

7 October 1980

The A.C.S. Fall Meeting had to be transferred to Las Vegas at one week's notice because of a strike of hotel and restaurant staff in San Francisco which threatened to disrupt it but the programme for the 'Emulsion Polymers' Symposium apparently proceeded smoothly nevertheless. Since the Division of Organic Coatings and Plastics Chemistry was the prime sponsor, the full preprints of the 35 Contributed Papers appear in 'Organic Coatings and Plastics Chemistry' Preprints Vol. 45 (1980) No. 2. Only the abstracts appear in the Polymer Division's 'Polymer Preprints' Vol. 21 (1980) No. 2. Fuller versions of most of the papers should appear in a volume in the A.C.S. Symposium Series later.

The Symposium on 'Science and Technology of Emulsion Polymers' at the 54th Colloid and Surface Science Symposium held at Lehigh University in June was also very successful: 29 papers were presented but no collective publication is planned.

'Polymer Colloids II' edited by R. M. Fitch containing the papers from the A.C.S. Miami Beach meeting of September 1978 was published in June by Plenum Press (ISBN 0-306-40540-1). It is a massive volume of 696 pages. The price is \$25.40 outside the U.S.. Within the U.S. the price is \$ 69.50 but, by using the form included in 'Polymer Preprints' A.C.S. Polymer Division members and affiliates can obtain the volume for \$ 52.12.

Plenum Press have also published an English translation of 'Emulsion Polymerization and Its Applications in Industry' by Elisavva, Ivanchev, Kuchanov, and Lebedev (ISBN 0-306-10961-1). The prices in this case are U.S. \$ 49.50 (\$ 57.12 with discount), Elsewhere \$ 59.40.

It is intended that the papers given at the Symposium on 'Emulsion Polymerization of Vinyl Acetate' held at Lehigh in April should be published as a book. The publishers will be Applied Science.

The Plastics and Rubber Institute are planning a 2nd International Polymer Latex Conference for May 1982. Formal inquiries should be made to Mr R.H.Craven, The Plastics and Rubber Institute, 11 Hobart Place, London SW1W 0HL. Telephone 01-245 9555. Informal inquiries to David Blackley.

Refer to the Annual Business Meeting Minutes for information currently available on the 3rd 'Polymer Colloid' Gordon Conference 1981, the 'Emulsion Polymers' section of the IUPAC Macromolecular Symposium 1981, and the proposed 2nd 'Polymer Colloids' NATO ASI in 1982.

A Conference volume entitled 'Polimery na Osnove Vinilatstata' ('Polymers based on Vinyl Acetate') was published by Nauka, Moscow in 1978 but no one outside the U.S.S.R. seems to have been able to acquire a copy. The titles of the papers appeared in 'Chemical Abstracts' 91 (1979) but these had simply been translated from 'Referatnye Zhurnal' (which presumably gives abstracts).

Copy for the Spring 1981 should be sent to me at the Chemistry Department, UMIST, P.O. Box 88, Manchester M60 1QD, England to arrive by 5th May 1981.

MINUTES of the ANNUAL BUSINESS MEETING of the POLYMER COLLOID GROUP held on Saturday, 14th June 1980 at 4.45 p.m. in the Sinclair Auditorium of Lehigh University, Bethlehem, Pennsylvania.

Present: J. S. Dodge, A. S. Dunn, M. El-Aasser, R.M.Fitch, N. Furlong, A. A. Robertson, and F. Saunders with Theo van de Ven (representing S. Mason) and B. Kronberg (representing P. Stenius).

Future Meetings. As Chairman of the 5rd Gordon Conference on Polymer Colloids, Bob Fitch announced that the Conference would be held at Tilton School, Tilton, New Hampshire, July 12-17, 1981. John Vanderhoff would be the Vice-Chairman. The 1981 Annual Business Meeting would be convened during the week. Speakers would include Overbeek, Tadros, and Stone-Matsui. The 1981 IUPAC Macromolecular Symposium would be held in Strasbourg, France in the preceeding week, 6-9 July and would include a section on Emulsion Polymers at which he had been invited to be the Main Lecturer.

Gary Poehlein had prepared a draft submission for a second NATO Advanced Study Institute to be held at Bristol, June 29-July 11, 1982. This had been circulated for comment to some but not to all of the members present and it was decided to meet again on Sunday at 5 p.m. when Gary would be present to consider the draft submission in detail. It was noted that Ron Ottewill was now a member of the Scientific Committee of NATO.

New Members. It was noted that, in fact, Dr Furlong had been nominated to represent the University of Melbourne group rather than Professor Healy. Nothing had been heard from Professor Watillon and it was decided that the representative of his group should be Dr Stone-Matsui. It was proposed that Theo van de Ven (McGill), Pranab Bagchi (Kodak, Rochester) and Dave Bassett (Union Carbide, South Charleston) should be members and they were elected unanimously.

Other Business Dr Furlong drew attention to a new journal 'Colloids & Surfaces' which had commenced quarterly publication in January from Elsevier: it was hoped that it could achieve more rapid publication than the 'Journal of Colloid and Interface Science'.

The meeting closed at 5.30 p.m.

Addresses of New Members

Dr T. C. M. van de Ven, Department of Chemistry, Pulp and Paper Building, McGill University, 3120 University Street, Montreal, PQ, Canada, H3A 2A7.

Dr P. Bagchi, Research Department, Eastman Kodak Co., Chemical Division, Kodak Park B-21, Rochester, N.Y. 14650, U.S.A.

Dr D. Bassett, Technical Center 120-150, Union Carbide Corporation, South Charleston, West Virginia 25305, U.S.A.

Substitute Dr J. Stone-Matsui for Prof. A. Watillon
Dr N. Furlong for Prof. T. Healy.

Change of Address Dr J. I. Gardon is now at Sherwin-Williams Co., 11541 South Champlain Avenue, Chicago, Illinois 60628, U.S.A.

30 SEP 1970

EFFECT OF n-ALKYL TRIETHYL AMMONIUM BROMIDES UPON MECHANICAL STABILITY OF NATURAL RUBBER LATEX

D. C. Blackley, National College of Rubber Technology, The Polytechnic of North London, Holloway, London N7 8DB.

It is usually assumed that the addition of cationic surfactants to an anionically-stabilised aqueous colloidal dispersion, such as natural rubber latex, will always reduce the colloidal stability, possibly to the point of coagulation, at least if the cationic surfactant is not added in sufficient quantity to reverse the charge on the particles. Rather surprisingly, we have recently found that this is not always true of natural rubber latex. Some results which I presented briefly at the recent A.C.S. Emulsion Polymerization Symposium held in Las Vegas indicate that under some circumstances the addition of small quantities of a cationic surfactant to natural rubber latex can result in small increases in mechanical stability.

