Polymer Colloid Group

Quarterly Newsletter

Vol. 1, No. 1, November 1971

D.J. Williams, Editor

The format, style, and contents of our first newsletter is
quite a mixture. I made no attempt to unify these elements, and
your documents were copied just as they were received. Are there
any comments or preferences for a more uniform approach? At this
time, my only suggestion is that all copy should be headed by the
following information: title, author, and date.

Of those invited to join, Morton, Dunn, and Wallace have
accepted. Time limitations prevented Morton from contributing
to this issue. I am corresponding with Napper about his possible
membership. Robertson and Stannett have not yet responded to
my letter of invitation. An address list of the current member-
ship is attached. I trust that this will bring a flood of re-
prints, preprints, etc. to my desk.

Polymer Colloid Group

Membership List

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Much of work recently has been directed towards obtaining polymer latices by polymerisation in the absence of a surface active agent, in order to avoid the problem of removing the emulsifying agent at a later stage by dialysis or ion-exchange resin treatment.   The work has been carried out by Mr. C.C. Ho and Mr. J.W. Goodwin.

A number of variables have been examined including initiator concentration, ionic strength, electrolyte type, stirrer type and speed, and temperature.   Styrene has been used as the monomer (redistilled at low temperature and pressure under nitrogen) and potassium persulphate as the initiator.

The success of the method depends upon obtaining a balance between initiator and monomer and using uniform stirring in the vessel.   We now have evidence that orthokinetic flocculation, in addition to perikinetic flocculation, plays an important role in determining the final particle size and hence the latter can be changed by varying the ionic strength of the medium.   Introduction of temperature as an additional variable means that a particle size range between 2000 and 10,000 Å can conveniently be covered (see Table 1).

Latex particles prepared in this way contain polymer of lower molecular weight than that found in particles obtained by emulsion polymerisation and hence the particles have a higher surface charge density arising from polymer end-groups.

Table 1
Preliminary results from non-emulsifier polymerisation

No.	Temp. $^{\circ}$C	Total Ionic Strength	Particle Diameter Å	Coeff. of Variation	Stirrer speed (r.p.m.)	% Conv.	M_N
Monomer conc. = 0.871 moles/litre based on total volume;					initiator conc. = 2.76×10^{-3}M		
HCC 2	70	1.29×10^{-2}	5264	2.0%	350	80	140,000
HCC 3	70	1.99×10^{-2}	6783	2.4%	350	80	91,500
HCC 4	70	2.39×10^{-2}	7125	2.9%	350	81	104,000
HCC22	55	2.39×10^{-2}	9667	1.6%	350	57	249,000
HCC23	85	2.39×10^{-2}	6430	9.4%	350	91	103,000
Monomer conc. = 0.577 moles/litre based on total volume;					initiator conc. = 2.94×10^{-4} M		
JG5/1	95	2.94×10^{-4}	2418	8 %	350	--	--

Current Interests and Activities

Robert M. Fitch

1. Particle Formation Mechanisms in Latex Polymerization

(a) Particle Formation Kinetics by Flow Apparatus Studies

(i) Reaction times of ⁻0.05 - 20 seconds

(ii) MMA with ionic radicals ($\cdot SO_4^-$, $\cdot SO_3^-$) and nonionic ($\cdot OH$)

(b) Radical Decay Kinetics via Flow Apparatus coupled with EPR

(c) Nonaqueous latex polymerization

(i) Number of particles vs stabilizer concentration

(ii) Surface adsorption of polymeric stabilizers

(iii) Polymerization kinetics by dilatometry

2. Surface Chemistry of Polymer Colloids

(a) Alkali metal ion exchange equilibria

(b) Surface group titration of acrylic latexes

(c) Stereoselective catalysis of organic reactions by surface groups

3. Ionic Nonaqueous Latex Polyermization of Acrylic Monomers

4. Synthesis of Monodisperse Acrylic Aqueous Latexes

University of Connecticut

Institute of Materials Science Equipment

Robert M. Fitch

1. Electron microscopes:

    JEOL   50 kilovolts

    RCA   ⁻80 kilovolts

    Hitachi 200 kilovolts

2. GPC - Waters Anaprep

3. Lite Scattering:

    Phoenix-Brice Dual Detector with synchronized drive and recorder

4. Ultracentrifuges

    a) Preparative - Beckman Spinco

    b) Analytical - Beckman Spinco

5. Viscometer - capillary, 4 shear rates

6. Osmometers

    (a) Membrane - Hewlett Packard Automatic

    (b) Vapor Pressure - Mechrolab

7. DSC-Perkin Elmer

8. DTA/TGA - DuPont

9. Curve Analyzer - DuPont

10. Image Analyzing Computer - Quantimet 720

Robert M. Fitch

Publications "In the Works"

1. Reaction kinetics of a redox system in hydrocarbon solvent:
    cumene hydroperoxide and aliphatic thiol. This is a free
    radical initiator at room temperature.

