly(vinyl alcohol) added as the stabiliser to aqueous vinyl acetate polymerisations was investigated dilatometrically. The rate decreased with increasing concentration and acetyl content but showed no definite trend with molecular weight. The addition of potassium chloride had no effect on the rate up to a concentration of 0.05 M but, above this threshold, the rate decreased rapidly. The adsorption of poly(vinyl alcohol) on a poly(vinyl acetate) latex was investigated by an iodine photometric method. Seeded polymerisations on a latex on which had been previously adsorbed poly(vinyl alcohol) showed some correlation between the degree of adsorption and the rate of polymerisation.

"The contraction for complete polymerisation of aqueous vinyl acetate at 60°C is 15.7%, which is considerably lower than the value of 24.6% observed for bulk polymerisation. The anomalous value for the aqueous system has been explained on the basis of density measurements which indicated that both potassium peroxydisulphate and vinyl acetate dislocate the structure of the solvent, water, and thereby increase its density."

A paper on the material mentioned in the last paragraph of the summary above was drafted during the summer but has been awaiting some minor revisions. It should be submitted for publication soon, probably to the 'British Polymer Journal'. Papers on the other material will probably be submitted to the 'Journal of the Chemical Society, Faraday Transactions I' (the successor since the merger on 1st January of the Chemical Society, the Royal Institute of Chemistry, the Faraday Society, and the Society for Analytical Chemistry of the back end of the 'Transactions of the Faraday Society'). It should be possible to circulate preprints of these papers in due course.

Two final year undergraduates in the Polymer Chemistry Course in the Department have just started on one-term research projects in this area. One (D.A. Willdigg) is making a further attempt to prepare an azo-sulphonate initiator. The method is that of J.A. Phelisse & C.A. Quiby of Rhone-Poulenc (Fr.P. 1,233,582 (1960), U.S.P. 3,161,630 (1964)). Tonge was interested in this type of initiator since it was expected that it would not be liable to induced decomposition: however when he found that persulphate did not undergo induced decomposition at the concentrations used for initiating polymerisation there was no longer any motive for using the water soluble azo initiators. However it should be possible to overcome the difficulties he encountered and this type of initiator with moderately-strong acid solubilising groups not liable to hydrolysis is likely to have important advantages over persulphate in the polymer colloid field. The other (D.J. Nichols) is investigating the reports of stereospecific emulsion polymerisation from Medvedev's collaborators who use benzoyl peroxide with a cationic emulsifier in alkaline solution. The increase of syndiotacticity which the Russian workers observe might be attributed to the decreased polymerisation temperature when this redox interfacial initiating/emulsifying system is used except that the tacticity of the product is also observed to depend on pH and emulsifier concentration. It is hoped to determine tacticity quantitatively by the n.m.r. method which has not, so far, been applied to this problem.

We are completing a "retooling" phase, during which most of our projects were improving their apparatus or techniques, and little useful data were accumulated. I'll review the progress by project.

Emulsion Polymerization Studies (M. Juang)

Current effort is directed toward control of bound surface charge on monodisperse polystyrene latices; by incorporation of small amounts of a vinyl sulfo-ester as a comonomer. One method of determination of the bound sulfo-ester which seems promising is deionization followed by conductometric titration with an anionic surfactant.

Preliminary indications show that we have achieved the desired monodispersity with a wide range of bound charge of a strongly acidic type.

Electroviscous Effect (M. Eguiluz)

Mr. Eguiluz has completed calibration of capillary and rotational viscometers, and verified his techniques of non-Newtonian viscometry by studying an aqueous carboxymethyl cellulose system in both types of instrument. He is now ready to work on the non-Newtonian behavior of deionized monodisperse latices as functions of concentration, particle size, charge, and electrolyte level.

Order-Disorder Transition (S. Gottschalk)

At a given electrolyte level, there is a functional relationship between the temperature and the concentration of the disordered (white) phase which is in equilibrium with the ordered (iridescent) phase. Since the concentration is analogous to a solubility, the temperature coefficient should give the heat of the order-disorder transition.

Our first data show a very low ΔH , i. e., below 1 K cal/mole.

At this point, Mr. Gottschalk (a sophomore) dropped the optical cell needed for the diffraction measurements; we'll try to duplicate the result (not the dropping) as soon as the glassblower delivers a new quartz cell.

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

Our new oscillatory rheometer is still not operational, although we're very close. The locally constructed air bearing didn't work well the first time, and is being honed, and the analog interface between the instrument and the computer has finally been worked out in bread-board circuitry. Software works in blocks, but has not yet been assembled into a master program. A short-cut method has been found to produce the nonaqueous dispersions needed for this study. After the dialysis against methanol, the final medium is added, and the methanol pulled off in a rotary evaporator. This eliminates one dialysis step, and yields stable, iridescent redispersions in the final medium. This modification is of especial value in

resuspending latex in viscous media; these are the suspensions which are expected to show long thixotropic relaxations.

More Progress: Mr. Niu has taken a wife, and Mr. Juang has fathered a baby girl. I hope all your groups are doing as well!