The cationic surfactants which we used were the n-alkyl triethyl ammonium bromides, prepared by reacting triethylamine with the appropriate n-alkyl bromide. The number of carbon atoms in the n-alkyl group was varied over the range 6 to 18, so that the total number of carbon atoms in the surfactant varied over the range 12 to 24. The surfactants were purified by recrystallisation. Being quaternary ammonium salts, there seemed to be little likelihood that the surface activity would be adversely affected by the alkaline pH of ammonia-preserved natural rubber latex.

The latex used was a 60% high-ammonia centrifuged concentrate. Care had to be taken in adding the cationic surfactants to the latex, in order to avoid local coagulation. The latex samples were matured for about 48 hours at room temperature in order to allow some opportunity for adsorption equilibrium to be attained. After maturation, the latex was filtered through two layers of cheese cloth in order to remove any particles of coagulum, the presence of which might seriously distort the measured mechanical stability. Mechanical stabilities were determined at 35°C by a conventional high-speed stirring test, essentially according to the procedure specified in B.S. 1672:1972. However, the stabilities were determined at 50% total solids content instead of at 55%, and the latex samples were diluted with water instead of with 1.5% ammonia solution.

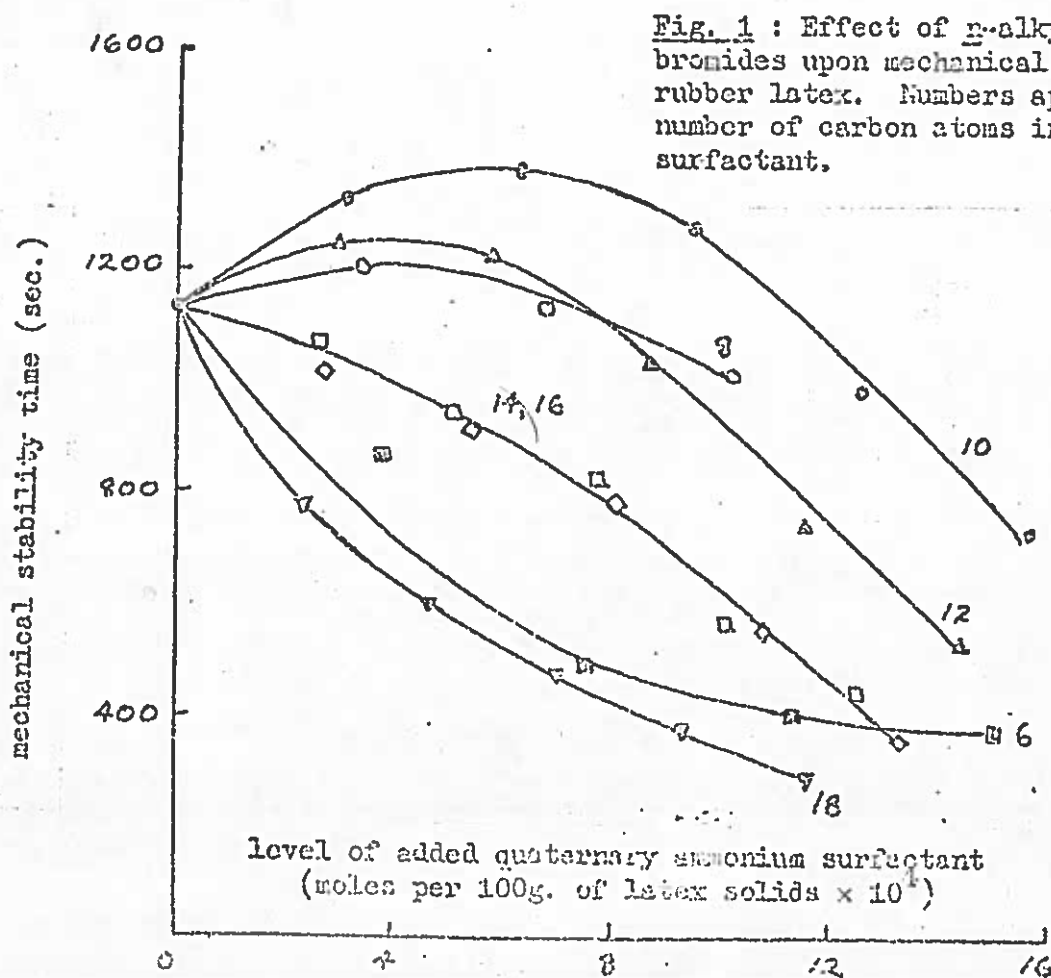
The results are summarised in Fig.1. Whilst these results show that in general the addition of these cationic surfactants does lead to a reduction in mechanical stability, however, they also show that this is not invariably the case. It appears that small additions of an n-alkyl triethyl ammonium bromide whose n-alkyl group contains between approximately 8 and 12 carbon atoms can bring about a small increase in mechanical stability.

It is usually assumed that the addition of a small amount of cationic surfactant to a rubber latex will invariably lead to a reduction in mechanical stability because the surface-active cations are adsorbed at the rubber-water interface, partially neutralise the charge at the particle surface, and thereby reduce the counterion cloud which surrounds the particles. There seems to be little reason to doubt that the cations of all the surfactants used in this investigation were adsorbed at the rubber-water interface, that the charge at the particle surface was partially neutralised, and that the counterion clouds surrounding the particles were reduced in consequence. What is clear is that the reduction in particle charge was not always accompanied by a reduction in mechanical stability; it appears that in some cases the destabilising effect of reduced particle charge is more than offset by some other effect which accompanies the adsorption of the surface-active cations at the particle surface, and which causes the mechanical stability to increase. One possible effect which meets these requirements is that the molecules of the added surfactant become mixed with the

molecules of indigenous soaps already adsorbed at the rubber-water interface, and that, in consequence, the lateral cohesion between the hydrophobic parts of the adsorbed molecules is reduced. It may be recalled that an effect of this type has been postulated by us previously in order to explain the ability of small additions of certain carboxylic-acid soaps markedly to increase the mechanical stability of natural rubber latex (1,2). In our previous publications we have made a case for supposing that reduction of lateral cohesion between the molecules in the adsorbed layer at the rubber-water interface may enhance the ability of those molecules to stabilise the particles against coagulation. In any event, regardless of the detailed mechanism which is proposed, the present results seem to indicate clearly that the mixing of the added soap or surfactant molecules with the molecules of adsorbed indigenous surface-active substances can have an important effect upon the mechanical stability of the latex, and that this effect can be more significant than any effect which arises merely from enhancement or reduction of the density of charge at the rubber-water interface. One aspect of the present results which is particularly interesting is that, of the cationic surfactants which were included in this investigation, the one which was able to effect the greatest enhancement of mechanical stability was the one which contained 10 carbon atoms in its *n*-alkyl chain. This is approximately the hydrophobe chain length at which added anionic surfactants (*n*-alkyl carboxylates, *n*-alkyl sulphates and *n*-alkyl sulphonates) are most effective in enhancing the mechanical stability of natural rubber latex.

