Polymer Colloid Group
Quarterly Newsletter

Vol. 2, No. 1, October 1972

21 DEC

D.J. Williams, Editor

It is with great pleasure that I present you with our first anniversary issue. I trust that you will find it as informative and stimulating as the first.

Congratulations are due Gary Poehlein who has just received an NSF grant to support his research on continuous emulsion polymerization.

Ron Ottewill and Tom Wallace have excused themselves from this issue, but we look forward to hearing from them next time.

Which reminds me. Contributions to the February issue are due in my office by mid-January. I look foward to hearing from you then.

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Polymer Colloid Group Newsletter - September 1972

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

The results of the two projects mentioned in the February Newsletter are now available.

Nichols investigated the tacticity of polymethyl methacrylate produced in an emulsion system with interfacial initiation. Cetyl pyridinium chloride is used as emulsifier: in alkaline solution it is partially hydrolysed and also acts as the reductant in a redox initiating system in which benzoyl peroxide is the oxidant. Medvedev and his collaborators (c.f. references cited in the May Newsletter and others cited therein) have repeatedly claimed that initiating systems of this type effect stereospecific polymerisation which is supposed to occur in the emulsifier layer, e.g. Trubitsyna, Margitova, & Medvedev, Doklady Phys. Chem. 166 (1966) 92: in some cases the amine reductant/emulsifier is itself an isotactic polymer e.g. partially hydrolysed isotactic poly-2-vinyl pyridinium bromide (Chernikhov & Medvedev, Dokl. Phys. Chem. 182 (1968) 795). If this effect could be verified it might have some potential industrial interest as a means of varying the properties of films formed from polymer latices besides the academic interest of the surfactant influencing the course of the polymerisation.

However the redox initiated polymerisation proceeds at a high rate at room temperature and the syndiotacticity of polymethyl methacrylate is known to increase with decreasing temperature so that careful quantitative measurements are required to establish whether the tacticity of the polymer produced with these emulsifier systems differs from that obtained by radical polymerisation in a homogeneous system at the same temperature. Although the Russian workers refer to kinetic measurements with other monomers they do not report any tacticity determinations on other polymers.

The high reaction rates obtained with the CPC/peroxide initiating system mean that efficient cooling is required to prevent the temperature of the reaction mixture rising. If the temperature is not controlled well enough the product might be characterised as a stereoblock polymer when, in fact, it was a mixture of molecules of different tacticities formed at different temperatures.

Polymers from four preparations were characterised by infra-red, D.T.A. determination of T_g, and n.m.r. The Preparations were:

(2) 3.3% CPC on water and 0.4 % Bz_2O_2 on monomer in bicarbonate buffer at 14°C, pH 10.

(5) 6.6% CPC on water and 0.4 % Bz_2O_2 on monomer with 0.05 % bromotrichloromethane (as a transfer agent to reduce the molecular weight and thereby improve the n.m.r. spectra) in bicarbonate buffer at pH 10 at 20°C.

(3) 3.3 % CPC and 0.4 % Bz_2O_2 at pH 7 with 0.2 % dimethylaniline as the reductant (an incidently also acting as an efficient transfer agent) at 20°C

(4) Photochemical bulk polymerisation of methyl methacrylate as 50 % solution in toluene at 20°C with 1% benzoyl peroxide as photosensitiser,

Since the glass transition temperature T_g depends also on the molecular weight which varied widely between these products it did not prove a very useful parameter for the characterisation of the tacticity of the products.

J values were calculated with an estimated error of 4% from i.r. spectra according to the method of Goode et al. (J. Polym. Sci. 46 (1960) 317). Values obtained were:

Run No.	2	5	3	4
J	119	116	122	120

Values for radical polymerised polymethyl methacrylate at ca. 60°C are usually in the range 95 - 100 whilst more syndiotactic specimens fall in range 100 - 115 and isotactic material in range 25 - 35. All the specimens appear to have closely similar tacticity corresponding to that to be expected from the temperature of polymerisation.

Although n.m.r is generally agreed to be the best method for the characterisation of tacticity, it proved difficult to get good spectra in which the appropriate peaks were well resolved. A preliminary evaluation of the spectra gave results in accord with those from the i.r. spectra but the use of a DuPont curve resolver seems to be indicated to obtain quantitative results. So far, I have not been able to trace such an instrument in Manchester, but Bob Fitch has kindly promised to do the necessary work on the University of Connecticut's machine so that the hope that members of the Group would be able to help others out in such circumstances looks like being realised!

Our preliminary conclusion isthat there is no stereospecific effect and that the Russian workers probably did not realise the effect of temperature on the tacticity of polymethyl methacrylate.

DIVISION OF

TITLE OF PAPER

Time Required: F-1

AUTHORS	Complete Business Mail Address	ACS Member?	Division Member?	American Chemist or Chemical Engineer?
<u>Robert M. Fitch</u>	Department of Chemistry and Institute of Materials Science, University of Connecticut, Storrs, Connecticut 06268	yes	yes	Chemist
Yashavanth K. Kamath	Department of Chemistry and Institute of Materials Science University of Connecticut Storrs, Connecticut 06268	yes	yes	Chemist

Work done at UConn, IMS

Plan ACS ___ nonACS X publication. Where? J. Indian Chem. Soc. ___ No ___ Uncertain

Presentation requires projector: 2x2" (35 mm) X 3¼x4" (standard) ___ Overhead ___ Vu-Graph ___ Film: 8 mm ___ 16 mm ___ Sound ___ Other equipment (specify) ___

ABSTRACT. 200 words or equivalent. TITLE OF PAPER, Authors' Names, Addresses with Zip Code. One-Line Space. Abstract. Single-space typing. Use *full width* of ruled area below.

SURFACE CHEMISTRY OF AMPHIPATHIC GRAFT COPOLYMER STABILIZERS IN POLYMETHYL METHACRYLATE ORGANOSOLS. <u>Robert M. Fitch</u> and Yashavanth K. Kamath, Department of Chemistry and Institute of Materials Science, University of Connecticut, Storrs, Connecticut 06268.

The intrinsic stabilizing capacity of two amphipathic polymeric organosol stabiilzers has been assessed. A "feather"-type molecule, whose lyophilic portions were based on polylauryl methacrylate (LMA), was found to stabilize ca. 2.6 x 10^6 cm^2 per gram of polymer adsorbed. A "comb"-type molecule, whose lyophilic moieties were based on poly-12-hydroxy stearic acid (PSA), stabilized ca. 1.6 x 10^6 cm^2 per gram. We propose that the superior performance of the "feather"-like polymer arises from its greater density of lyophilic chain segments in the solvated layer which it creates at the sol particle/diluent interface. Entropic factors are probably responsible for a higher repulsive potential upon interparticle collisions.