This quarter I thought it might be of interest to the group to describe current areas of interest in Bristol in work jointly directed by Mr. J.W. Goodwin and myself. These projects can be broken down into four main areas:

I. Mechanism of Latex-Particle Formation

This has been subdivided into two streams, the mechanism in the presence of surface active agent and that in the absence of such materials. The following factors have been investigated:

- 1) influence of initiator concentration,
- 2) effects of initiator type, e.g. persulphate, hydrogen peroxide, diazo cyano valeric acid;
- 3) monomer concentration and type,
- 4) temperature,
- 5) stirring using both laminar and turbulent flow,
- 6) ionic strength,
- 7) type of electrolyte, in particular, variation of counter-ion valency,
- 8) removal of surface active agent by dialysis

II. Characterization of Latices

We have tried to characterize all the good monodisperse latices by a wide variety of techniques including,

- 1) particle size analysis on ca. 3,000 particles
- 2) surface area determination - by gas adsorption on freeze dried samples - by negative adsorption on wet samples
- 3) molecular weight determination by membrane osmometry - mainly with polystyrene using toluene or dioxan as solvents
- 4) microelectrophoresis
- 5) conductometric titration
- 6) potentiometric titration - in a limited number of cases as we find this a slow technique
- 7) dye adsorption following the methods of Santi-Palit et al.

In some cases the adsorption of cationic surface active agents has been employed as an alternative means of estimating the number of negatively charged groups on the particle surface.

III. Control of Surface Groups on Particle Surface

We should like to obtain some particles where all the groups have the same chemical form. At present we find sulphate, carboxyl and hydroxyl groups on the latex surface and would like to convert these all to carboxyl. Persulphate catalysed by Ag^+ works well but flocculates the latex. We are now seeking reagents which carry out the conversion, but leave the latex in a stable form. Currently we are trying sodium periodide-potassium permanganate. Any suggestions welcomed!

IV. Properties of Latices

This might be more appropriately entitled the use of polymer latices as a model colloidal dispersion, i.e. one in which the particle shape is spherical, the range of particle size is narrow and where the surface charge

is known. Current and past (unpublished) activities include :

- 1) studies of flocculation - orthokinetic and perikinetic
- 2) electrophoresis - relaxation effect
- 3) compression studies, to determine interaction forces and the role played by secondary minima in determining packing. We would be interested in using Krieger's technique in this experiment to determine interparticle distances at different pressures.
- 4) Adsorption of surface active agents, particularly cationic and non-ionic.
- 5) Rheological studies
 - a) in absence of additives to investigate effects of: particle size, particle charge, electrolyte concentration and the effects of secondary minima
 - b) in the presence of additives such as cellulose ethers and surface active agents

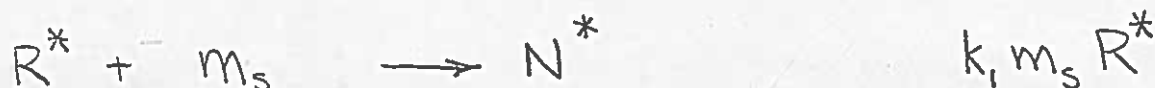
CONTINUOUS EMULSION POLYMERIZATION

Gary Poehlein; Dept. of Chemical Engineering; Lehigh University

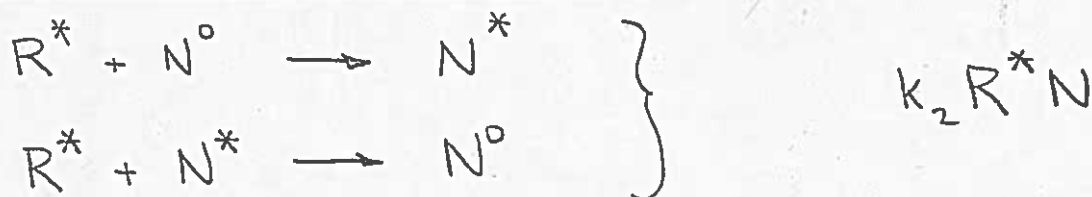
Since the last newsletter our paper (DeGraff & Poehlein, J. Poly. Sci. A-2, Vol. 9, 1955-1976 (1971)) has been published and all of you should have reprints. Two other papers which have been published lately give some different results which are worth reviewing in this note.

I. Nomura, et.al. (J. Appl. Poly. Sci., Vol. 15, 675-691 (1971)) suggest a different model for particle formation. The following mechanism and rate equations are suggested.

NEW PARTICLE FORMATION:



RADICAL MOVEMENT INTO EXISTING PARTICLES



where: R^* is aqueous phase free radical concentration, m_s is micelle concentration, N^* is the concentration of particles containing radicals, N^0 the concentration of inactive particles, and k_1 and k_2 are rate constants.

Please note that

$$N^* + N^0 = N = \text{total particle concentration}$$

and

$$S_m = m_s M_m$$

where S_m is the concentration of emulsifier which is not adsorbed on particles and M_m is the micelle aggregation number.

Using the rate equations above the particle concentration in the effluent from a CSTR is given by:

$$N = R_i \Theta N_A \left\{ \frac{k_1 m_s R^*}{k_1 m_s R^* + k_2 R^* N} \right\}$$

or

$$N = R_i \Theta N_A \left\{ \frac{1}{1 + \frac{\epsilon N}{S_m}} \right\}$$

where $\epsilon = \frac{k_2 M_m}{k_1}$ is a new parameter determined by fitting experimental data.

Nomura, et.al. show that the above model fits their data from transient start-up experiments and steady-state experiments at low values of Θ (CSTR mean residence time) better than a model based on S-E Case 2 kinetics. While the better agreement with the data cannot be questioned the use of a model which predicts radical flux into particles to be proportional to particle number and independent of particle size just doesn't seem correct.