2. Synthesis of Acrylic Polymer Colloid Liquid Crystals; an
    Undergraduate Laboratory Experiment.

Dr A. S. Dunn,
Chemistry Department,
The University of Manchester Institute of Science and Technology,
P.O. Box 88, Manchester M60 1QD, England.

I have passed the page proofs of the lecture which I gave to the Surface and Colloid Chemistry Group of the Society of Chemical Industry in London in December 1971 on 'The role of the emulsifier in emulsion polymerisation': it should be published in "Chemistry and Industry" during October. Reprints should be available later.

Mr C.J.Tonge has completed his Ph.D. Thesis on 'Aspects of emulsion polymerisation'.   Provided that the Examiners accept it in November, the abstract could be included in the February News Letter.   This work is mainly concerned with the possibility (c.f. A.I.Yurzhenko & O.P.Brazhnikova, J. Gen. Chem. USSR, 26 (1956) 1481) that peroxydisulphate initiator decomposes at an enhanced rate at a latex or emulsion surface. We find, however, that the effect reported is really an induced chain decomposition which does not occur in the presence of monomer at initiator concentrations in the range used in polymerisation experiments. We had thought it probable that the particle surface was an important locus of polymerisation in the case of vinyl acetate because it seemed more reasonable to suppose that the rate of polymerisation would be first order in the monomer concentration in the aqueous phase than half order in the monomer concentration in the polymer phase. (A.S.Dunn & L.C.H. Chong, Brit. Polymer J., 2 (1970) 49, esp. p.57 col. 1 and Fig. 8). However Litt (J. Polym. Sci. A-1, 8 (1970) 3607) has now put forward a mechanism for this polymerisation which can (c.f. his eqn. (13)) account for a dependence of the rate of polymerisation on the square root of the monomer concentration in the polymer phase although this depends on the intervention of an isomerisation step in which a vinyl acetate radical is converted into a highly water soluble butyrolactonyl radical for which independent evidence is, so far, lacking. Nevertheless, Litt's mechanism seems to account for the evidence very plausibly so that we are now inclined to abandon the surface reaction idea again.

.Newsletter Contribution for November, 1971

Irvin M. Krieger, Case Western Reserve University

Work in progress falls into three main areas:

(1) Emulsion polymerization studies (M. Juang).

(2) Rheological studies (T.-F. Niu, M. Eguiluz)

(3) Studies of ordering in uniform sphere dispersions (unstaffed at present).

(1) Emulsion polymerization: The objective here is to be able to produce uniform polymer colloids of well-characterized charge, over a wide range of particle size. Current work is focused on styrene and divinylbenzene as comonomers, with persulfate initiation and mixtures of ionic and nonionic surfactants. Some polymerizations have been conducted with azo-bis-isobutyronitrile (VAZO) initiation, in an effort to obtain low charge densities. The purpose of incorporating divinylbenzene is to permit the polymer spheres to be subsequently redispersed into organic media, without dissolution or swelling.

The charge is determined by conductometric titration with NaOH after deionization with mixed-bed resins. A puzzling result is the fact that the oil-soluble nonelectrolyte VAZO initiator and the water-soluble electrolyte persulfate usually give similar particle sizes and charges. Some work has been done with the method of Greene, Sheetz and Filer (J. Colloid + Interface Sci. 32, 90 (1970)) to polymerize a surface-active monomer onto the particle surface, thereby augmenting the charge without significantly changing particle size. This work has been tabled, because we want strong-acid sulfate groups rather than weak-

acid carboxyls. Following Vanderhoff's suggestion, we are now looking at the incorporation of a vinyl sulfo-ester comonomer in various proportions in order to accomplish charge variation.

(2) <u>Rheological Studies</u>: Already completed (J. Colloid and Interface Sci. 34, 91, 126 (1970)) is a study of steady-shear viscometry of a "hard-sphere dispersion". Now under way is a time-dependency study on the same systems, using oscillatory shear with Fourier analysis of the response. A new instrument is under construction, utilizing computer generation of the oscillation and computer acquisition and analysis of the data. It will really be something . . . if it works! Plans are to relate thixotropic relaxation times to the time constant $t^* = \eta v/kT$, where η is the viscosity of the suspension and v the particle volume.