We have confirmed the findings of Osmond and Walbridge that the surface concentration of stabilizing groups is relatively independent of organosol particle size and total surface area, in spite of the fact that we used different techniques in the synthesis of both organosols and LMA stabilizer.

These results also support our previously proposed mechanism of particle formation of polymer colloids, both aqueous and organic, in which homogeneous nucleation and limited flocculation determine the final particle concentration.

MAIL ABSTRACT TO PERSON NAMED IN ACS DIVISIONAL DEADLINES PUBLISHED (JUNE & DEC.) IN C&EN

K-1

CASE WESTERN RESERVE UNIVERSITY

POLYMER COLLOID NEWSLETTER, OCTOBER, 1972

Emulsion Polymerization Studies (M. Juang)

Our work has concentrated on the emulsifier-free recipes for producing monodisperse polystyrene latices, which were recommended by Dr. Ottewill. We have found our resin kettle reactors to be satisfactory; with their slow "folding action" stirring using wide paddles as stirrer blades, the solids content can be raised to 20%. High initiator levels give larger particle sizes, as reported by Ottewill. We find that addition of an inert electrolyte such as K_2SO_4 has the same effect on particle size as additional initiator. With seeding, uniform particle sizes up to 2μ have been achieved.

In order to augment particle charge, vinyl sulfo-ester comonomer was added to the emulsifier-free recipes. Smaller monodisperse particles result, down to 0.11μ. Conductometric titration (after ion exchange) shows charge densities of from 3 to 30% of monolayer coverage, whereas coverages up to 85% were achieved with the mixed-emulsifier recipes.

Electroviscous Effect (M. Eguiluz)

Deionized monodisperse latexes have been found to exhibit yield points; and their viscosity vs. shear rate behavior is well approximated by the Casson equation. Current work is aimed at "roughing out" the dependence of the flow behavior on polymer content and on electrolyte level. Electrolyte type and specific ion effects are also under study.

K-2

For example, Ca^{++} and Mg^{++} ion concentrations produce the same electroviscous effect at high and at low electrolyte levels, but there is a marked difference at intermediate levels, with Ca^{++} producing the greater effect.

Order-Disorder Transition (S. Gottschalk)

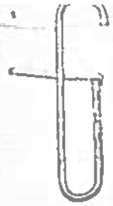
During the summer, a computer program was written to integrate the Poisson-Boltzmann equation for a shell model of the ordered spherical-particle colloid. Since Mr. Gottschalk is an undergraduate student, work in this area has made no progress as yet this semester. We hope to put a full-time graduate student to work on this project some time this Fall.

Time-Dependent Rheology (T.F. Niu)

The computer-rheometer coupling has received most of Mr. Niu's attention during the past few months. With the aid of a summer pre-college student (Larry Rogers), a program was written whereby the computer generates a ramp function, driving the rheometer from zero shear to a maximum and then back to zero. This program measures steady shear behavior over a range of shear rates when the period of ramp generation is long, and generates "thixotropic loops" when the period is comparable to the relaxation time of the fluid.

The 8-bit digital-to-analog converter provided with our Lab-8 computer proved to be the factor limiting our experimental accuracy. It was replaced by a 12-bit converter, which was constructed from commercial modules. This necessitated some rewriting of our computer programs. This work is almost completed, and we hope to get on with our measurements of thixotropic relaxation processes in polymer colloids.

You should all have received reprints of a review article on "Rheology of Monodisperse Latiçes".



POLYMER - COLLOIDS NEWSLETTER - D.H.NAPPER

AQUEOUS ENTROPICALLY STABILIZED LATICES

One of the features that distinguishes sterically stabilized dispersions from electrostatically stabilized dispersions is their response to temperature changes. Some sterically stabilized dispersions flocculate on heating; others flocculate on cooling; still others (in principle at least) do not flocculate either on heating or on cooling.

This behaviour can be understood in terms of the thermodynamic factors that control stability. Those dispersions that flocculate on heating are prevented from flocculating at lower temperatures by enthalpic interactions; the accompanying entropy changes actually promote flocculation. Only if the temperature is high enough does the $-T\Delta S$ term exceed the ΔH term and flocculation result . Stability imparted in this way is termed enthalpic stabilization. Several industrially important steric stabilizers, such as poly(ethylene oxide) and poly(vinyl alcohol), are good enthalpic stabilizers in water. For dispersions that flocculate on cooling the position is just the reverse: the entropy changes on close approach of the particles oppose flocculation whereas the enthalpy changes promote it (so-called entropic stabilization). Poly(ethylene oxide) in methanol is a good example of an entropic stabilizer. Dispersions that do not flocculate at any accessible temperature may be stabilized by a combination of enthalpic and entropic interactions.

Ottewill some years ago rightly pointed out in an Annual Reports review that enthalpic stabilization appeared to be the most common form of steric stabilization in aqueous systems whereas entropic stabilization was the most common mode in non-aqueous systems. Indeed at that time no examples of entropic stabilization in water were apparently known.

We have now prepared two examples of polymer latices which are entropically stabilized in water. Poly(acrylic acid) in 0.2 M HCl (to suppress any electrostatic effects) has been shown to function as an entropic stabilizer in water because dispersions that are stabilized by PAA flocculate on cooling. Interestingly poly(methacrylic acid) appears to be an enthalpic stabilizer in water. Polyacrylamide in water is also an entropic stabilizer, the latices obtained exhibiting robust stability to most good flocculants (e.g., addition of 36 N H_2SO_4 results in the latices charring rather than flocculating). The methods for preparing these latices have been published in Polymer Letters, <u>10</u>, 449 (1972).

EMULSION POLYMERIZATION RESEARCH -- G. W. Poehlein -- October Issue, Polymer Colloid Newsletter

I began this summer by starting to try to develop a more general model for emulsion polymerization in a single continuous stirred-tank reactor. While some progress was made in this direction, the most complete fruits of my efforts involved the exploration of several side tracks. These are outlined briefly below. More complete preprints on these topics have been sent to members of the Polymer Colloid Group.

1. Competive Growth of Polystyrene Particles: A widely-accepted particle-growth relation for single latex particles is given by Equation 1.

$$\frac{dV}{dt} = \frac{\pi D^2}{2}\frac{dD}{dt} = K_1 \; [M] \; \bar{n}$$

where V is particle volume, D is particle diameter, $\bar{n}$ the number of free radicals in the particle, [M] the monomer concentration at the polymerization site, t is time, and K_1 a constant dependent on the propagation rate constant, reaction conditions and particle swelling.