Other possible explanations for the better fit would be:

1. The new model introduces an additional experimental parameter which improves the fit.
2. Perhaps a trace of inhibitor in the feed could cause the problem in fitting the S-E model. Inhibitor traces in the feed to a CSTR can have significant effects during start-up periods and in low Θ steady-state runs.

II. Gerrens and Kuchner: (Br. Poly. J. Vol. 2, Jan. 1970) reported data for methyl acrylate which agreed reasonably well with theoretical predictions for particle formation but deviated considerably for polymerization rate. They found that

$$R_p \propto R_i^{0.65} \theta^{0.43} [M]^{1.2}$$

whereas theory predicts

$$R_p \propto [S]^{1.0} \theta^{-0.67}$$

where $[S]$ is the emulsifier concentration.

Gerrens suggests that \bar{n} might be less than 1/2 due to the movement of radicals out of the particles. This, he claims, would cause the observed differences between theory and experiment.

Since our future work will be with monomers more water-soluble than styrene (e.g. methyl methacrylate and vinyl acetate) the observations of Gerren's are interesting. We would like to be able to change our theoretical model to account for experimental observations including those of Gerrens. First attempts will probably involve altering our particle growth equation to allow \bar{n} to be different from 1/2 (esp. below 1/2). Perhaps we can incorporate the results of Stockmayer or O'toole directly into the growth equation and obtain a solution numerically. Any other suggestions?



10 January 1972

PULP AND PAPER RESEARCH INSTITUTE OF CANADA

570 ST. JOHN'S BOULEVARD, POINTE CLAIRE 72Q, CANADA
TEL (514) 697-4110 CABLE-PAPRICAN TELEX 0120797

CONTRIBUTION TO POLYMER COLLOID GROUP QUARTERLY NEWSLETTER

February 1972

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

Current activity related directly to polymer colloids is being carried on by two graduate students M.S. El-Aasser and A. Homola. The work was undertaken to investigate the physical chemistry of coalescence and film formation of latexes and represents our first venture into this area.

The initial approach was to attempt measurement of the force required to produce initial coalescence of latex particles. This was done by a centrifugal method (J. Colloid & Interface Sci. 36, 86(1971)) and the required pressure was evaluated when some of the more obvious variables were changed in a styrene-butadiene latex stabilized by lithium stearate.

More recently efforts have been made to correlate results with theory and to consider the contributions of electrostatic repulsion and steric repulsion. To this end techniques have been developed to measure electrophoretic mobility (mass transport), to replace soap as the stabilizer (dialysis and ion exchange) and to measure the force-separation relationship by a filter membrane technique (cf. Barclay and Ottewill, Spec. Disc. Faraday Soc. 1 138 (1970)). The work is still in progress but two observations of interest have been made that complicate the picture.

One of these relates to the removal of soap (lithium stearate) from the latex by dialysis or ion exchange. The removal is followed by determining residual soap by conductometric titration in the usual way. It has been found

that a latex showing little residual soap immediately after dialysis will, on storage, again show a titratable soap content. The present suggestion is that stabilizer is occluded in the latex particles during polymerization and then slowly diffuses out as accessible soap is removed. This hypothesis has been checked by carrying out an accounting of soap introduced in the emulsion polymerization and the total soap recoverable after long storage times.

The second observation is that the mechanical expression of serum from a latex through a membrane sets up a system in which Donnan equilibrium phenomena can play a role in affecting the ionic concentrations and consequently the stability of soap-stabilized latexes.

Mr. El Aasser has submitted his thesis and upon its acceptance, further reports will become available.

AAR:es

R-

FINAL REPORT

RESEARCH AND DEVELOPMENT STUDIES INTO THE BASIC TECHNOLOGY OF

RADIATION INDUCED EMULSION POLYMERIZATION INCLUDING

SMALL SCALE PILOT PLANT SYSTEMS

for

Division of Isotopes Development, USAEC

V. T. Stannett

E. P. Stahel

Department of Chemical Engineering

North Carolina State University

Raleigh

June 1971

ABSTRACT

The radiation induced emulsion polymerization of butadiene, styrene-acrylonitrile and butadiene-acrylonitrile comonomer systems has been studied. In addition vinyl chloride has been investigated both in emulsion and in bulk under precipitating conditions. Butadiene was found to polymerize extremely slowly in bulk and in emulsion. The styrene comonomer system was faster but also slow. However, extremely pure butadiene polymerized much faster and future efforts should be directed towards the use of exceptionally pure materials. Butadiene-acrylonitrile and acrylonitrile itself polymerized much more rapidly but exhibited a complex kinetic behavior. It was found difficult to produce true emulsion polymers with acrylonitrile itself although the emulsifier did change the course of the polymerization process and increase the rate considerably. G (monomer) values of more than 75,000 were readily obtained with pure acrylonitrile in "emulsion" systems.

The bulk polymerization of vinyl chloride is interesting in that the polymer precipitates initially as a fine powder which later coalesces to an opaque mass. G (monomer) values of about 10,000 were obtained; little post effect and a square root dependency of the rate on the dose rate were found. The emulsion polymerization proceeded smoothly with G (monomer) values of more than 100,000. The kinetics were found to be complex and not to fit any standard or known scheme. The molecular weights in both systems were found to be essentially dependent only on the temperature, i.e. were governed by chain transfer to monomer.