References

1. D. C. Blackley, bt. A. A. Nor Aisah and R. Twaits, *Plastics and Rubber : Materials and Applications*, 1979, 4, 77
2. D. C. Blackley and M. Azas, *Plastics and Rubber : Materials and Applications*, 1980, 5, 57



OSMIUM TETROXIDE FIXATION OF VINYL CHLORIDE EMULSIONS. Henry M. H. Yang, Charles N. Bush, David J. Polelino, and Ronald W. Smith. McGraw-Hill Company, Chemical Group, Technical Center, P. O. Box 122, Aven Lake, Ohio 44012.

Introduction

In studying the mechanism and the kinetics of polymerization, it is essential to understand the locus of polymerization and the particle growth mechanism. For example, in emulsion polymerization, polymer particles grow from the micelle phase (50-200 Å) to the final particle size. Depending on the conditions, this size may be from 1,000 Å to 4,000 Å. In suspension polymerization, polymer particles are nucleated inside the monomer droplets. In this case, the initial monomer droplet size is directly related to the final particle size ranging from 60 to 300 micrometer.

Recently, Ugelstad and others¹ also indicated that the locus of initiation and propagation in emulsion polymerization can be shifted from micelles to the monomer droplets if the diameter of the monomer droplet is reduced sufficiently, for instance to one micrometer, prior to the initiation of the polymerization process. Under this circumstance it is evident that monomer droplet size also plays an important role in the polymerization mechanism.

Unlike monomers such as styrene and alkyl acrylates, vinyl chloride is in the gaseous state at the standard condition. Thus, it is hard to measure its droplet size using any of the conventional methods such as the sedimentational, optical, or the electrozone current measurements. In this report, a new technique to measure the vinyl chloride monomer droplet size is demonstrated. This technique utilizes the rapid reaction of osmium with Osmium Oxide₂, resulting in stable hard particles which are capable of being measured by an electron microscope.

Osmium Tetroxide staining has been widely used in studying biological and polymer systems.² Recently, this technique was used to study the effects of surfactants on styrene monomer droplet size distribution and particle nucleation.^{4,5}

To the author's knowledge, this is the first work applying the Osmium Tetroxide fixation technique to measure vinyl chloride droplet size. This is a useful technique to study the particle growth mechanism and the effect of soap type and concentration on emulsion droplet size.

Experimental

Osmium Tetroxide with a 99.82 purity was obtained from Aldrich Chemical. A 2% solution in distilled water was prepared for use. Staining experiments were performed in a high pressure Luerlock syringe obtained from Ideal/Nicholson of Chicago. In all experiments, the molar ratio of vinyl chloride monomer to Osmium Tetroxide was kept at 1:1.5 to ensure complete reaction. In a typical staining experiment, a 10 ml sample of a vinyl chloride emulsion was taken from a reactor using a 10 ml Luerlock syringe. A second 10 ml Luerlock syringe which contained 9.9 ml 2% Osmium Tetroxide solution was immediately connected to the first syringe through a Luerlock connection. When the connecting lock was opened, 0.1 ml of the VCI emulsion was pushed into the second syringe, and the lock was immediately closed. The syringe which contained Osmium Tetroxide solution was gently tumbled for 10 minutes. The solution gradually turned black as a result of the reactions between Osmium Tetroxide and vinyl chloride

monomer. The syringe was left in the hand for another 15 minutes to ensure complete reaction. Thirty droplets of the darkened solution were diluted to 40 ml using distilled water. Sample grids for electron microscope measurement were then prepared by either placing one drop of this dilute solution onto the carbon substrate side of the copper grid or dipping the copper grid into the diluted sample solution. After either preparation had dried it was examined and photographed in a Philips EM 100 B transmission electron microscope.

Osmium Tetroxide vapors are extremely poisonous, highly irritating, and damaging to the eyes, respiratory tract, and skin. All the preparations were done in a good ventilation hood. A mask and gloves were worn for protection.

Results and Discussion

The chemistry of the reaction of Osmium Tetroxide and alkenes has been described elsewhere.⁵⁻⁷

As a demonstration of this staining technique, a 3-liter steel reactor was charged with 50% demineralized water, 49% vinyl chloride and 2x10⁻³% Sodium Alkyl Sulfonate. No initiator was added. The whole mixture was stirred at 400 RPM and 40°C for 15 minutes, then 10 ml of the emulsion sample was taken using a high pressure syringe. The procedure described in the Experimental Section was then followed. Figures A and B show the results of staining this emulsion sample. Spherical droplets with broad size distribution can be seen. The monomer droplet size generally depends upon the agitation rate, the type of surfactant, and the surfactant level. The Critical Micelle Concentration (CMC) is 1.4 g/liter for the surfactant we used here, so it is well below CMC.

When staining samples during polymerization, the monomer droplets can easily be distinguished from the polymer particles by comparing the results with a sample stained after the vinyl chloride was vented.

This technique has been found very useful in studying the locus of the particle growth in different polymerization processes and recipes.

References

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 - b) Riemersma, J. C., Acta Metalleum, Suppl. 12 233-235 (1972).
 - c) Kato, K., Polymer Letter 4, 35-38 (1966).
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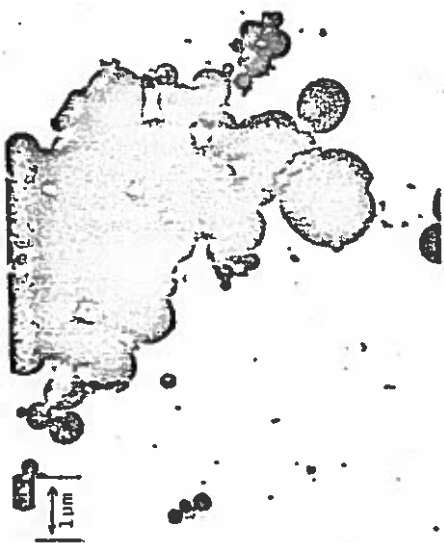