Smith and Ewart Case-2 kinetics, which seem to be valid for small polystyrene particles, indicate that $\bar{n} = 1/2$. Thus for these small particles Eq. 1 could be written as follows:

$$\frac{dV}{dt} = \frac{K_1 [M]}{2} \qquad (2)$$

For very large particles one would assume that bulk kinetics would apply and $\bar{n}$ would be proportional to particle volume. In this case Eq. 1 becomes:

$$\frac{dV}{dt} = K_2 [M] \; D^{3.0} \qquad (3)$$

where K_2 is a constant.

Vanderhoff and coworkers measured competitive growth for bimodal mixtures of polystyrene particles and fitted the experimental results to the equation.

$$\frac{dV}{dt} = kD^c \qquad (4)$$

The data confirmed a near-zero exponent (c) for small particles but yielded a value of 2.5 for large particles; in apparent disagreement with theory. Theory and experiment can be brought together if one considers rates of free radical movement into different size particles. If free radical uptake per unit of surface is constant the radical input per unit volume is smaller for the larger particles. Thus $\bar{n}/V$ is smaller in the larger particles and the theory predicts a competitive growth exponent of 2.5.

2. MMA Polymerization in a CSTR; Multiple Steady States and Cyclic Conversion.

One can demonstrate that multiple steady state conversions are possible when MMA is bulk polymerized in a CSTR. This effect results because of the strong Tromsdorf effect. This same phenomena is suggested as one possible reason for cyclic conversion observations when MMA is polymerization in emulsion in a CSTR. The evidence is not conclusive and work will be continued to resolve uncertainties.

19 September 1972

PULP AND PAPER RESEARCH INSTITUTE OF CANADA
570 ST. JOHN'S BOULEVARD, POINTE CLAIRE 720, P.Q., CANADA
TEL. (514) 697-4110 CABLE-PAPRICAN TELEX 01-20797

CONTRIBUTION TO POLYMER COLLOID GROUP QUARTERLY NEWSLETTER

September 1972

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

Studies of particle interactions in latexes are being continued by Mr. A. Homola. A statement of recent activities follows.

The resistance of latex particles to coalescence can be quantitatively measured by ultracentrifugation or flow methods as previously reported. However, it should be noted that while both techniques allow us to measure the minimum force required for latex coalescence, neither yields any information relating the interaction energy or force to the interparticle separation. Such results are vital in any quantitative evaluation of latex stability in relation to the DLVO theory and especially in elucidating the role of steric repulsion in the stability. Consequently an apparatus has been constructed for the measurement of the pressure-volume relationship of latex confined by a semi-permeable membrane. Recently, the apparatus was considerably modified to allow for continuous automatic operation and recording of data.

The preparation of suitable latexes for these experiments has proceeded in two ways. Monodisperse styrene and styrene-butadiene latexes have been produced using lithium stearate as an emulsifier and stabilizer. It has been found possible to control the stabilizer content by treatment with ion exchange resins or by dialysis. Partial or complete removal of the soap, or its replacement by other stabilizers, can be effected.

Preparation of soap-free polystyrene latexes following the procedure by Kotera et al. has also been successful. These latexes are stabilized presumably by strong acid groups, bound to the surface, that result from decomposition of the potassium persulphate initiator.

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The particle size, molecular weight and colloidal properties are varied by concentrations of initiator, of monomer and of added electrolyte. Stirring speed also affects the properties of the latex and at extremes produces novel effects. At low speeds, coexisting suspension and solution polymerization can result in very large (~3 mm dia.) polystyrene spheres with occluded drops of monodisperse latex. At high speeds, very small particles are formed (0.1-0.2 µm) and these coalesce to a whipped cream consistency probably as a result of a decreased stabilization/area ratio.

Characterization of "soap-free" polystyrene latices have led to the following observations, related to the structure, stabilization and deformability.

The hydrodynamic density was determined by ultracentrifugation using sucrose, dextran, Ficol, and D_2O gradients and found to be 1.052±002. Experimentally the same density in various media suggests the absence of internal hydration and rather negligible surface hydration. Also electron micrographs of thin sections of polystyrene particles embedded in Spurr resin and stained with Br_2 or OsO_4 did not reveal any noticeable pores. Previously reported results with styrene-butadiene latexes suggested a porous structure.

Microelectrophoretic measurements as a function of pH strongly suggest the presence of more than one ionizable group on the surface, most probably sulphate and carbonate.

Electron microscopy and measurements on the filtration-formed latex cakes revealed a definite deformation of particles in ordered packing as a result of capillary forces operating during room-temperature drying.

5-1

Radiation-Induced Graft Polymerization in Emulsion System

K. Ishigure*, K. Yoshida** and V. T. Stannett

Department of Chemical Engineering
North Carolina State University
Raleigh, North Carolina
U. S. A. 27607

Abstract

The radiation-induced polymerization of styrene was conducted under emulsion conditions in the presence of polybutadiene latex in an attempt to induce grafting and the results were compared with the corresponding chemically initiated system. The propagation rate constants, kp, for styrene estimated on the assumption of the Smith-Ewart theory and the activation energies derived from the temperature dependence were found to be in good agreement with the values reported in the literature. The grafting efficiency was also measured and the results are discussed in association with the molecular weight of the polystyrene chains on the basis of a simple model. This is presented to explain some aspects of the experimental results and to give clearer ideas of the reactions involved.

*On leave from Dept. of Nuclear Engineering, U. of Tokyo.
**On leave from J.A.E.R.I., Takasaki, Japan.

VINYL ACETATE EMULSION POLYMERIZATION

Part I. Ionic Strength and Temperature Effects on Monomer Solubility in the Ionically-Stabilized Polymer Particle

A. Klein, C. H. Kuist, National Starch and Chemical
Company, Plainfield, New Jersey, and V. Stannett,
North Carolina State University, Raleigh, N. C.

Abstract

The monomer solubility in the polymer was strongly affected by ionic strength variation; with increasing ionic strength, solubility was found to increase. At constant temperature, this was entirely due to the decrease in interfacial tension, as the condensation of surfactant proceeded at the interface. The temperature affected both the polymer-solvent interaction parameter as well as the interfacial tension. These are the two parameters on which solubility depends. The interfacial tension variation with temperature was found to be complex, but entirely dependent on the entropic consideration of adsorption. The polymer-solvent interaction parameter vs. inverse temperature dependence was found to be linear, as expected.