A recirculating flow reactor system is used to study the radiation induced emulsion polymerization of styrene. Emulsion is recirculated through

an all stainless steel six liter system from a stirred vessel through relatively long transfer lines to a helical flow reactor positioned within a high intensity Co-60 irradiation. The pilot plant is equipped with automatic temperature measurement and control for operating above and below room temperature. Constructed of standard stainless steel tubings and fittings, the system is modular in design to facilitate changes in configuration. Mathematical analysis of the engineering flow system is carried out utilizing the model styrene system for which Smith-Ewart kinetic behavior is assumed. Polymerization rate expressions so formulated are incorporated into a mathematical model for the conversion history in the system using engineering models for each of the flow elements.

Major departure from standard batch kinetic behavior is found in the flow reactor scheme employed. The mixing of fluid elements of different reaction time histories gives rise to a major second effect believed to be the rapid transfer of emulsifier. Operating conditions of the flow system minimizing this effect are shown to yield results consistent with the theory of Smith-Ewart including the 0.6 power rate dependence on soap concentration. Operation under conditions where conversion per pass in the flow reactor is high and the total volume of the system is large compared to the reactor volume, is accompanied by a markedly higher soap dependence. Effects of the system engineering variables of temperature, agitation, emulsion composition, system volume ratios and flow rate are presented. Rates as high as 15 percent per minute are reported for a standard styrene emulsion. The pilot plant demonstrates the engineering feasibility of flow reaction systems utilizing radiation initiation to carry out emulsion polymerization.

Rate of Drying of Latex Films

JOHN VANDERZOFF, LEHIGH

The earlier work concerned the measurement of drying rates of latex films in small circular dishes. The thickness of the latex films was limited to about 1 mm or greater because that amount of latex had to be added to cover the bottom of the dish. These drying experiments were analyzed by plotting the cumulative water loss as a function of elapsed time. This gave a curve (Fig. 1) which could be separated into three stages: (1) an initial stage in which the rate of water evaporation is constant and about the same as that of pure water or emulsifier solution; (2) an intermediate stage in which the rate drops off rapidly; (3) a final stage in which the rate is constant (or nearly so) and about 100-1000 fold smaller than the initial rate. These three stages can be correlated with our ideas on the film formation process: (1) in the first stage, the particles are free to move about with characteristic Brownian motion and the surface available for evaporation is the cross-sectional area of the dish; (2) in the second stage, the particles come into irreversible contact with one another and the water fills the interstices between them, so that the area of the water-air interface is reduced progressively; (3) in the third stage, the particles are coalesced, and the water evaporates by diffusion through capillary channels or through the polymer itself.

More recently, thinner latex films have been studied, i. e., latex films on glass slides prepared using a drawdown bar with a 10-mil or 20-mil gap. In these cases, the elapsed time to dryness is shorter, and the drying process can be characterized by several areas (Fig. 2); (1) the total area of the film A_0 ; (2) the area of wet fluid latex A_I ; (3) the area of wet fluid latex plus the surrounding area in which the particles have come into contact with one another but have not yet coalesced A_{II} . The latexes used in these studies are monodisperse styrene-butadiene copolymer latexes formulated with additional sodium lauryl sulfate so that their surface tension-emulsifier concentration curves have leveled out at a low value. Typical results are shown for the latex of 0.444 μ diameter (39.6% solids, 10-mil drawdown, dry bulb temp. 73° F, wet bulb temp 62° F) in Figure 3 (variation of cumulative water loss with time relative to the areas A_0 , A_I , A_{II}), Figure 4 (variation of A_I and A_{II} with time) and Figure 5 (variation of rate of water loss with time relative to the areas A_0 , A_I , and A_{II}). The rate of water loss based on A_{II} is constant over a larger part of the drying schedule than that based on the other areas*. This result is to be expected since this area represents that part of the film in which the particles have not yet coalesced. Similar results have been obtained with the other latex particle sizes ranging from 0.165 to 0.589 μ . Some variation with particle size has been observed, but these differences must be confirmed.

*Please do not be misled by the scattered points of Figure 5. In these experiments, the areas are estimated using a grid underlying the glass slide. Thus the accuracy of the drying rate measurements is better than that of the area measurements. The scatter is greatly reduced by drawing a smooth curve through the points of an area-time plot (Fig. 4) and reading off the area values from this curve. This type of plot has not yet been prepared for the sample shown.

These results indicate that the drying process can be described by only two stages: (1) an initial stage corresponding to stage 1 of the earlier model; (2) a final stage corresponding to stage 3 of the earlier model. That is, the intermediate stage observed earlier may be only a transition between the initial and final stages which disappears when the film thickness is decreased far enough. And the practical applications of latexes are in films closer to 10-20 mil thickness than to 1 mm thickness.