The other rheological topic is the "second electroviscous effect", arising from particle-particle repulsions in concentrated suspensions. Here we really need to know particle charge. The soap-free recipes of Ottewill would be most useful here. Of especial interest is the possible existence of a yield point. At present, we are still in the process of calibrating equipment and preparing and characterizing our spherical colloid suspensions.

(3) <u>Ordered Polymer Colloids</u>: Accomplishment to date is summarized in my article in Fitch's book "Polymer Colloids". My only researcher now working in this area is a part-time sophomore, but it is high on the priority list. The sophomore will measure temperature-dependence of the transition concentration. By analogy with the temperature variation of solubility, this should give the heat of the order-disorder transition. Projects stacked up awaiting staff and funds are:

October 15, 1971

Dr. David Williams
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City College of New York
New York City, New York 10031

Dear David:

Enclosed is a complete list of my publications for this first quarterly "newsletter."

Our current experimental work concerns the mechanism of latex film formation, specifically, the rate of drying of latex films and how it can be correlated with the various postulated stages of the process. This work was begun while I was still at Dow and is being continued at Lehigh. Preliminary results were reported, for the first time, at the Gordon Conference "Chemistry and Physics of Coatings" in August, 1971.

The experiments comprise measuring the variation of weight loss with time for a latex sample in a small dish (film about 1 mm thick) or a "drawdown" on a glass plate (about 0.01-0.02 in thick) in a controlled environment (72° F; 50% RH). The work done at Dow used the following latex copolymers, all of a type similar to those used in commercial applications: vinylidene chloride-$\underline{n}$-butyl acrylate; ethyl acrylate-methyl methacrylate; $\underline{n}$-butyl acrylate-methyl methacrylate; styrene-butadiene. All of these are film-formers. The work done thus far at Lehigh uses non-film-forming monodisperse polystyrene and film-forming monodisperse styrene-butadiene copolymer latexes.

The variation of polymer volume fraction with time follows a sigmoidal or S-shaped path, a form difficult to analyze; however, if the data are plotted as the total weight of water lost by evaporation as a function of time, the drying process can be divided into three distinct stages: 1. an initial stage in which the rate is constant and about the same as for pure water, and which persists up to about 50-75% by volume polymer; 2. an intermediate stage in which the rate falls off rapidly; 3. a final stage in which the rate is again approximately constant, but at a value very much smaller than that observed initially.

We propose that this initial period corresponds to the "wet" latex, i.e., the stage in which the latex particles move about with the characteristic Brownian motion. This stage ends when the particles come into contact with one another and the particle motion ceases. The intermediate stage corresponds to that in which the particles in contact with one another undergo coalescence to form a continuous film. In the final stage, the small amount of water remaining evaporates through capillary channels in the film or by diffusion through the polymer.

The current experiments comprise the measurement of the drying rates of the polystyrene latex as a function of air velocity across the face of the sample. The purpose is to study the intermediate stage, i.e., the rate of evaporation of water from a porous solid with capillaries of known dimensions. The other experiments comprise measurement of the drying rates of a series of monodisperse styrene-butadiene copolymer latexes, to determine the effect of particle size and, also, to relate the drying rate to the area of "wet" latex as opposed to the total area of the latex film (as was done heretofore).

The results will be described in later reports.

Best regards.

Sincerely yours,

John W. Vanderhoff
Associate Director-Coatings

rm

enclosure

cc: Dr. Gary D. Poehlein

(a) Systematic study of transition conditions (concentration, temperature, energy) as functions of inter-particle forces (as determined by particle charge, electrolyte level and dielectric properties of the medium).

(b) Elasticity studies on the ordered (crystalline) form, either by a modification of Ottewill's osmotic piston or by sonic velocity.

(c) Brownian movement of spheres on the lattice, by laser Doppler studies.

(d) Effect of polydispersity and nonuniformity of charge on the stability of the ordered phase.

(e) Rheo-optical effects. The ordered phase should be destroyed by rapid shearing.

TECHNICAL PUBLICATIONS — J. Vanderhoff

1. "Optical Properties of Uniform Particle Size Latexes" (Co-authors T. Alfrey, E.B. Bradford, and G. Oster) J. Opt. Soc. Am. 44, 603 (1954).

2. "Electron Microscopy of Monodisperse Latexes" (Co-author E.B. Bradford) J. Appl. Phys. 26, 864 (1955).

3. "A Motion Picture Investigation of Polymer Latex Phenomena" (Co-author E.F. Gurnee) Tappi 39, 71 (1956).

4. "The Use of Monodisperse Latexes in an Electron Microscope Investigation of the Mechanism of Emulsion Polymerization" (Co-authors E.B. Bradford, T. Alfrey) J. Colloid Sci. 11, 135 (1956).