S-3

Polymerization of Vinyl Chloride in the Presence of Precipitants. I

Koichiro Arita* and V. Stannett
Department of Chemical Engineering
North Carolina State University
Raleigh, North Carolina 27607

Synopsis

The kinetics of bulk and precipitation polymerization of vinyl chloride has been studied over wide range of reaction temperature using γ-ray induced initiation. The auto-acceleration effect, which has been observed by many investigators in the case of chemically initiated bulk polymerization of vinyl chloride above 40°C and has been the most controversial aspect of the bulk polymerization of vinyl chloride, was found to disappear in the bulk polymerization below 0°C. In the bulk polymerization at 40°C, the autoacceleration effect was observed up to 20%, in agreement with the results of previous investigators, and a pronounced effect of the size of polymer particles on the time-conversion curve was observed. The kinetics of precipitation polymerization of vinyl chloride in the presence of some non-solvents was successfully described by a one parameter equation. A kinetic scheme, which clearly explains the zero-order reaction behavior of bulk polymerization at low temperature and the kinetic behavior of precipitation polymerization described by the empirical equation is proposed. The autoacceleration effect in the bulk polymerization at 40°C was considered to be essentially the same phenomenon as the small retardation period observed in the bulk polymerization observed at low temperature.

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*Present address: Central Research Laboratory, Daicel Ltd.,
171 Tsurugaoka, Ohi-machi, Iruma-gun, Saitama, Japan.

EMULSION POLYMERIZATION WITH MIXED EMULSIFIER SYSTEMS. INITIATION IN MONOMER DROPLETS.

John Ugelstad.

In some recent papers we have discussed emulsion polymerization with systems consisting of anionic emulsifiers and different fatty alcohols of high chain length. Certain systems like Na-lauryl sulphate and cetyl alcohol may lead to a very fine dispersion of the monomer. We suggested that in this case the monomer droplets might serve as loci for initiation by radical capture from the water phase. Originally this idea was based upon results with vinyl chloride and was mostly based upon the kinetics of the reaction. During my stay at Lehigh University the author in cooperation with Vanderhoff carried out some work with styrene with the mixed emulsifier systems. In this case the idea of initiation in the monomer droplets was supported by the similarity of the size and size distribution of the monomer droplet emulsion and that of the polymer particles in the final latex.

In our research work in Trondheim we have continued this work along two different lines:

1. Investigation of the kinetics of emulsion polymerization with mixed emulsifier systems leading to initiation in monomer droplets.
2. Investigation of the emulsifier capacity for different monomers of different mixed emulsifier systems.

<u>Ad. 1:</u>

The specific kinetic features of the mixed emulsifier systems when applied with vinyl chloride was that the rate was very much decreased compared to what it was without the fatty alcohol. This reduction in rate was most pronounced at low degrees of conversion. In the presence of fatty alcohol there was, however, a relatively much higher autocatalytic effect at higher conversion.

The previous results with styrene show the same kinetic features. Addition of fatty alcohol leads to a very drastic decrease in the rate. Again there was a marked autocatalytic effect in the presence of fatty alcohol.

We are for the moment analysing these kinetic data in view of the mechanism suggested i.e. initiation in monomer droplets.

Ad. 2:

We have investigated a lot of different systems both for their ability to emulsify the monomer and the mechanism of polymerization which is encountered. There is a striking correlation between the emulsifying capacity of the system and the mechanism of polymerization. In all cases where we get a stable monomer emulsion with finely dispersed droplets we get initiation in monomer droplets, and the polymer particles are much bigger than experienced with the ionic emulsifier alone.

The systems we have found effective are up to now:

Ionic emulsifier	
Na-lauryl sulphate	Cetyl alcohol
" "	Stearyl alcohol
Na-cetyl sulphate	Cetyl alcohol
" "	Stearyl alcohol
Na-lauryl	Cetyl amine
"	Stearyl amine
Na-cetyl sulphate	Cetyl amine
" "	Stearyl amine
Kationic emulsifier	
Trimethyl sulphate	Cetyl alcohol
" "	Stearyl alcohol

Lower chain alcohols and amines were much less effective, also lower sulphates are less effective.

John Ugelstad

RATE OF DRYING OF LATEX FILMS: LIQUID-WATER TRANSMISSION RATES

J. W. Vanderhoff*
Center for Surface and Coatings Research
Lehigh University
Bethlehem, Pennsylvania 18015

and

E. B. Bradford and W. K. Carrington
The Dow Chemical Company
Midland, Michigan 48640

Introduction

Latex-drying experiments were carried out by measuring the rate of water evaporation from a thin film of latex in a small dish. Three latex copolymers were used: (1) 70:30 vinylidene chloride-n-butyl acrylate; (2) 67:33 ethyl acrylate-methyl methacrylate; (3) 67:33 styrene-butadiene. Latex samples were placed in a 2-in Teflon dish or 25-mm stainless steel planchet positioned on the pan of a Mettler Gram-O-Matic analytical balance in a constant-temperature (72° F), constant-humidity (50% RH) room, and the weights were recorded as a function of time.

Figure 1 is a schematic representation of the latex-drying process, as the variation of cumulative water loss with time. The drying process can be divided into three stages: (1) an initial constant-rate stage in which the particles move about freely and the rate of evaporation is about the same as for water; (2) an intermediate stage of rapidly-decreasing evaporation rate in which the particles come into irreversible contact with one another and the water-air interfacial area decreases sharply; (3) a final stage in which the particles have coalesced so that the water-air interfacial area is very small, and the small amount of water remaining evaporates by diffusion through capillary channels or the polymer itself.

The purpose of this report is to describe experiments carried out in conjunction with the foregoing work, in which the liquid-water transmission rate was measured for latex-film samples taken at different times during the drying and ageing process. In some cases, the latex-film sample was taken as soon as it became transparent -- near the end of the intermediate stage or beginning of the final stage. In other cases, the latex-film sample was aged at room conditions for a time sufficient for completion of the further, gradual coalescence (1). The objective of the work was to compare the rate of water evaporation in the final stage of drying with that expected from the diffusion of water through the polymer itself.

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* - work done at The Dow Chemical Company

V-2

Experimental Details

The cells were prepared from aluminum 35-mm film containers (diameter 1.2 in; height 1.8 in) which are fitted with a domed rubber-gasketed 1.4-in-diameter screw cap. This domed cap was cut away to give a circular 1-in diameter opening. Circular latex-film samples were fitted in to these caps so that a 1-in diameter circle of film was exposed. A weighed amount of water was placed in the cell, and the cap was screwed on carefully so that the lip of the cell pressed the film against the rubber gasket without cutting it. The filled cells were then weighed to provide the tare.

For measurement of liquid-water transmission rates, the filled cell was inverted, placed on a small stand made of metal screen, and the total weight was measured as a function of time. The water in the cell contacted the latex film, diffused through it, and escaped by evaporation. The latex film was prevented from contacting the metal screen by the lip of the screw cap; however, the water evaporating from the film was free to escape through the metal screen (positioned several inches above the bench top). The experiments were carried out in a constant-temperature (72° F), constant-humidity (50% RH) room.