Fig. A Vinyl Chloride Droplets Stained by 0.04 Dilute Solution

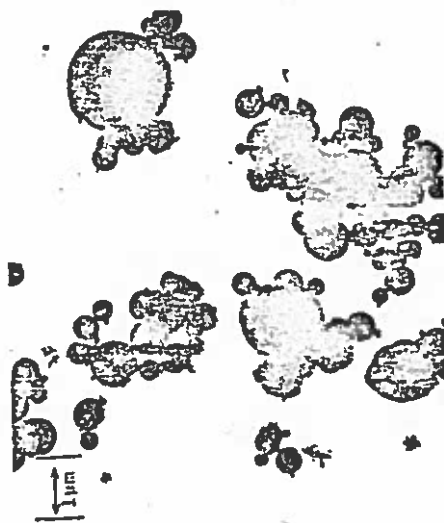


Fig. B Vinyl Chloride Droplets Stained by 0.04 Dilute Solution

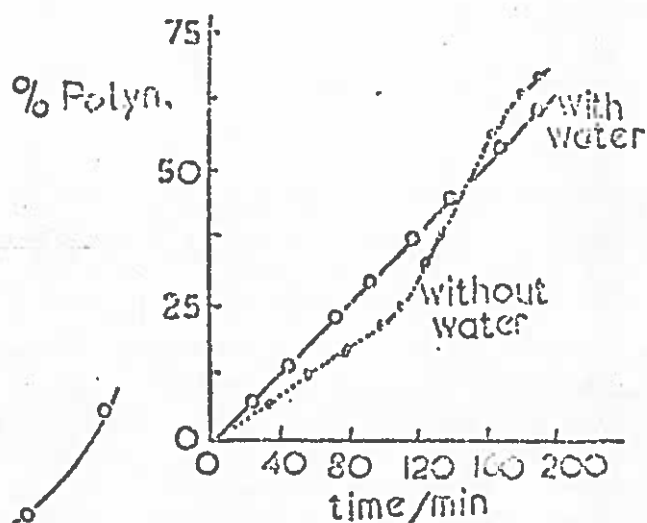
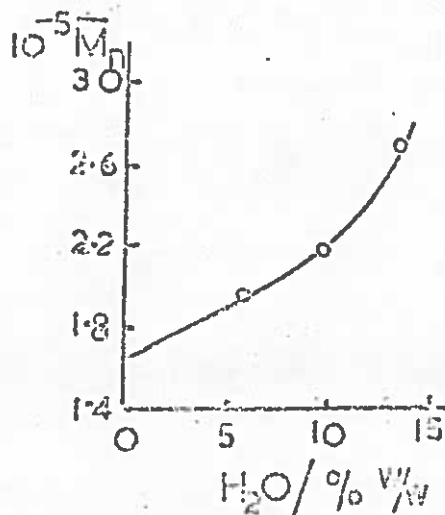
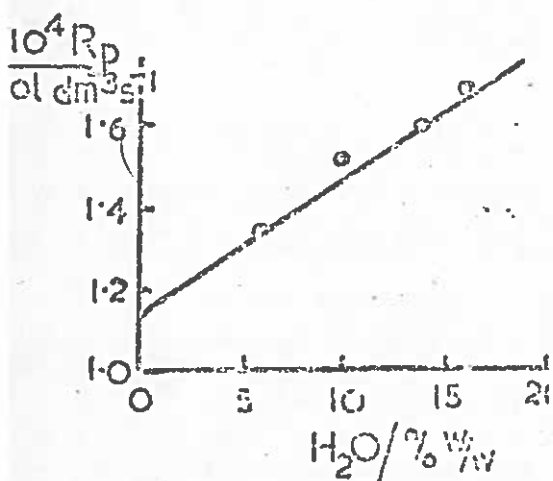


The Origin of Structural Variations in Polyvinyl Alcohol

There is some evidence in the literature that the water content of methanol used as a solvent in the polymerisation of vinyl acetate from which polyvinyl alcohol is subsequently prepared may affect the properties of the polyvinyl alcohol obtained probably as a result of variations in the extent of non-hydrolysable short-chain branching resulting from intramolecular transfer during the polymerisation. Kamachi, Liaw, and Nozakura (Polym. J. **11** (1979) 921) find that the propagation rate constant found for vinyl acetate in solution polymerisation varies markedly with the solvent and attribute this to solvation of the polymerising radical. If this is correct a similar variation of the rate constant for intramolecular transfer leading to the formation of short-chain branches is also likely. The results of Beileryan, Egoyan, & Marmaryan (Arm. Khim. Zh. **26** (1973) 442) show that the polymerisation of vinyl acetate is sensitive to the water content of methanol water mixtures

Effect of Water on Polymerisation of Vinyl Acetate in Methanol

Vinyl acetate 6.7 mol dm^{-3}	Benzoyl peroxide $3.5 \times 10^{-3} \text{ mol dm}^{-3}$		
	Bulk	Methanol	Methanol-water
$k_p/k_t^{1/2}$ at 50°C	0.288	0.425	0.516
$E_{\text{overall}}/\text{kJ mol}^{-1}$	-	114	108
$E_p/\text{kJ mol}^{-1}$	34	52	46
Solvent transfer constant, k_f/k_p	-	7.75×10^{-5}	3×10^{-5}
Long-chain branch points (mole %) (hydrolysable)	-	0.14	0.08



A Hoechst patent (B.P. 1,224,113 (1971)) on the continuous polymerisation of vinyl acetate in methanol also claims that a more consistent polyvinyl alcohol of higher viscosity is obtained on complete hydrolysis when some water is added to the methanol.

Parts by wt. AIBN	Per 100 parts by weight Vinyl Acetate ca. 32% conversion		Viscosity (cP) of a 4% solution of a 100% hydrolysed PVCH
	Methanol Parts by wt.	Water Parts by wt.	
0.017	9.40	-	47 - 54
0.017	9.40	0.50	59 - 62
0.017	9.40	1.69	76 - 84
0.010	6.40	-	53 - 68
0.010	6.40	1.10	83 - 90