J. W. Vanderhoff
2/14/72

FIGURE 1

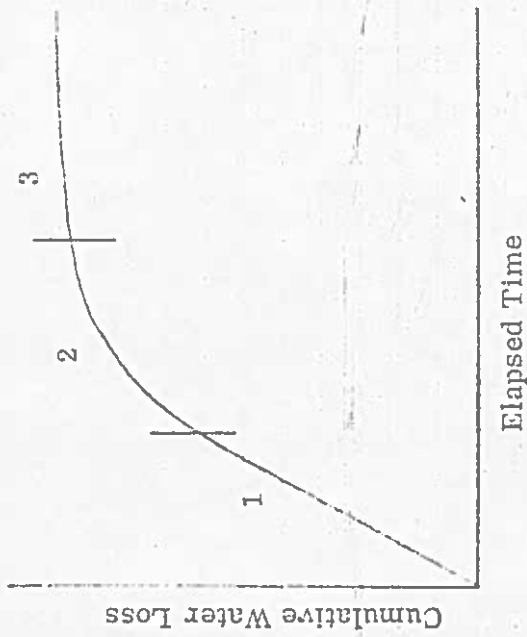


FIGURE 2

Latex Film - Drawdown on Glass Slide

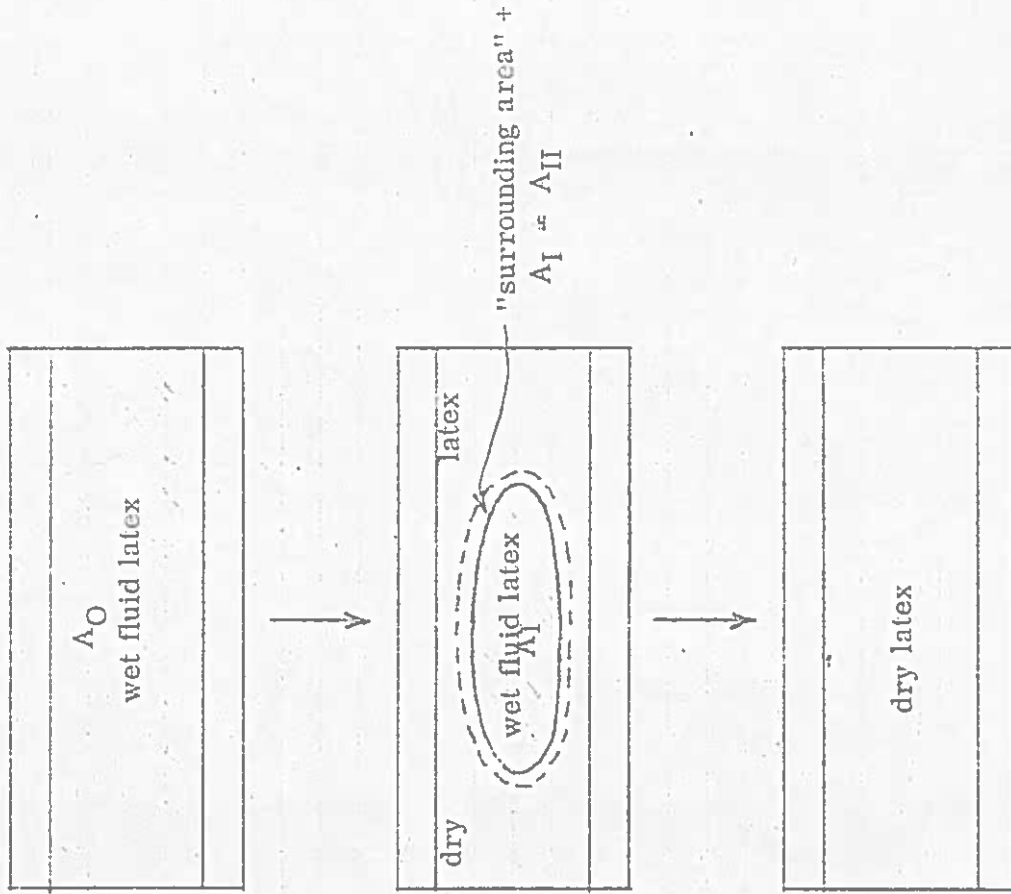


FIGURE 6

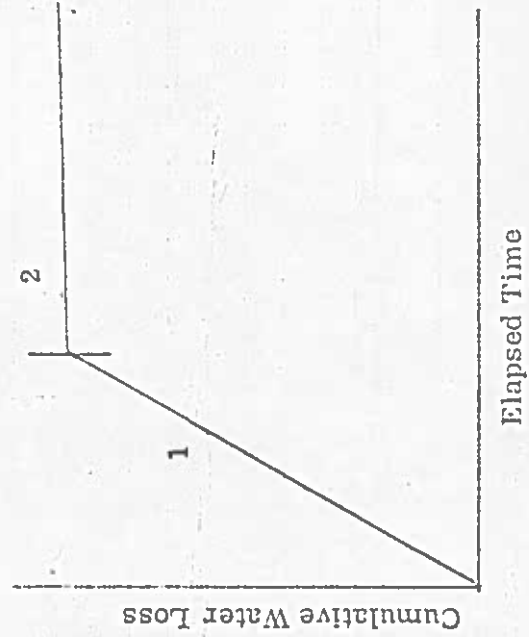


FIGURE 3 Variation of Cumulative Water Loss with Elapsed Time Relative to Areas A_0 , A_I , and A_{II}

Monodisperse 60:40 Styrene-Butadiene Copolymer
 Latex; 0.44- μ Diameter; 39.6% Solids; 10-mil
 Drawdown; Dry Bulb Temp. - 73°F; Wet Bulb
 Temp. - 62°F