5. "Some Factors Involved in the Preparation of Uniform Particle Size Latexes" (Co-authors J.F. Vitkuske, E.B. Bradford, T. Alfrey) J. Polymer Sci. 20, 225 (1956).

6. "An Investigation of the Mechanism and Kinetics of Emulsion Polymerization" (Co-author E.B. Bradford) Tappi 39, 650 (1956).

7. "The Particle Diameter Determination of Film Forming Latexes by Electron Microscopy" (Co-author E.B. Bradford) J. Colloid Sci. 14, 543 (1959).

8. "The Use of High-Energy Irradiation in Emulsion Polymerization Kinetic Studies" (Co-authors E.B. Bradford, H.L. Tarkowski, B.W. Wilkinson) J. Polymer Sci. 50, 265 (1961).

9. "The Particle Diameter Determination of Film-Forming Latexes by Electron Microscopy of Their Deformed Particles" (Co-author E.B. Bradford) J. Colloid Sci. 17, 668 (1962).

10. "Inverse Emulsion Polymerization" (Co-authors E.B. Bradford, H.L. Tarkowski, J.B. Shaffer, R.M. Wiley) Advances in Chemistry, Series No. 34, "Polymerization and Polycondensation Processes" p. 32, 1962.

11. "The Morphology of Synthetic Latexes" (Co-author E.B. Bradford) J. Polymer Sci. C3, 41 (1963).

12. "Mechanism of Film Formation of Latices" (Co-author E.B. Bradford) Tappi 46, 215 (1963).

13. "Self-Extinguishing Polystyrene Foaming-in-Place Beads" (Co-author A.K. Jahn) J. Appl. Polymer Sci. 8, 2525 (1964).

14. "The Use of Monodisperse Latex Particles in Medical Research" Preprints, American Chemical Society Division of Organic Coatings and Plastics Chem. 24, 223 (1964).

15. "Morphological Changes in Latex Films" (Co-author E.B. Bradford) J. Macromol. Chem. 1, 335 (1966).

16. "Theoretical Consideration of the Interfacial Forces Involved in the Coalescence of Latex Particles" (Co-authors H.L. Tarkowski, M.C. Jenkins, E.B. Bradford) J. Macromol. Chem. 1, 361 (1966).

17. "Film Formation of Latices" Proceedings, European Conference of Pulp and Paper Industrial Technology, London, September 4-9, 1966.

18. "Well-Characterized Monodisperse Latexes" (Co-author H. J. van den Hul) J. Colloid & Interface Sci. 28, 336 (1968).

19. "Desorption of Emulsifiers from Polystyrene Latexes" (Co-author H. J. van den Hul) Proc. Vth International Congress on Surface Active Substances, Barcelona, Sept. 1968, Sect. B, p. 319.

20. "Radioiodination of Latex Particles" (Co-authors J. M. Singer, C. J. Van Oss) J. Reticuloendothelial Soc. 6, 281 (1969).

21. Chapter 1. "Mechanism of Emulsion Polymerization", "Vinyl Polymerization Vol. I, Part II", G. Ham, ed., Marcel Dekker, New York, pp. 1-138, 1969.

22. "The Preparation of Monodisperse Latexes with Well-Characterized Surfaces" (Co-authors H. J. van den Hul, R. J. M. Tausk, J. Th. G. Overbeek) "Clean Surfaces: Their Preparation and Characterization for Interfacial Studies" G. Goldfinger, ed., Marcel Dekker, New York, 1970, p. 15.

23. "Inferences on the Mechanism of Emulsion Polymerization from Characterization of the Polymer Endgroup" (Co-author H. J. van den Hul), Brit. Polymer J. 2, 121 (1970).

24. "Mechanism of Film Formation of Latices", British Polymer J. 2, 161 (1970); Paint & Varnish Production 60 (12), 25-37 (1970).

25. " 'Clean' Monodisperse Latexes as Model Colloids" (Co-author H. J. van den Hul), "Polymer Colloids", R. M. Fitch, ed., Plenum Press, New York, 1971, p. 1.

26. "Effect of Ion Exchange on Latex Stability", (Co-authors G. D. McCann, E. B. Bradford, H. J. van den Hul), "Polymer Colloids, R. M. Fitch, ed., Plenum Press, New York, 1971, p. 29.

27. "Effect of Ion Exchange on Latex Particle Size Distribution", (Co-authors G. D. McCann, E. B. Bradford, H. J. van den Hul), J. Colloid & Interface Science, 36, 1, May, 1971.

28. "The Characterization of Latex Particle Surfaces by Ion Exchange and Conductometric Titration" (Co-author H. J. van den Hul), submitted October, 1971, to J. Electroanal. Chem. & Interfacial Electrochem.