The measurement of the water-vapor transmission rate was carried out in the same way except the the filled cells were left upright, so that water vapor contacted the film instead of liquid water. In some cases, the experiment was begun with the measurement of the liquid-water transmission rate and then, at some predetermined time, the cell was inverted to the upright position and the experiment continued with the measurement of water-vapor transmission rate.

Experimental Results and Discussion

Figure 2 shows the results for the 70:30 vinylidene chloride-n-butyl acrylate copolymer. The open points show the results for a film sample (estimated thickness 14 mils) aged several months (electron microscopic examination of surface replicas showed that the further, gradual coalescence was complete in about 14 days; therefore, the film can be considered homogeneous and representative of that copolymer composition). The liquid-water transmission rate (LWTR) was initially zero, then increased slowly to a constant rate of 4.6×10^{-8} g/min/cm^2 within 7 days. This constant rate persisted for about 40 days. During this time (at 33 days), the cell was inverted, and the experiment was continued, measuring the water-vapor transmission rate (WVTR). There was no observable difference between the liquid-water and water-vapor transmission rates.

The closed points show the results for a film sample (thickness 13 mils) dried until it first became transparent (88.0% solids), then placed in the cell. The liquid-water transmission rate was initially great, but soon decreased to a constant 4.4×10^{-8} g/min/cm^2, which persisted for 32 days.

The variation of liquid-water (and water-vapor) transmission rates with time is as expected. The film sample taken during drying when it first became transparent had not undergone the further, gradual coalescence process that renders it homogeneous. The water in contact with the film finds many capillary channels through which to diffuse, and thus the liquid-water transmission rate is high. However, as the further, gradual coalescence proceeds, the water-soluble components that are incompatible with the polymer are squeezed out, and the liquid-water transmission rate decreases progressively, reaching a constant value representative of the polymer within 10 days.

The film sample aged several months had already undergone further, gradual coalescence and thus was a homogeneous mass of copolymer. Consequently, the liquid-water transmission rate was zero initially, but increased progressively to a rate representative of the copolymer within 7 days. The close agreement of the two rates (4.6×10^{-8} and 4.4×10^{-8} g/min/cm^2, respectively) and the times required to attain them (10 and 7 days, respectively) indicate that these values are representative of this particular 70:30 vinylidene chloride-n-butyl acrylate copolymer, without any influence of the polymer-incompatible components of the system.

Figure 3 shows the results for the 67:33 ethyl acrylate-methyl methacrylate copolymer. The open points show the results for a film sample (thickness 20 mils) aged several months (electron microscopic examination of surface replicas showed that the further, gradual coalescence was complete in about 14 days; therefore, the film can be considered homogeneous and representative of that copolymer composition). The liquid-water transmission rate was substantial even in the beginning of the experiment (initial rate 1.6×10^{-6} g/min/cm^2) and decreased slightly to a constant rate of 1.4×10^{-6} g/min/cm^2 after 12 days. The insert of Figure 3 shows that the liquid-water transmission began immediately when the film was contacted with water. The closed points show the results for a film sample (thickness 15 mils) taken from the cell as soon as it became transparent (85.0% solids). The liquid-water transmission rate was initially 3.6×10^{-6} g/min/cm^2, but soon decreased to a constant 2.0×10^{-6} g/min/cm^2 at about 10 days. This constant rate persisted for 34 days. Thus, the liquid-water transmission rate for the sample taken when the latex film first became transparent was greater than that for the aged sample, but the difference was not great. However, these values are about two orders of magnitude greater than those of the vinylidene chloride-n-butyl acrylate copolymer (as expected).

Figure 4 shows the results for the 67:33 styrene-butadiene copolymer. The open points show the results for a film sample (thickness 16.8 mils) aged for one month (electron microscopic examination of surface replicas showed that the further, gradual coalescence was complete within 14 days; therefore, this film can be considered homogeneous and representative of that copolymer composition). The liquid-water transmission rate quickly increased to a constant 7.7×10^{-5} g/min/cm^2. The results for the samples aged 3 hours and 40 hours coincide at a constant rate of 9.6×10^{-5} g/min/cm^2, slightly greater than that of the sample aged one month. Another sample aged one month, then washed thoroughly with water to extract residual water-soluble ingredients, displayed a much lower (but constant) rate of 2.8×10^{-6} g/min/cm^2. That this latter value is probably representative of that copolymer composition is shown by the agreement with the value of 3.1×10^{-6} g/min/cm^2 obtained for a film prepared by coagulating the latex, washing it thoroughly with water, drying, then pressing a film under heat and pressure.

Summary and Conclusions

The liquid-water transmission rates are summarized in the following table.

Liquid-Water Transmission Rates of Latex Films

(g. water/min/cm^2 at 72° F, 50% RH)

Sample	Initial Rate	Constant Rate
VeCl$_2$-nBA fresh	2×10^{-5}	4.4×10^{-8}
VeCl$_2$-nBA aged	0	4.6×10^{-8}
EA-MMA fresh	3.6×10^{-6}	2.0×10^{-6}
EA-MMA aged	1.6×10^{-6}	1.4×10^{-6}
S-B fresh	---	9.6×10^{-5}
S-B aged	---	7.7×10^{-5}
S-B aged and washed	---	2.8×10^{-6}
S-B coagulated, washed, and molded	---	3.1×10^{-6}

The following conclusions can be drawn from this work to date:

(1) the latex drying process can be separated in three stages which correlate with the mechanism of latex film formation;

(2) the rate of water evaporation in the first constant-rate stage is the same as that for pure water or dilute emulsifier solution (2.0-2.8 x 10^{-4} g/min/cm^2);

(3) the rate of water evaporation in the third stage is about 100-1000 times smaller than that of the first stage;

(4) the liquid-water transmission rate of the latex copolymers is less than the rate of water evaporation in the third stage --- this difference is about 100-fold for the vinylidene chloride-n-butyl acrylate copolymer but less for the ethyl acrylate-methyl methacrylate and styrene-butadiene copolymers --- indicating that the water evaporates through capillary channels rather than by diffusion through the polymer;

(5) the liquid-water and water-vapor transmission rates of latex-cast films are the same (as expected).