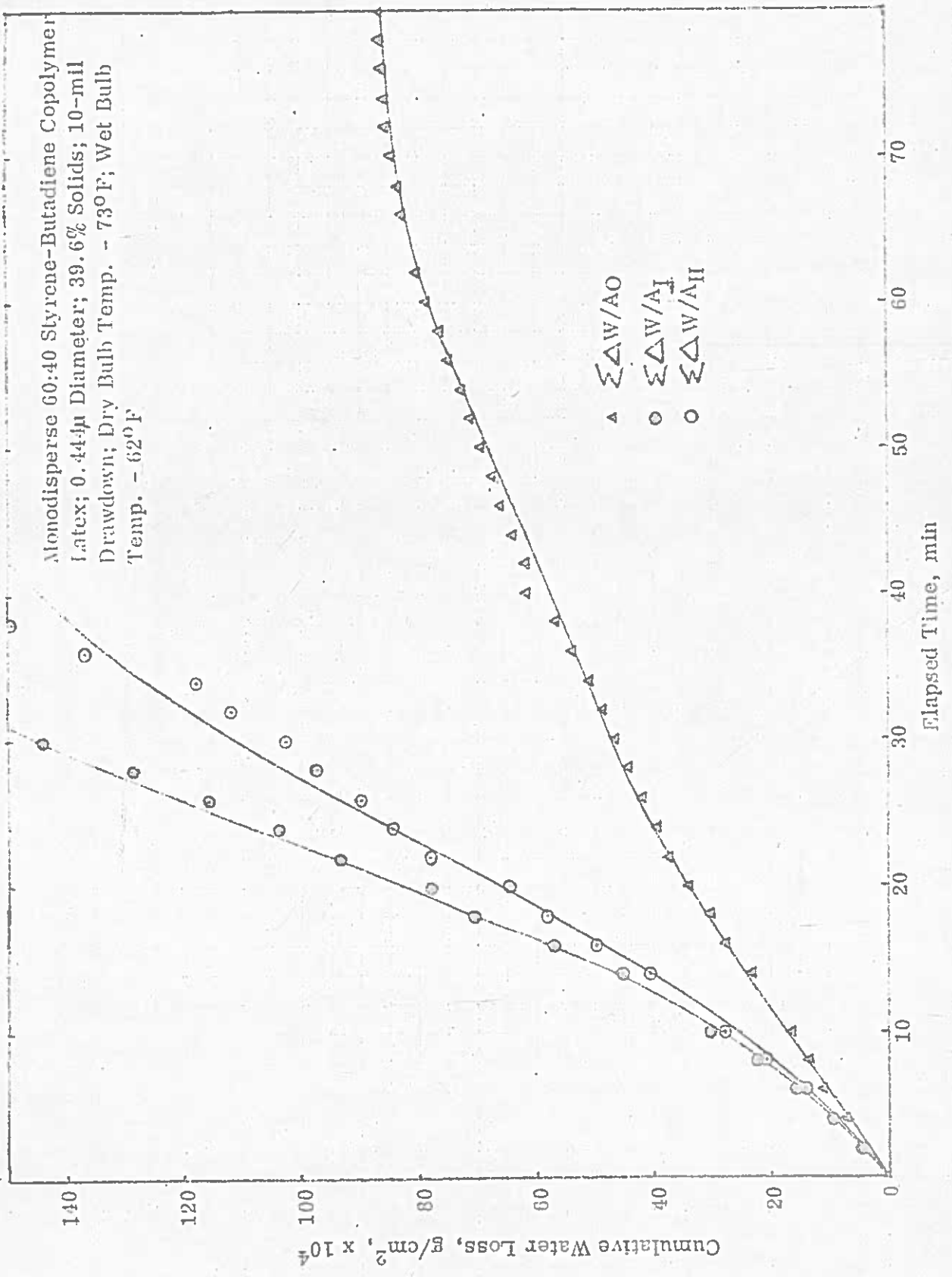
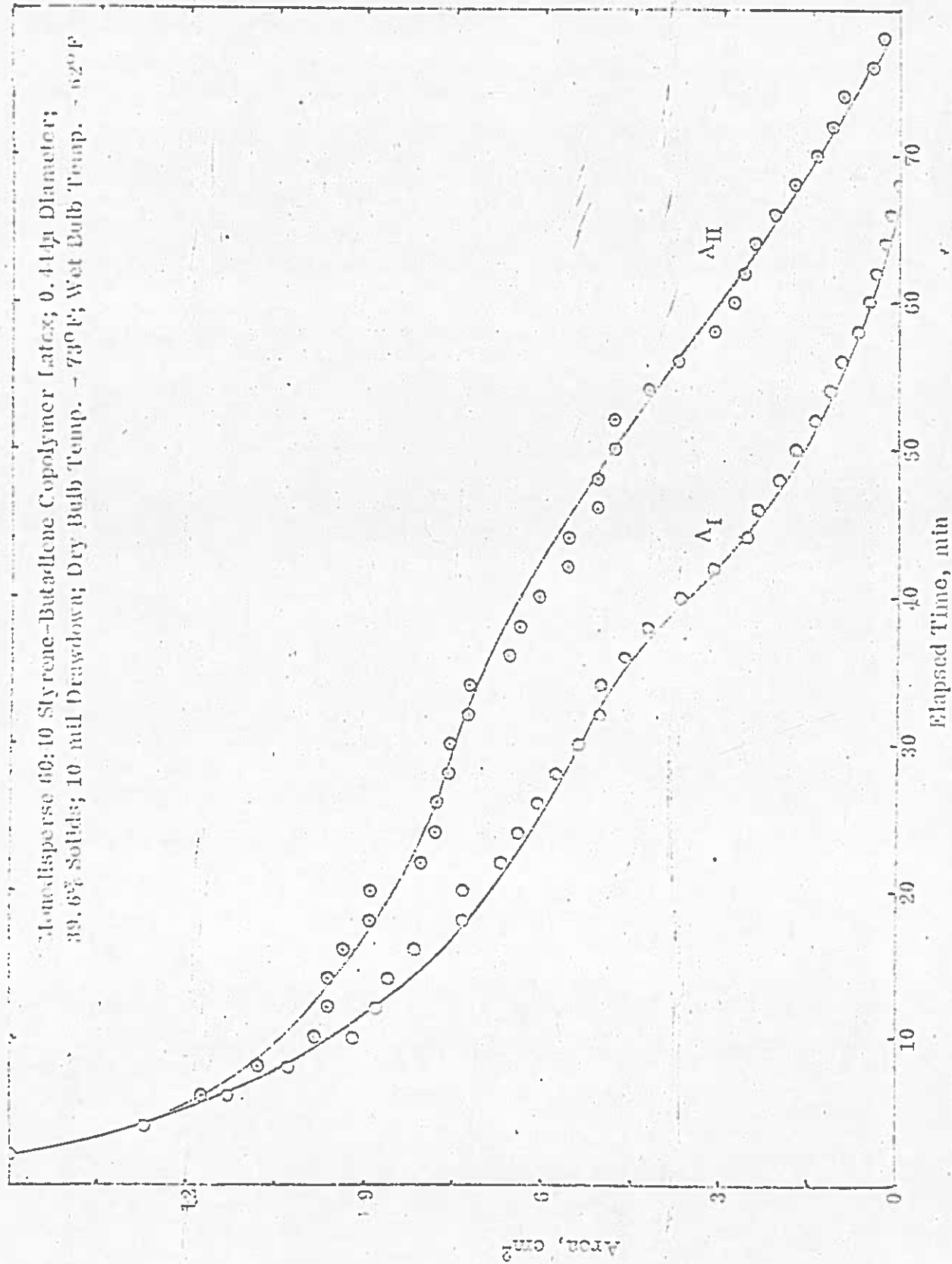