For his M.Sc. project, Mr M.H.Mahmood has tested the effect of methanol containing 0.1% water compared with methanol dried over a 4 Å Molecular Sieve. A 50% solution of vinyl acetate with 0.115% azodiisobutyronitrile was polymerised at 55 °C for 21 hrs when the conversion was found to be 84% in the dry methanol and 51% when water was present. Previous work indicated that the time required to reduce the acetyl content to 12 mole % by alkaline methanolysis using 1.6% w/v NaOH was 31 min. but, in fact, the acetyl content found after this time was 4.0 mole % in each case. This just goes to show how critical the precise method of carrying out this reaction is. The product is a stiff gel which has to be cut up and dumped into a solution of the equivalent quantity of acetic acid to stop the reaction. The absorbance at the maximum (440 nm) of the red complex formed by the residual sequences of more than 14 vinyl acetate residues with aqueous iodine in potassium iodide differed being 1.16 for the sample polymerised in dry methanol and 0.92 for that obtained in the presence of water. Since the average acetyl content is the same, this either means that the formed sample has a broader acetyl sequence length distribution or that there is more short-chain branching (or conceivably a higher 1:2-glycol content) in the latter sample. Since the conditions of methanolysis were the same for both samples the acetyl sequence length distributions would be expected to be identical so the latter explanation seems the more plausible. The latex viscosity of polyvinyl acetate latices is known (cf. Shiraishi, Moro) to be very sensitive to the structure of the polyvinyl alcohol used to prepare them. Accordingly the two polyvinyl alcohol-acetate specimens were used in the emulsion polymerization of an 8% v/v at a concentration of 3% on the aqueous phase. A minor proportion of sodium dodecyl sulphate (0.08%) had to be used to obtain a stable latex. Persulphate initiation was used at 60 °C. The polyvinyl alcohol-acetate from the dry methanol synthesis gave a conversion of 60% in 5 hrs, that from the PVAc prepared in presence of water 59%. But the latex viscosities (measured in a capillary viscometer) were 4.4 and 2.3 cP respectively. Thus it appears that a small amount of water present in the methanol used in the preparation of the polyvinyl acetate can be responsible for a large difference in latex viscosity when the polyvinyl alcohol prepared from it is subsequently used in an emulsion polymerisation. Variation in the water content of the methanol is just the sort of adventitious factor which could account for variations in the properties of the product if its importance were not realised so that it could be controlled.

Polymer Colloids Newsletter

University of Connecticut

26 SEP 1980

Shu-Jan Liang:

The kinetics of the swelling of organic colloids are being studied under three circumstances: (1) different activities of diffusant in the aqueous phase, (2) different migration rates of diffusant through the interface, and (3) different mobilities of diffusant within the latex particle.

A light scattering photometer is used to measure the swelling rates of latexes. The particle sizes are determined by both angular dependence of scattering and 90° scattering of vertically polarized light. Mono-disperse, aqueous latexes of polymers and a liquid disulfide, which show higher order of Tyndall spectra, were prepared for this study. The effects of the polymer glass transition temperature and relaxation kinetics on swelling rates are investigated by swelling glassy and rubbery polymers with good solvents. Tetrahydrofuran and p-dioxane are used as the swelling agents. Polymeric and monomeric surfactants are used to coat the surface of the latex particles, and their effects on swelling rates are studied in terms of the amount of adsorption and the conformations of macromolecules adsorbed on the liquid-solid interface.

The accompanying figure shows the results for the swelling of polystyrene latex by tetrahydrofuran in water at various THF concentrations. Acceleration in the swelling rate is observed when the T_g of the polystyrene/THF mixture within the particles falls to room temperature. At this point the swelling mechanism changes from Fickian to polymer-relaxation-controlled. The latex was ion-exchanged and steam-distilled to remove traces of residual monomer.

We believe swelling kinetics determined with styrene monomer are subject to error because (1) the monomer may be polymerized by trapped radicals in the glassy polymer, and (2) fine droplets of monomer, under agitation, will have an activity greater than that of the monomer at a planar interface and variable because of variations in particle size, due to the Kelvin effect. Therefore swelling kinetics should only be done with solutions that are below saturation.

This work is in cooperation with John Ugelstad under the sponsorship of NATO.

Tor Henrik Palmgren:

Laser Light Scattering Studies on the Early Kinetics of Emulsion Polymerization

Work is being done on the kinetics of the earliest stages of the emulsion polymerization of Methyl Methacrylate in aqueous medium. The study is a continuation of earlier work done by Fitch, Tsai, Watson and

others, and attempts to further clarify the mechanism of particle nucleation in homogeneous systems.

In our experiments the monomer concentration is varied below the point of saturation. Other variables are initiator and stabilizer concentration. Currently sodium dodecyl sulfate is used as stabilizer, and the photodegradable compound biacetyl is used as initiator. The intention is to look at systems that are initiated by other water-soluble photosensitive initiators, as well. Present experiments are carried out under continuous illumination.

The instrumental approach is an improvement over the one used by Watson for work on coagulation kinetics of latex formation. A Brice-Phoenix 2000 DM light scattering photometer was used for the in situ detection of the polymerization process. However, to achieve higher sensitivity, the instrument has been modified as follows: A He/Ne laser is employed as the scattering light source allowing for high signal stability. The signals are detected simultaneously at two photomultiplier tubes, one at 0° and the other at 90 degrees to the laser beam. These signals are then fed to a differential amplifier, and the difference signal is subsequently recorded. The advantage of this approach is that external noise thus can be minimized by subtraction. A secondary Hg-vapor light source is mounted at right angles to the incoming laser beam (270°), to provide the energy necessary to decompose the initiator molecules.

The differential signal is recorded as a function of time, and subsequently converted to Rayleigh ratios versus time. Theoretical computations based on Hansen's and Ugelstad's equations for particle formation have been carried out.

The following experimental observations have been made: Experiments performed under otherwise identical conditions indicate that the initial rate of polymerization is the same, regardless of the presence or absence of stabilizer. This is to be expected from the theory and can be further illustrated by the equation below.

$$\frac{dN}{dt} = R_i - R_c - R_f \quad , \text{ where}$$

N = number of particles, R_i is the rate of initiation, R_c is the rate of capture, R_f is the rate of coagulation. It is clear from this that capture and coagulation can be ruled out during the first few seconds of polymerization. However, later during the reaction it was noticed how the coagulation process was clearly retarded by the presence of emulsifier, as expected.

Finally an interesting observation was made, while comparing experiments with different monomer concentrations. Quite the contrary to what could be anticipated from theory, higher monomer concentration resulted in a slower rate of increase in the Rayleigh ratio. The monomer concentrations studied

were 0.1 M (close to saturation) and 0.05 M. Intuitively one would expect the critical chainlength to be reached sooner with a higher monomer concentration, thereby resulting in a higher rate of increase in Rayleigh ratio. However, the contradiction between theory and practice seems to suggest that the critical chainlength may be a function of monomer concentration. The explanation for this may be a binary solvent effect, where a higher monomer to water ratio would result in a higher solubility of the oligomeric chains, thus allowing oligomers to grow longer in a case where the monomer concentration is higher. Our theoretical calculations tend to support this idea, in that they predict nucleation rate to be strongly dependent on the critical chainlength. Further experiments and curve fittings have to be done in order to assess the validity of these ideas.