Georg Pochten - Lehigh

I shall attempt, in this first report, to outline my past and present work in the emulsion polymer field. This should not be too time-consuming since my tenure in polymer research is shorter and my contributions fewer than those of the other members of our group. I came to Lehigh in 1965 with a background that included one polymer survey course and an M.S. Project on the theoretical aspects of molecular weight distributions of polymers produced in bulk free-radical systems.

While looking around for suitable academic polymer kinetics research I was motivated toward emulsion polymerization for two reasons. First, an article describing a bottle polymerizer convinced me that nothing could be simpler. Stories of high viscosities, mixing problems, reactor control, etc. associated with bulk and solution reactions were frightening. But here was a system that was as easy as turning a bottle under water.

The second motivation stemmed from a belief on my part that continuous reactors were destined to become more important commercially. At that time I could find almost no fundamental research on using continuous reactors to carry out emulsion polymerizations. In addition to the potential practical application of data from a continuous stirred-tank reactor, I also felt that the data could be of considerable fundamental value. Hence research in this area was begun in 1966, with Mr. Andrew DeGraff, a graduate student who finished his Ph. D. in 1970. At present I have a Ph. D. continuing this work and an undergraduate working on semi-continuous systems.

Continuous Emulsion Polymerization: Dr. DeGraff's work involved a theoretical and experimental study of the emulsion polymerization of styrene in a single continuous stirred-tank reactor. Fig. 1 shows a rough flow diagram of the experimental system.
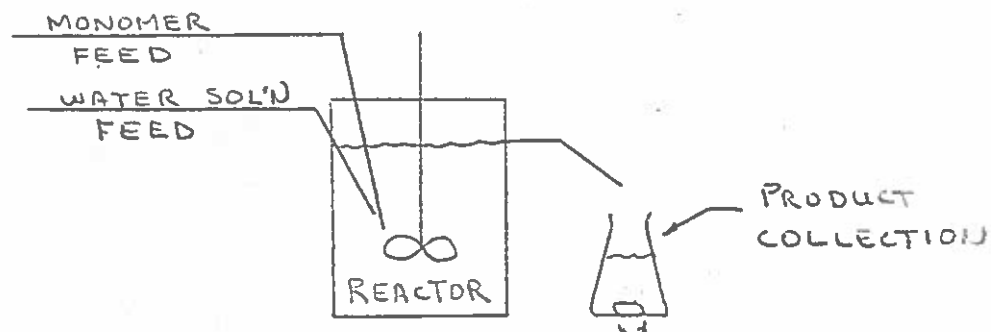

FIGURE 1   SIMPLIFIED FLOW DIAGRAM

The CSTR is different than batch reactors for several reasons. First, the three distinct polymerization intervals referred to by Harkins and Smith & Ewart cannot exist here. Instead, particles must be formed in the presence of many particles. Second, the age distribution of particles in the reactor product is very broad, as given by Eq. 1.

1) $f(t) = \dfrac{1}{\theta} e^{-t/\theta}$

where θ is the mean residence time; i.e. the reactor volume divided by the volumetric feed rate.

DeGraff assumed that particle formation could be described by Eq. 2.

2) $N = R_i \theta \dfrac{\{A_f\}}{\{a_s S\}}$

Where N is particle concentration in the product stream, R_i is the rate of initiation, a_s is the adsorption area per molecule of surfactant, S the surfactant concentration in the feed stream, and A_f is the area covering capability of the unadsorped surfactant. Using Smith-Ewart Case 2 concepts as modified by Stockmayer we were able to develop theoretical predictions for the particle concentration, rate of polymerization, particle size distribution, and molecular weight averages. If the particles were small enough that Stockmayer's modification was not required the following results were obtained for N and R_p:

3) $N \propto [s]\, \theta^{-2/3}$

4) $R_p \propto [s][M]\, \theta^{-2/3}$

where R_p is the rate of polymerization and [M] is the monomer concentration in the particles. Our experimental data for styrene and that of Gerrens and Kuchner (1) and Gershberg and Longfield (2) followed the predictions of Eqs. 3 and 4 with some deviations in N at larger mean residence times, θ.

Gerrens and Kuchner (1) also studied methyl acrylate. They found the particle concentration to be as predicted by Eq. 3 but the measured polymerization rate was considerably different from that predicted by Eq. 4. R_p for methyl acrylate was found to follow Eq. 5.

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

This data raises some questions like:

1. Where is the reaction taking place?

2. What is $\bar{n}$?

3. Can free radicals transfer out of a particle?

We plan to examine Gerrens' data more carefully in the near future in an attempt to answer these questions.