References

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John W. Vanderhoff
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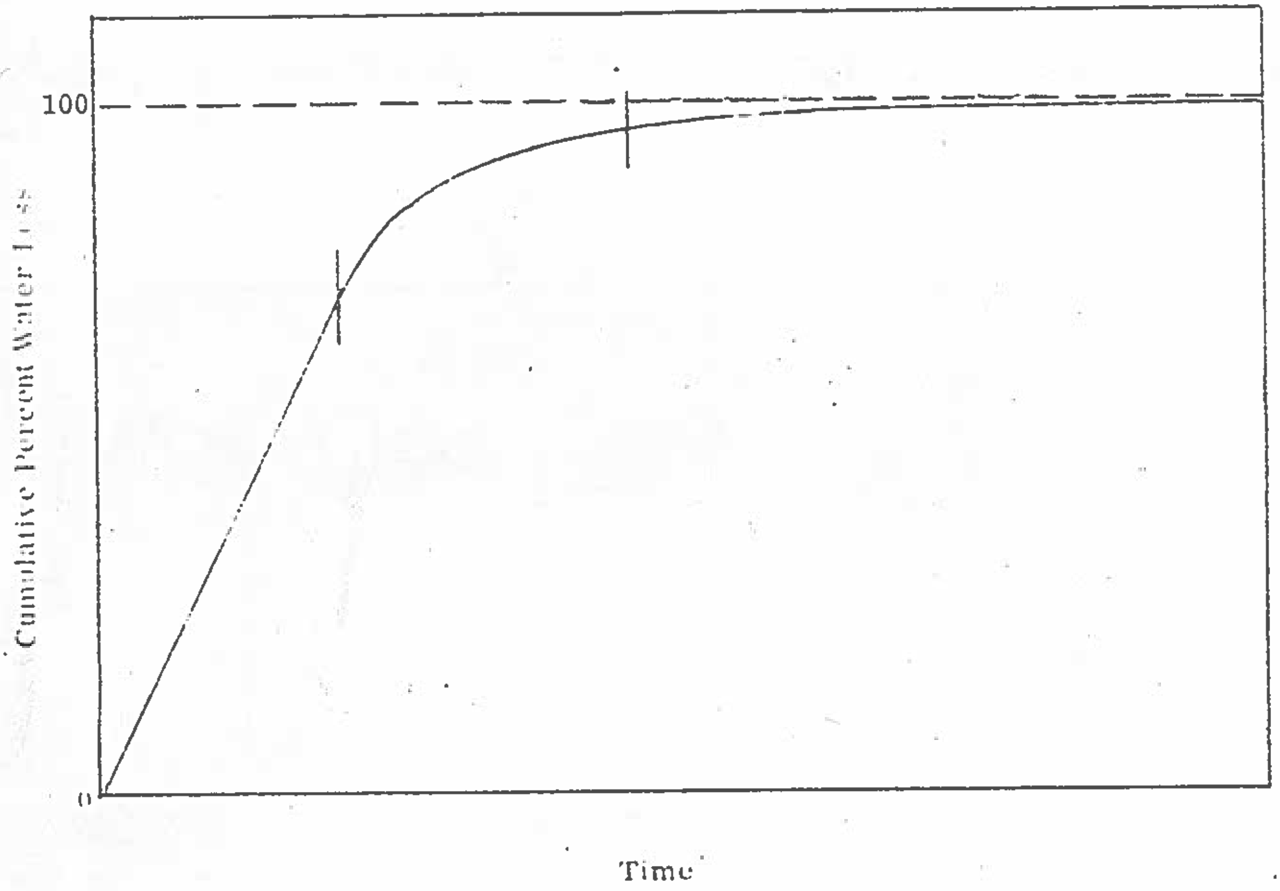

Figure 1. Schematic Representation of Three-Stage Latex Drying Process as the Variation of Cumulative Water Loss with Time

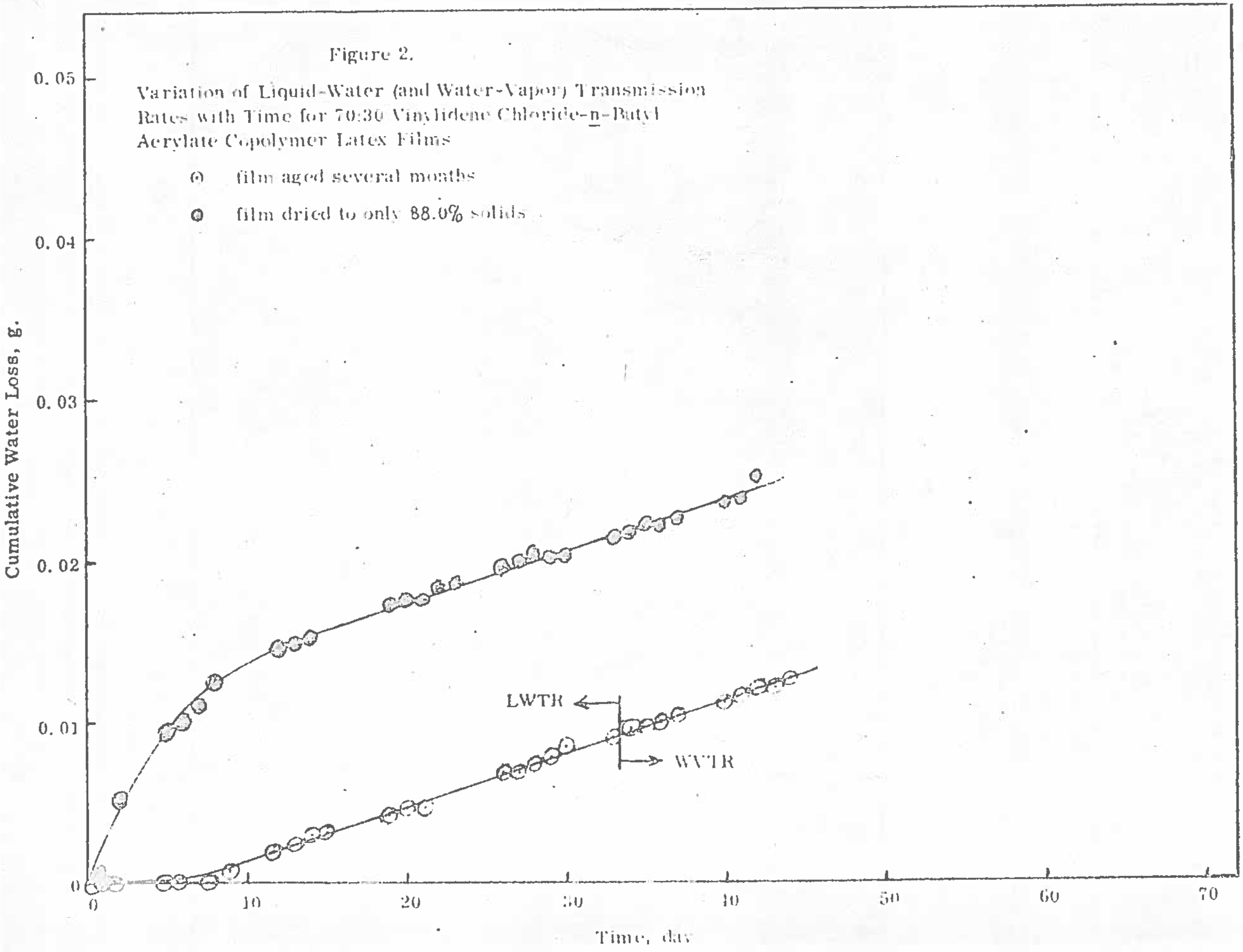

Figure 2.