Charles Fifield:

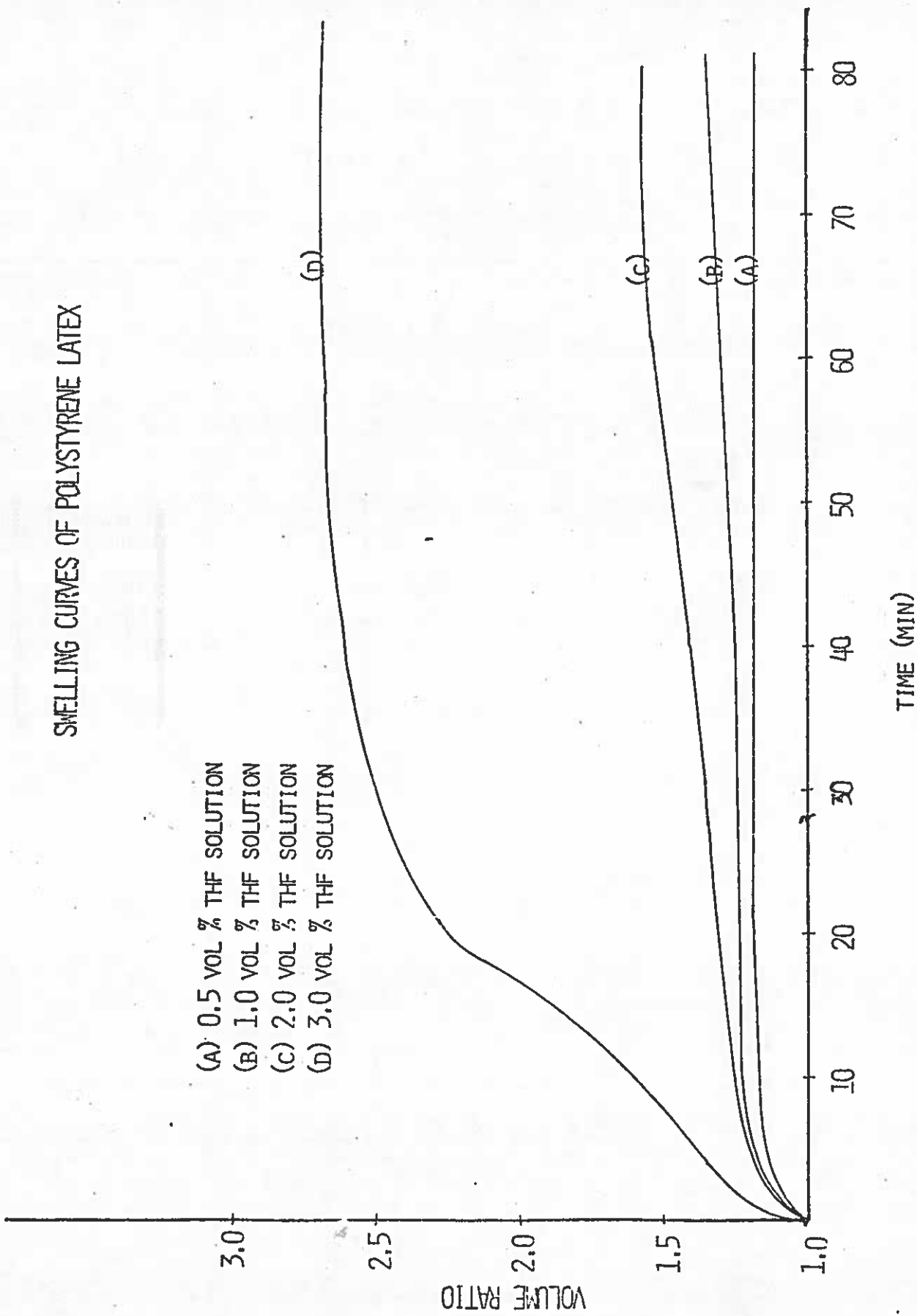
We are investigating Ion Scattering Spectroscopy (ISS) and Secondary Ion Mass Spectrometry (SIMS), two highly sensitive methods for surface chemical analysis.

In ISS, sensitive to only the outermost one or two atomic layers, a beam of monoenergetic ions such as $^3\text{He}^+$ or $^{20}\text{Ne}^+$ is directed at a sample and their energy distribution after being scattered is determined at a given angle. The ratio of the energies of the scattered and incident ions, E/E_0 , depends on the mass of the given surface atom. Identification of surface atoms is thus possible. In SIMS, charged species which are ejected from the surface as a result of ion beam bombardment are analyzed by a mass spectrometer.

Dried polystyrene latex samples were mounted on Au/Pd-coated plates. Elements such as C, O, Na and S, among others, were identified. The detection of sulfur could not be used to provide a measure of sulfonate or sulfate groups since the sensitivity of ISS/SIMS to the element in this form was found to be quite low. Latexes containing only sulfonic acid groups were converted to the rubidium sulfonate form by ion exchange and this element was detected because of the high sensitivity of the method for Rb, even though the level of sulfur was below the limit of detectability. A series of well characterized latexes will be used as calibrating standards to determine the correlation between quantity of sulfonate determined titrimetrically and the Rb peak-intensity in the ISS/SIMS.

SMELLING CURVES OF POLYSTYRENE LATEX

- (A) 0.5 VOL % THF SOLUTION
- (B) 1.0 VOL % THF SOLUTION
- (C) 2.0 VOL % THF SOLUTION
- (D) 3.0 VOL % THF SOLUTION



CURRENT POLYMER COLLOID RESEARCH AT MCMASTER UNIVERSITY

A.E. HAMIELEC, Department of Chemical Engineering. 8 SEP 1980

This is my first contribution to the Newsletter and on this occasion I thought it appropriate to introduce the various projects which are currently in progress or have just been completed.

1) Liquid Size Exclusion Chromatography (LSEC)

LSEC is similar to hydrodynamic chromatography (HDC) except that porous glass packings are employed. LSEC is under investigation as an analytical technique for the measurement of particle size distribution of latices in the submicron range. Emphasis has been placed on the development of calibration techniques for a turbidity detector where peak broadening is significant. Calibration techniques are now considered satisfactory. The LSEC method works well for particles of up to 1 micron in diameter that are monodispersed. Polymer particles greater than about 4000 Å may be trapped in the packing and as a consequence, LSEC works well with broad particle size distributions only when particles greater than 4000 Å in diameter are not present.