Our theoretical predictions of particle size distribution were within the accuracy of experimental measurements. At low to moderate values of θ (7 to 30 minutes) a particle growth model based on S-E Case 2 kinetics was adequate. At high values of θ it was necessary to incorporate Stockmayer's modification into the model in order to predict the skewing of the distribution toward larger particles. Gerren's did not measure PSD so I don't know how methyl acrylate particles might grow.

Katz, Shinnar, and Saidel (3) suggest that polymer ^(in monodisperse particle systems,) formed during interval 2 should, in the absence of transfer reactions, have an Mw/Mn value of 2.0. If this is accepted and we worry about the way free radicals move into particles we should be able to compute an Mw/Mn ratio for our widely dispersed particle sizes. In fact, if one assumes a free radical entry rate proportional to particle area as suggested by Gardon, it can be shown that Mw/Mn should be 4.84 for product from a CSTR. Our measurements of Mw/Mn averaged 3.07 for 37 runs; considerably less than 4.84. Values near 3.0 have also been reported for batch and semi-continuous systems. Questions:

> 1. What mechanism controls the rate of entry of free radicals into particles?
>
> 2. What is the degree of polymerization of the free radicals when they enter the particles?

A paper describing our work with styrene should appear in the next issue or two of the J. Poly. Sci., A-1. Sorry, but I don't have any preprints.

Current and future work will involve similar CSTR studies (θ, Ri & S will be varied) with monomers more water soluble than styrene. Tentative plans include work with vinyl acetate, methy methacrylate, and methyl acrylate.

Semi-Continuous Systems: In addition to the continuous work I have an undergraduate working on semi-continuous emulsion polymerization of styrene. He has developed a theory for particle size distribution and is now attempting experimental verification.

By varying the rate and timing of post emulsion additions to the reactor one should be able to produce narrow or broad distributions. We are attempting to make narrow and bi-modal products at the present time.

Drying of Latex Films: Outside of the kinetics area I am involved with John Vanderhoff on some film drying work. I assume John will describe this in his report.

References Cited

1. H. Gerrens and K. Kuchner, British Polymer J., 2:(1-2), 18 (1970).

2. D. B. Gershberg and J. E. Longfield, Preprint 10, Sym. Poly. Kinetics and Catalyst Systems, 45th A.I.Ch.E. Meeting, New York (1961).

3. S. Katz, R. Shinnar, and G. Saidel, Ch. 8 in "Addition and Condensation Polymerization Processes", Adv. in Chem. Series, 91, ACS, Washington, D.C. (1969).

Equipment

Our equipment is rather limited at Lehigh. We have:

1. Continuous reactor system.
2. Electron microscope.
3. Normal analytical equipment, e.g. vacuum ovens, balances, etc.
4. Light scattering devices.
5. Ultracentrifuge.
6. Couette viscometers.

Our molecular weight measurements were made on a GPC at Air Products & Chemicals, Inc. in Trexlertown.

PROGRESS REPORT — T. Wallace - R.I.T.

Recent reports from this laboratory have outlined methods of size

distribution analysis of polymer latex systems based on the observed

extrema in the angular light scattering pattern of either the

vertically polarized component of scattered light or the

polarization ratio (i.e., ρ, the ratio of the intensities of the

horizontal and vertical components of scattered light). Both

methods initially require extensive Mie calculations, and the

subsequent preparation of diagrams for use in future size distribution

analyses. The observed angular position of the minima enables

one 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. The study presently

underway has the same basis but is designed to determine the

feasibility of using unpolarized and horizontally polarized scattered

light as the basis for size distribution analysis.

T. P. Wallace
R.I.T.

Report of David J. Williams

The City College of New York

November 1971

D.H. Napper recently published a note in The Journal of
Polymer Science to express his reservations concerning the
acceptability of the core-shell model in styrene emulsion poly-
merization. My reply was recently submitted to the J.P.S., and
it is attached for your reference.