Variation of Liquid-Water (and Water-Vapor) Transmission Rates with Time for 70:30 Vinylidene Chloride-n-Butyl Acrylate Copolymer Latex Films

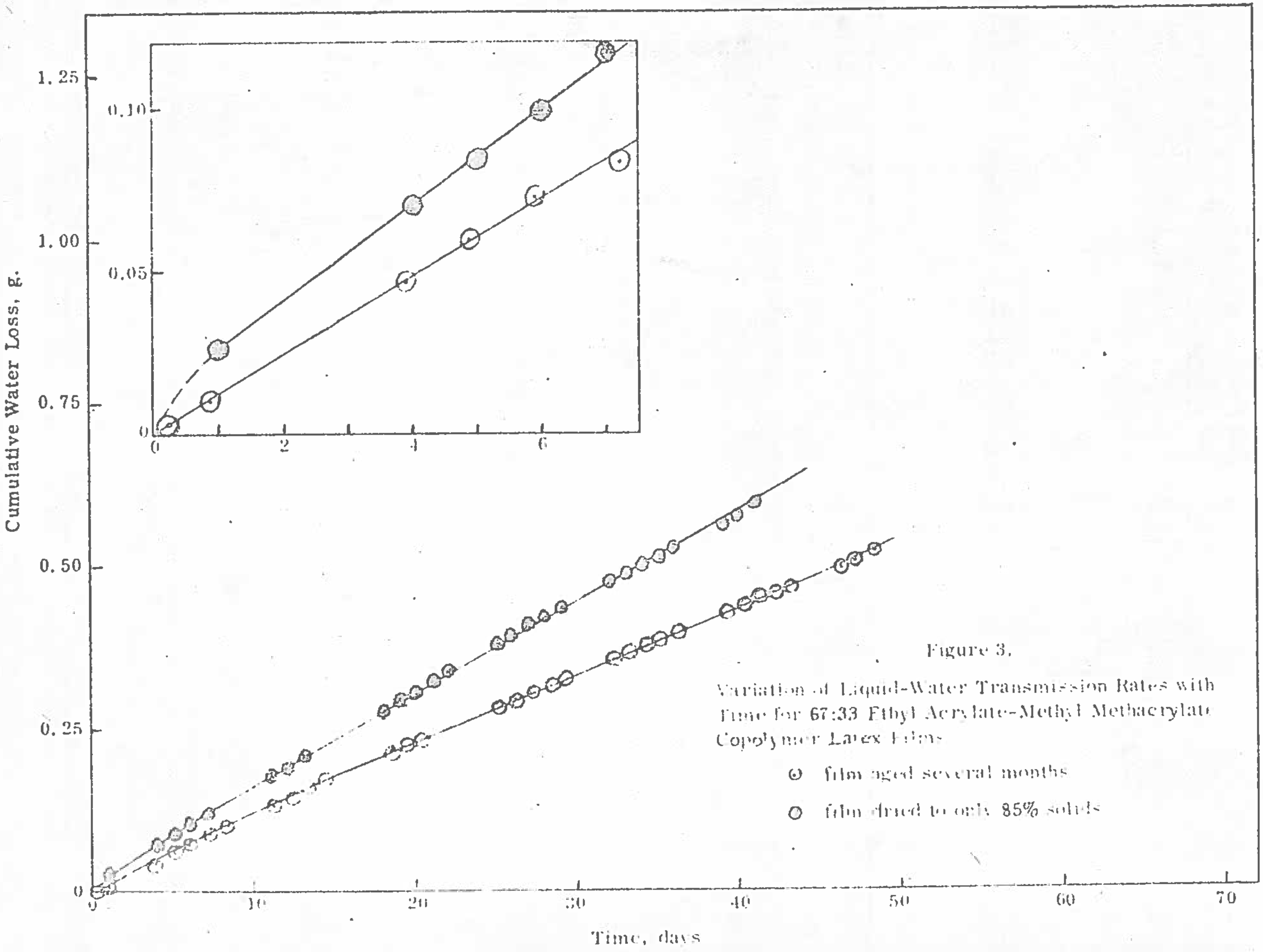

Figure 3.

Variation of Liquid-Water Transmission Rates with Time for 67:33 Ethyl Acrylate-Methyl Methacrylate Copolymer Latex Films