2) Continuous Emulsion Polymerization of Vinyl Acetate

An attempt is being made to develop practical control strategies to control conversion, particle size distribution, weight-average molecular weight and long chain branching frequency. Control strategies are being tested experimentally with the aid of online sensors to measure surface tension, conversion (densitometer), particle size distribution (turbidity-spectra) and weight-average molecular weight (KMX6-low angle laser light scattering photometer).

3) Free Radical Polymerization Kinetics at High Conversion

Models are being developed to account for diffusion-controlled termination and propagation reactions due to chain entanglements and glassy-state transition. These models are being used to predict abnormal molecular structures (such as excessive terminal double bonds and long chain branching) which seem to occur at high conversions in the bulk, suspension and emulsion polymerization of vinyl chloride. Copolymerizations of styrene-acrylonitrile at high conversions are being done to measure abnormal microstructure when propagation reactions are diffusion controlled.

(Contribution to Polymer Colloids Group Newsletter, from Dr. A.E.Hamielec, Department of Chemical Engineering, McMaster University, Hamilton, Ontario, Canada).

Polymer Colloid Group Newsletter

S.G. Mason, T.G.M. van de Ven and A.A. Robertson

Department of Chemistry, McGill University
and
Pulp and Paper Research Institute of Canada

23 SEP 1980

Current studies in our graduate student research program include the following.

(a) Rheo-optical behavior of ordered latexes.

The behavior of ordered latex under shear was investigated using a visible-light Bragg diffraction technique. When the Bragg angle is fixed at 90° , the Bragg diffraction peak corresponds to the spacing of the lattice planes parallel to the walls. Before applying shear the latex exhibited a clear peak. When the latex was subjected to a low shear rate (0.33 s^{-1}), the peak became broader and was shifted towards longer wave lengths. This might be due to a deformation of the electric double layer by the shear, thus causing a difference in the distance between the lattice planes of the latex.

Under higher shear, one might expect the occurrence of a larger shift of the peak. However, it was found instead that the peak was separated into two peaks, one of which had a shorter and one of which had a longer wave length than the original peak.

Ordered latex suspensions are, in general, non-Newtonian. The above phenomenon can provide insight into this non-Newtonian behavior. The presence of two peaks suggests that two kinds of spacing exist in the latex, one shorter and the other larger than the original spacing (see Fig. 1). This could explain the difference with the simple shear flow pattern.

Other interesting phenomena are:

- (1) The separation of the spacing does not recover after removal of the shear. In contrast the peaks which were shifted by low shear returned to their original position after removal of the shear, but remained broadened.
- (2) As first reported by S. Hachisu, we confirmed that the spacing of the latex at rest is smaller than the value calculated from the volume fraction of the latex. In other words, the size of the particles determined by Bragg diffraction is smaller than that determined by electronmicroscopy.

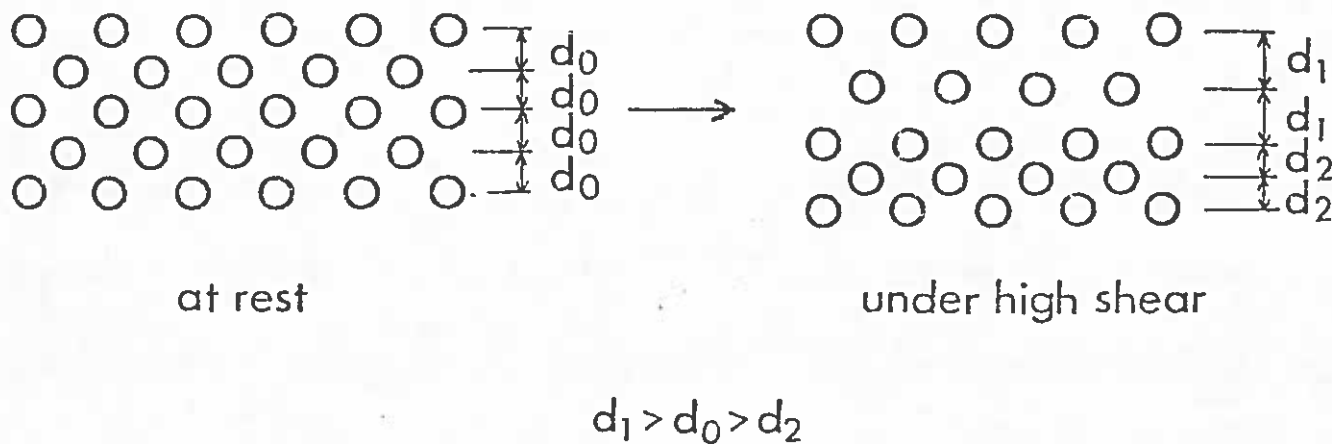


Fig. 1 Schematic presentation of the structure of ordered latex under high shear.

(b) Particle deposition from flowing suspensions.

The objective of this study is to determine particle deposition rates from flowing suspensions by solving complete transport equations including terms describing specific surface interactions and external forces. The results are relevant to deposition onto pulp fibers subjected to flow.

Rigorous equations were formulated describing deposition kinetics of spherical Brownian particles onto walls of parallel plate and cylindrical channels. Hydrodynamic corrections, dispersion and electrical double-layer forces as well as external forces, e.g. gravity, were simultaneously considered in an exact form. These equations were solved numerically using the weighted average Crank-Nicolson scheme and the particle flux (mass transfer Sherwood number) was determined as a function of dimensionless parameters introduced, such as Péclet number Pe , gravity number Gr , and Ad , Dl , τ accounting for the dispersion and electrical double-layer effects.

The results of numerical calculations have revealed that the particle flux is strongly influenced by the presence of attractive surface interactions, i.e. in the case when particle and channel surfaces are oppositely charged. This effect is especially well pronounced for

distances close to the origin (i.e. where the deposition starts) and for larger values of the Péclet number. This is due to the fact that under such conditions the diffusion boundary layer is comparable with distances over which surface interactions play a dominant role. Accordingly, the effect of surface interactions diminishes as $Pe \rightarrow 0$ and $x \rightarrow \infty$ (x is the longitudinal distance from the origin), i.e. for small particles and for remote distances from the origin where the diffusion boundary layer thickness becomes large. This is illustrated when the effect of attractive double-layer interactions on mass transfer rate (Sh number) is presented as a function of the dimensionless longitudinal distance \bar{x} . It is found that for small distances (i.e. $x < 1$) the calculated flux values differ considerably from the analytical formula:

$$Sh_1 = \frac{1}{\Gamma(4/3)} \frac{2 Pe}{9 \bar{x}}^{1/3} \quad (1)$$

which is widely used for interpretation of experimental results. However, for $Pe < 10^{-3}$ (i.e. for particles smaller than about $0.2 \mu\text{m}$) and in the absence of external forces, this formula may be successfully used for predicting particle deposition rates. Even for relatively strong double-layer interactions the deviation between exact results and those obtained by using Eq. (1) does not exceed 10%. Similarly, for particles smaller than $0.2 - 0.1 \mu\text{m}$ in diameter the influence of gravity becomes negligible. For larger particles, however, especially when the orientation of channel walls is perpendicular to the direction of gravity, this equation cannot be used to estimate the particle flux, not even as a crude approximation, giving results much too small for the lower channel surface and much too large for the upper one. Thus, for larger particles, i.e. above $1 \mu\text{m}$ in diameter, the influence of specific interactions on the particle deposition rate remains important even at remote distances from the origin.