Our efforts of the past two years have been directed toward
two objectives: (1) to obtain additional physical evidence for
the existence of the core-shell morphology and (2) to derive a
theoretical explanation for its formation. I will review pro-
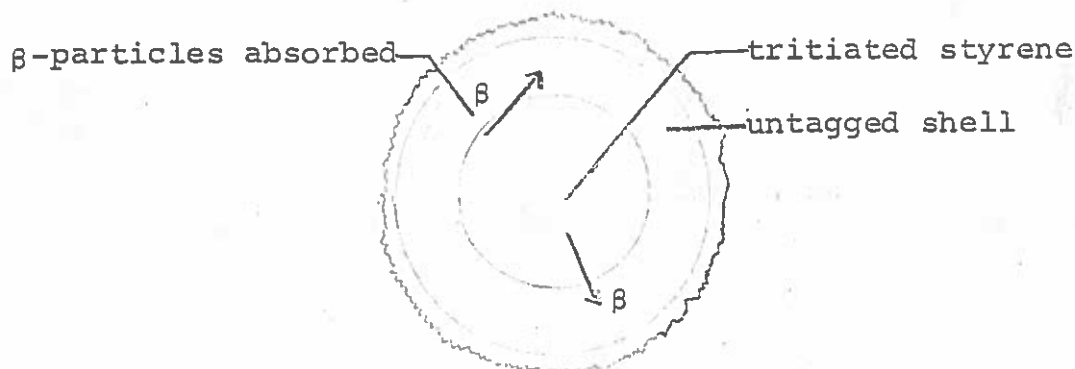gress on item (1) in the present communication and item (2) in
the next.

The core-shell morphology was suggested by the results of
kinetic studies (J.P.S., A-1, $\underline{8}$, 2617 (1970)). Direct physical
evidence was obtained by "spiking" a run in progress (at 20%
conversion) with trace amounts of butadiene so that the final
product was comprised of a polystyrene-core surrounded by a
poly(styrene-co-butadiene)-shell. Upon embedding, slicing,
staining and viewing in the electron microscope, doughnut struc-
tures were observed, thereby corroborating the proposed model.
Subsequent work with butadiene-tagging was executed with seed
lattices, reswollen to conditions of equilibrium saturation
(Polymer Preprints, $\underline{12}$, No. 1, 464 (1970)). This work showed
that when fresh monomer (or solvent) is added to seed particles,
equilibrium encapsulation occurs rather than uniform swelling

and that the two-phase behavior is observed over a wide range of
particle diameters - 500 to 6000$\overset{\text{o}}{\text{A}}$.

There are two limitations inherent in the use of butadiene
tagging and subsequent particle slicing as a means of physically
observing the core-shell morphology. One could argue that the
two-phase morphology revealed in our butadiene tracer work was
caused by the incompatibility between the polystyrene molecules
of the seed particle and the poly(styrene-co-butadiene) mole-
cules of the second generation of growth. The problem of in-
compatibility was first discussed with reference to the experi-
ment in which a run in progress was "spiked" with butadiene.
In subsequent works we utilized less than 0.7 (wt)% butadiene
and never observed evidence of incompatibility. Although we had
good reason to conclude that incompatibility was not affecting
our arguments, we felt it imperative to establish an insolubil-
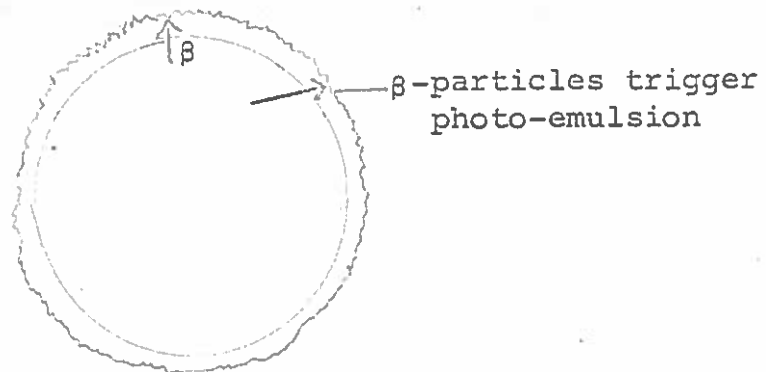ity free test.

A second limitation is imposed by the method used to ob-
tain the ultra-thin sections for viewing in the electron micro-
scope. We find that only isolated, single-particles in the im-
bedding resin yield effectively to ultra-microtomy. In pre-
paring the samples for slicing, we have been unable to effec-
tively disperse the particles, and they tend to agglomerate in
the embedding resin. The knife merely scrapes over these agglom-
erates, and singly dispersed particles are uncommon. Finding
the confirming structures in the electron microscope is then
akin to looking for the proverbial needle in the haystack. Con-
sequently, this approach could never have a statistical basis.