FIGURE 4 Variation of Areas A_I and A_{II} with Elapsed Time

Monodisperse 60:10 Styrene-Butadiene Copolymer Latex; 0.41 μ Diameter;
39.6% Solids; 10 mil Drawdown; Dry Bulb Temp. - 73°F; Wet Bulb Temp. - 62°F



Rate of Water Loss, $\text{g}/\text{cm}^2/\text{min}$, $\times 10^4$

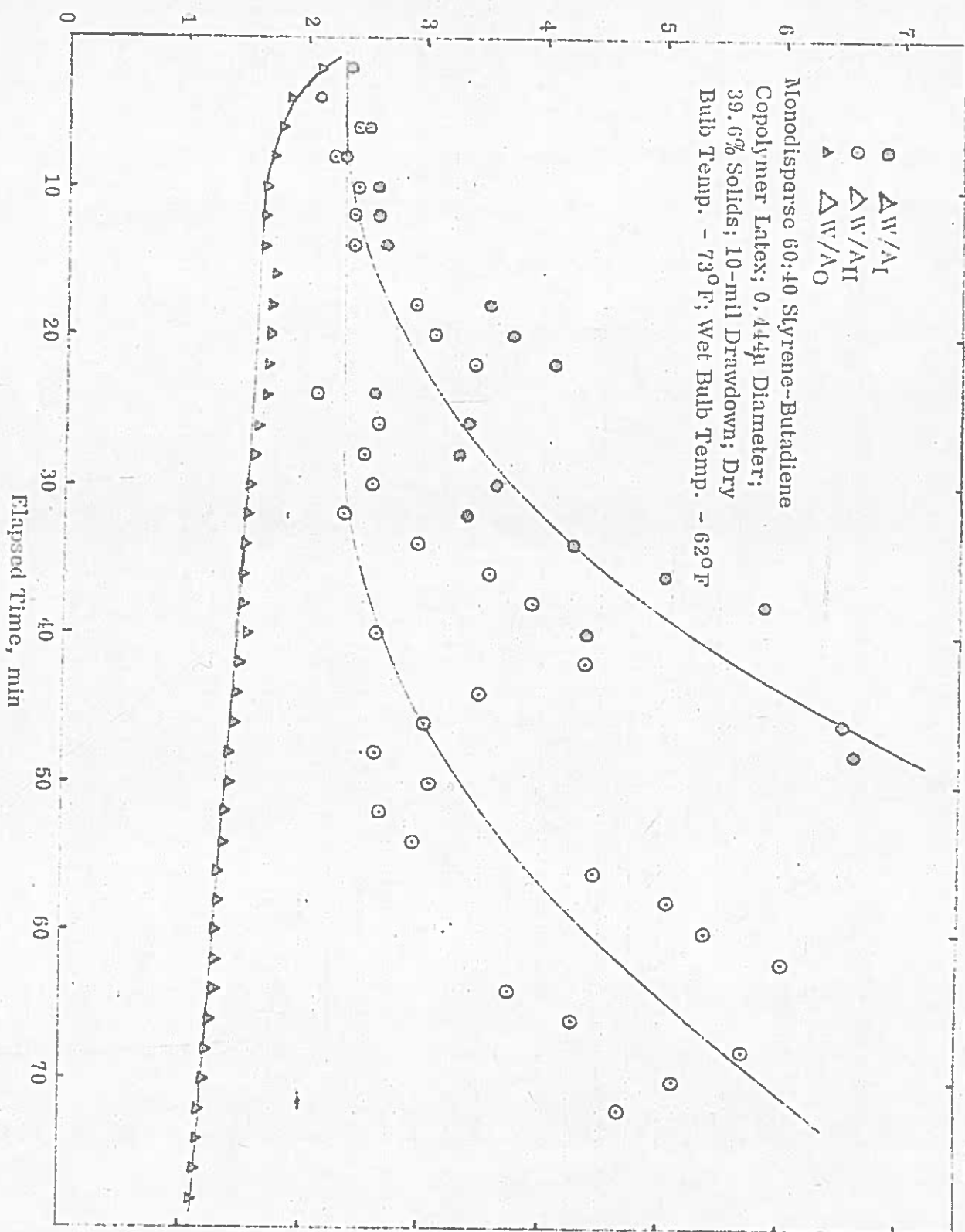


FIGURE 5 Variation of Rate of Water Loss with Elapsed Time Relative to Areas A_0 , A_1 , and A_{II}