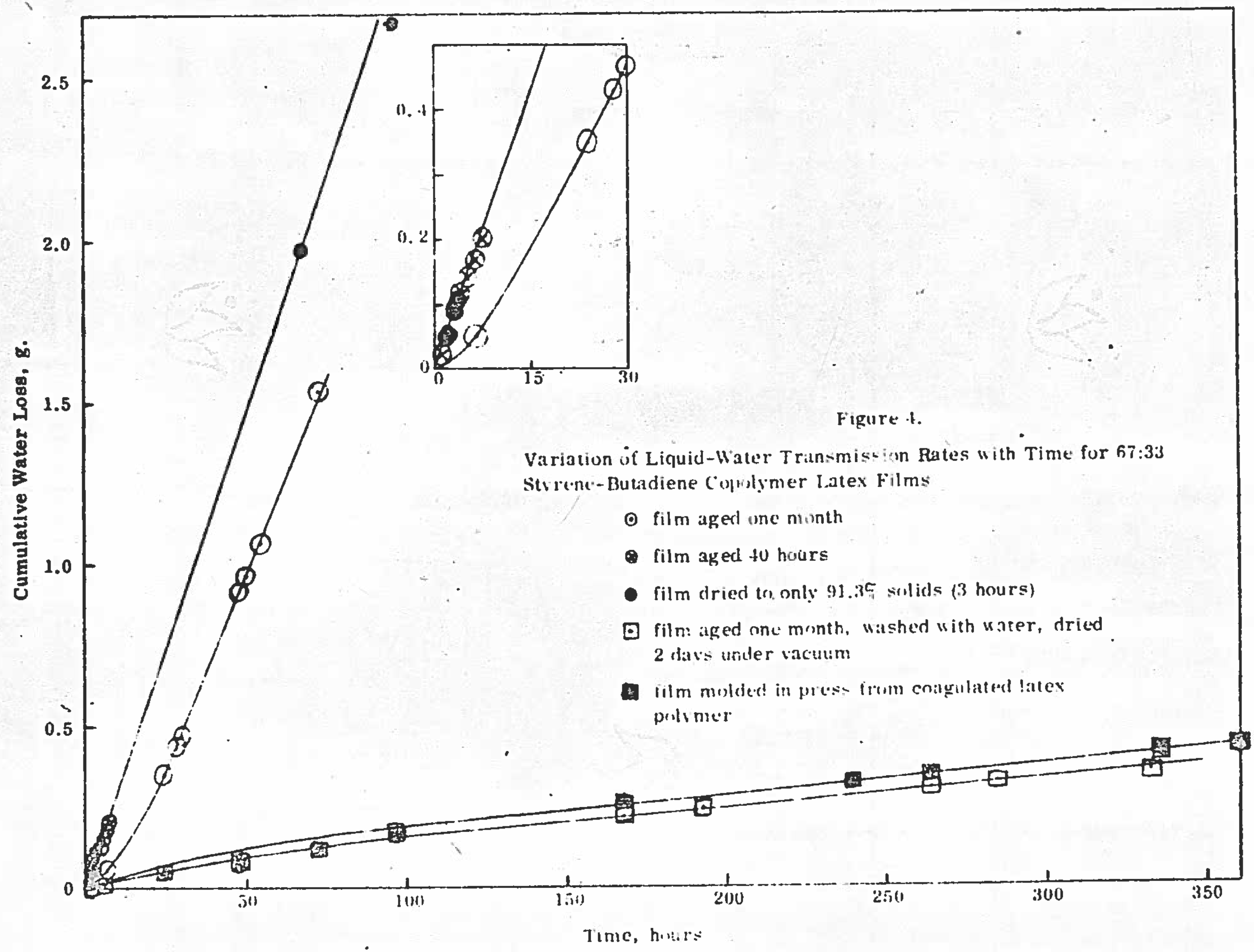

Figure 4.

Variation of Liquid-Water Transmission Rates with Time for 67:33 Styrene-Butadiene Copolymer Latex Films

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David J. Williams
The City College of New York
October 1972

We have executed one of the experiments I proposed in the last issue to further elucidate the factors controlling the core-shell morphology, and we have recently resubmitted our paper, on "The Equilibrium Encapsulation of Polystyrene Latex Particles" to The J. Polymer Sci., with a modified presentation, hoping to make the core-shell concept more palatable to the reviewers. Our revised manuscript includes an experiment describing the morphology resulting from a re-seeding with the oil soluble initiator, benzoyl peroxide. In this issue of the newsletter, I will describe how we have revised our presentation and the oil soluble initiation experiment.

To review the experimental facts, recall that we have performed a series of seeded styrene emulsion polymerizations in which the second stage of growth was initiated only after the second stage monomer charge had achieved equilibrium saturation with the seed particles. The final particles were observed in the electron microscope using two means of distinguishing between the first and second generation polymer: (a) butadiene tagging and osmium tetroxide staining coupled with ultra-microtomy and (b) tritiated-styrene tagging coupled with autoradiographic detection. We have found that the first and second generation polymer chains are not uniformly mixed throughout the final latex product: rather, the second

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generation polymer overcoats the seed polymer in a core-shell fashion.

The most important feature of the seeded polymerizations was that they were initiated with the latexes in a state of equilibrium saturation with monomer. Furthermore, the core-shell morphology was observed to prevail in the final product for which the first generation seed polymer (polymer I) was fully compatible with both the charged monomer (monomer II) and the second generation polymer obtained therefrom (polymer II). Since the core diameters closely corresponded to the seed particle diameters and since there was no evidence of appreciable polymer I - polymer II interpenetration between the core and shell, it appears that the major portion of polymer II is located within the shell of the second generation latex particle.

It now remains [This is new material.] to develop an explanation for the experimental facts just summarized. First, it is clear that a diffusion controlled kinetic mechanism is not supported by the experimental results. We should also keep in mind the additional fact that, according to the studies of van den Hul and Venderhoff as well as Ottewill with persulfate initiation the major portion of sulfate end groups remain on the surface of the particles - even through successive generations of seeded polymerizations. This means that nearly all the polymer molecules are bound to the particle-water interface by their chain ends.

We next considered two possible explanations for the formation of the core-shell morphology. In the first, one could postulate that the monomer and polymer are uniformly distributed at equilibrium; upon reinitiation, each second generation polymer chain is bound to the swollen particle surface and must grow there; monomer II, which swells the entire network, migrates toward the periphery as the supply there diminishes. As monomer II migrates to the surface, it must displace polymer I chain segments toward the center. Hence, as polymerization proceeds polymer I chain segments collect at the center and polymer II segments collect in the peripheral region, thereby forming a core-shell structure. A most serious difficulty with the latter mechanism is that it requies the preferential migration of polymer I chain over polymer II chains; and, from a diffusional point of view, polymer I chains are indistinguishable from polymer II chains.

In an alternative explanation, one could postulate that monomer II does not uniformly swell polymer I but that a major portion of it collects in the peripheral region of the particle, i.e., encapsulation occurs. Upon reinitiation, monomer II converts to polymer II in the peripheral region, thus forming a core-shell structure. Any monomer II that might be located in the central region of the swollen particle would migrate to the peripheral region as the monomer located at the periphery was consumed.

The first mechanism is based upon the fact that the locus of polymer chain ends is the particle-water interface. The second is based upon the supposition that monomer II is located in the peripheral region at equilibrium saturation before the second generation·polymerization is initiated. The latter is in accord with our earlier proposed core-shell model for a growing latex particle. An experiment was devised to differentiate between the two foregoing explanations: First deionize the seed latex, by diluting with distilled water and amberlite MB3 mixed bed ion exchange resin, to remove residual initiator. Prepare the seeded charge, taking care to replace the soap lost in the deionizing process. Add trace amounts of butadiene, as before, with the monomer II. Utilize the oil-soluble initiator, benzoyl peroxide (0.1 (wt)%, based on monomer II) and recommence polymerization. The question is: Does the monomer distribute uniformly as per the first explanation or does it tend to locate in the peripheral region of the particle as per the second explanation? Now, before repolymerization, the benzoyl peroxide should distribute essentially throughout the particle in direct proportion to monomer II; furthermore, polymer II chains will not be attached to the particle surface. Hence, if uniform distribution of monomer II prevails, polymer II should be uniformly distributed throughout the final latex particle and no core-shell morphology should be observed. On the other hand, if monomer II tends to overcoat the particle, then a core-shell morphology should be observed in the final particle - provided there is no extensive remixing within the particle as polymerization proceeds.

As shown in Figure 1, the core-shell morphology is clearly evident. In this case the core diameter (2440A) observed by electron microscopy does not correspond to the seed diameter (1640A), and we do not yet have an explanation for this difference. Nonetheless, this result supports the notion that, at equilibrium saturation, monomer and polymer are not uniformly distributed but that a sheath of monomer actually encapsulates the swollen latex particle.