To eliminate these limitations, plus any others one might associate with the butadiene tagging and slicing technique, we undertook a series of experiments that utilized tritiated styrene as the tagging agent and autoradiography as the detecting method. Tritiated styrene could never be argued to introduce compatibility problems, and the experiments were performed in such a way that slicing was not required and thousands of particles could be observed. Ordinarily, the technique involves the use of radioactive tracer elements which have been incorporated into a given sample. The location of the tagged molecules within a sample can be ascertained by coating with a fine grained photographic emulsion. The exposed silver grains in the photographic emulsion then determines the position of the tagged molecules in the sample when observed in the electron microscope.
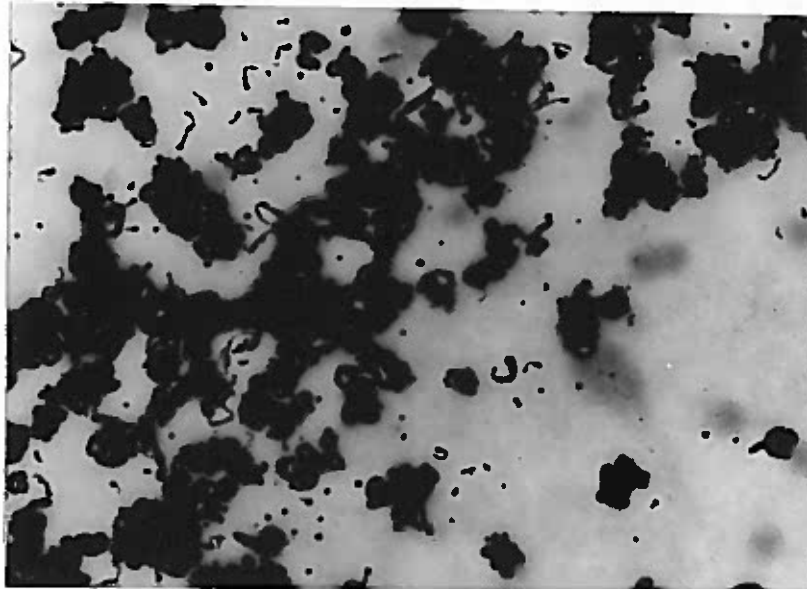

Tagged-core, untagged-shell particle
Core diameter = 1520Å, shell thickness = 1330Å

Figure 1-a

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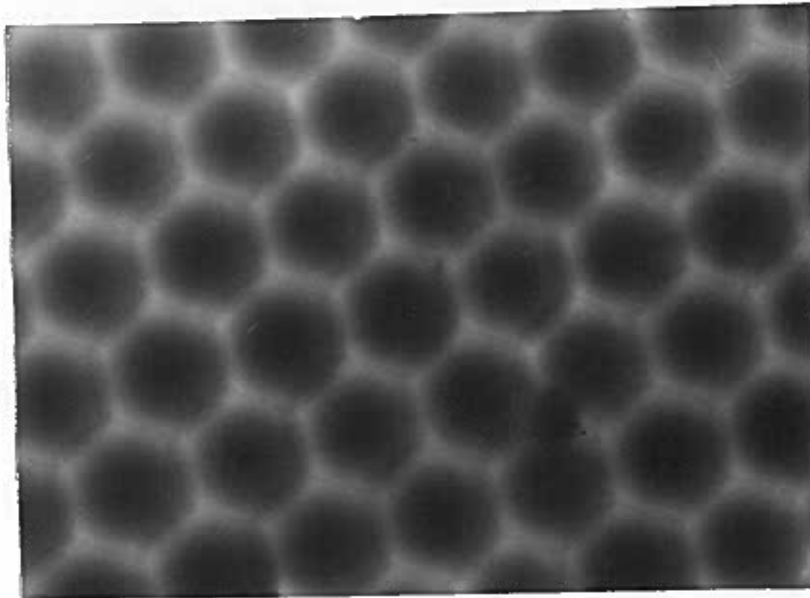The City College of New York

β-particles trigger
photo-emulsion

Uniformly tagged particle
Diameter = 3410Å

Figure 1-b

Control particle with tagging throughout

Figure 2-a

Tagged-core-untagged-shell particle

Figure 2-b

A 1520Å-diameter, tagged-seed particle was twice overcoated under equilibrium saturation conditions with untagged styrene to produce a final untagged shell thickness of 1330Å. Tritium as a low energy emitter (maximum of 18 KeV) has a track length of only 500 to 800Å in a material such as polystyrene. If the particles so constructed were truly core-shell in structure, adsorption should occur as depicted in Figure 1-a and the photographic emulsion coating the particles should not become exposed.

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In order to provide a basis for comparison a 3410$\overset{\text{O}}{\text{A}}$ diameter particle was prepared with tagging throughout. Such a particle (Figure 1-b) should show numerous traces.

Our results are shown in Figures 2-a and 2-b. As predicted innumerable traces are observed in the control (Figure 2-a) and none are observed in the tagged-core-untagged-shell particle (Figure 2-b). These results constitute the most convincing evidence yet presented to support the core-shell morphology.