Kinetics of Emulsion Polymerization

WALLACE

A search of the pertinent literature reveals many experimental and theoretical studies of the kinetics of emulsion polymerization. In every case only one parameter of the system was considered, namely the growth rate of a single particle or a system of particles which was considered to be monodisperse. However, an examination of the kinetics of emulsion polymerization should consider the entire distribution of particles, and the effect of growth on this distribution. Employing the light scattering method of Wallace and Kratochvil⁽¹⁾ for latex particle size analysis, based on the exact Mie theory calculations, the modal diameter and the distribution width parameter can be determined.

The kinetics of particle growth, as pointed out by Brodnyon⁽²⁾ can be expressed as:

$$dV/dt = kr^\alpha = k'V^{\alpha'}$$

where r and V are the radius and volume respectively, k is the rate constant, and α expresses the order of the reaction with respect to size. Literature values for α range from 0 to 2.5. Employing the step growth polymerization recipes of Woods, Dodge and Krieger⁽³⁾, four seed latex samples can be prepared having modal diameters in the range from 2000 - 8000 Å, in turn these samples can be accurately characterized as to modal diameter or modal volume, and the distribution width parameter. These seed latexes can then be subjected to an additional step polymerization, with aliquots removed and quenched at set intervals over the entire reaction time. Once these

samples have been characterized, the total volume per cm^3 integrated over the distribution width can be plotted vs time. Initial slopes and the rate of change in volume vs time can be determined accurately. Based upon a linear relationship of the log of the velocity (i.e. $\log dV/dt$) vs the log of the integrated volume, α can be determined from the slope and the rate constant k will be the intercept.

Employing the method of Vanderhoff et al⁽⁴⁾ two of these initial seed latexes are mixed, and the mixture subjected to a step growth polymerization after which the final modal diameters and distribution width parameter can be determined for each sample in the mixture. Instead of employing the initial and final diameters, as did Vanderhoff to calculate α , the entire distribution of particle sizes is utilized. This method can then be compared to α obtained from a single sample method, and the kinetics of the two systems can be accurately determined. The obvious extension of these methods will be a study of the kinetics under various reaction conditions.

Thomas P. Wallace and Richard S. Ehle
Chemistry Department
Rochester Institute of Technology

References

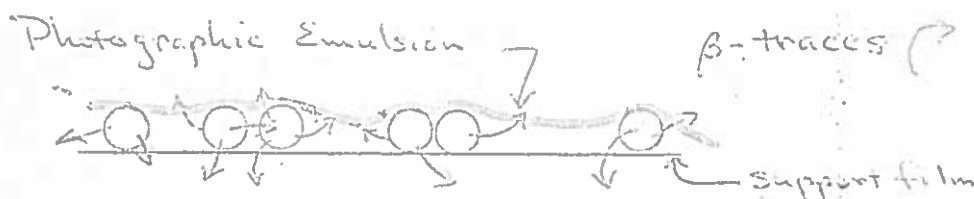
1. T.P. Wallace and J.P. Krathohvil, J. Polym. Sci. B, 5, 1139 (1967).
2. J. G. Brodnyon, J of Coll. Sci., 15, 573 (1960).
3. M. E. Woods, J. S. Dodge, I. M. Krieger, Proceedings of the Paint Research Institute, 40, 541. (1968).
4. J. W. Vanderhoff, J. F. Vitkuske, E. B. Bradford, T. Alfrey, J. Polym. Sci., 20, 225 (1956).

David J. Williams
The City College of New York

February 1972

Bob Fitch raised some questions on our autoradiographic evidence to support the core-shell morphology. I was apparently pretty fuzzy about it. With the expectation that what bothered him bothered others, I will try to present a clearer picture of what we did.

In practice it is impossible to uniformly coat the particles with photo emulsion as depicted in Figure 1-a and 1-b. Rather, the particles are placed on a parlodion coated microscope grid in the conventional manner, and then a film of the photographic emulsion is placed over them as depicted below. Exposure-time was 1608 hours. The photo emulsion was developed by standard methods.



The composite arrangement shown was then placed in the electron microscope and examined for evidence of β -particle emission. In the situation depicted not all the β -particles emitted from the particles will leave a recordable trace. Nonetheless, the fraction of β -particles directed toward the photographic film should be the same from sample to sample and no artifacts should be introduced with this technique.

The actual β -particle traces appear as the black splotches and squiggles seen in Figure 2-a. The latex particles can be seen somewhat diffusely as grey spheres under the photo film. The latex particles in Figure 2-a are the 1520A-diameter active seeds used to prepare the particles shown in Figure 2-b.

(The hexagonal close packing observed in Figure 2-b is, of course, coincidental). The particles in 2-b have a particle diameter of 4100A, i.e., a 1325A shell covers the active seed particles. The absence of splotches and squiggles means that no β -particles escaped from the active seed which is clear evidence supporting the core-shell morphology and the phenomenon of equilibrium encapsulation. Had the seed particles been uniformly swollen by the fresh inactive styrene monomer, numerous traces would have been observed, although they would have been less numerous than observed in Figure 2-a.