In the case of a cylindrical channel when gravity cannot be neglected, the particle flux and consequently the amount of particles deposited depends not only on the longitudinal coordinate but also on the angular coordinate θ ; this dependence is more pronounced for larger distances from the origin.

In contrast to the rotating disc or spherical collectors, the interception effect is unimportant for the parallel-plate and cylindrical channels even for large particles because of the lack of a normal component of the fluid velocity vector. Consequently, the specific interactions play a much more significant role in determining particle deposition rate within parallel-plate and cylindrical channels as compared to the rotating disc or spherical collectors.

A comparison of existing experimental results of Bowen and Epstein with our theoretical predictions shows, in cases of strong double-layer attractions, a better agreement between theory and experiment than comparison with Eq. (1), used by these authors to interpret their results.

25 SEP 1980

Contribution to Polymer Colloid Group Newsletter

by M. Nomura

Dept. of Industrial Chemistry, Fukui University, Fukui, Japan

We (M. Nomura, Dr. S. Muroi and Dr. S. Matsuo) organized The 1st Symposium on Polymer Microspheres, Japan to be held at Fukui University, Fukui, Japan in Oct.31 - Nov. 1, 1980. The program is included for reference in this Newsletter. Preprints will be provided in case somebody is interested. (Preprint is written in Japanese)

SYMPOSIUM ON POLYMER MICROSPHERES

FUKUI MEETING

OCT.31 - NOV. 1, 1980

Organized by The Hokuriku Branch of The Society of Polymer Science, Japan and cosponsored by Division of Colloid and Surface Chemistry of The Chemical Society of Japan and The Adhesives Society of Japan and other two societies.

PROGRAM

1. Effect of Polymerization Conditions on the Morphology of PTFE Particles. T. Shimizu, S. Yamaguchi and S. Koizumi (Daikin Kogyo)
2. Monomer Distribution in Particles During Seeded Polymerization. M. Okubo, Y. Katsuta and T. Matsumoto (Kobe Univ.)
3. Surface Structure of Composite Polymer Emulsion Particles. M. Okubo, A. Yamane and T. Matsumoto (Kobe Univ.)
4. Studies on the Polymer Gel Spheres with Functional Groups on their Surface-Copolymerization of Diallyl Phthalate with Unsaturated Carboxylic Acid- Y. Otsuka, H. Kawaguchi and T. Hamasaki (Keio univ.)
5. Preparation of Amphoteric Latex Via the Hoffman Reaction. H. Kawaguchi, H. Hoshino and Y. Ohtsuka (Keio Univ.)

Invited Lecture: New Development in Polymer Emulsion.
T. Matsumoto (Kobe Univ.)

Invited Lecture: Applications of Synthetic Latex Particles for Medical and Biological Studies: T. Suzuki (Tokyo Medical Colledge)

6. Preparation of Composite Polymer Porous Membrane Employing Emulsion Polymerization. S. Hayashi, T. Hirai and N. Hojo (Shinshu Univ.)
 7. Temperature Sensitive Behavior of Composite Polymer Emulsion Film. M. Okubo, M. Seike and T. Matsumoto (Kobe Univ.)
 8. Rate of Emulsion Copolymerization of Styrene and Methyl Methacrylate. M. Nomura, I. Horie, M. Kubo and K. Fujita (Fukui Univ.)
 9. Analysis of Rate of Emulsion Polymerization with Dominant Gel-Effect. S. Omi, H. Nagatomo and M. Iso (Tokyo Noko Univ.)
 10. Rate of Coagulation of Latex Particles. K. Higashitani, Y. Matsuno and G. Hosokawa (Kyushu Institute of Technology)
 11. Preparation of Self-Crosslinking Emulsion by Radiation-Induced Emulsion Polymerization. A. Katakai and K. Makuuchi (JAERI, Takasaki)
 12. Viscosity Control of Emulsion Polymerized by Radiation. K. Makuuchi, A. Katakai and S. Egusa (JAERI, Takasaki)
 13. Emulsion Polymerization of Styrene by Electron Beams. K. Hayashi and S. Okamura (JAERI, Neyagawa)
 14. Preparation and Surface Properties of Nonaqueous Dispersion of Poly(Methyl Methacrylate). A. Kitahara, T. Satoh, S. Matsumura, K. Kandori and K. Kon-no (Science Univ. of Tokyo)
 15. Structure of Electrical Double Layers on Synthetic Latices. K. Furusawa (The Univ. of Tsukuba)
 16. Studies of Ionizable Surface Groups on Various Latices by Conductometric and Potentiometric Titrations. M. Ozaki, N. Arai, H. Itoh and Y. Miyashita (Yokohama City Univ.)
 17. Acid Distribution and Stability in Carboxylated Styrene-Butadiene Latexes. M. Sekiya and T. Koike (Nippon Zeon)
- Invited Lecture: Hydrophilic Gel: Its Characterization and Application to Separation of Biological Substances.
F. Kamiyama (Sekisui Chem. Co.)
18. Dynamic Light Scattering Measurements of Polystyrene Latices. T. Kato, K. Nakamura and A. Takahashi (Mie Univ.)
 19. Preparation and Characterization of Alkali-Swellable Carboxylated Latex. S. Nishida (Japan Synthetic Rubber Co.) M.S. El-Asser and J.W. Vanderhoff (Lehigh Univ.)
 20. Effect of Neutralization on Water-resistance of Carboxyl-Containing Emulsion Film. Y. Doi, T. Kato and H. Ori (Showa Highpolymer Co.)
 21. Analysis of Plastisol Viscosity Using the Glass beads Models. T. Suzuki, S. Yonehara and M. Izumi (Nippon Zeon Co.)
 22. Electrokinetic Properties at the Liquid/Gas Interface. T. Imamura (Kao Soap Co.) F.J. Micale (Lehigh Univ.)
 23. Characterization of Poly(Methyl Methacrylate) Latex Grafted with Acrylic Acid by Using Light Scattering Method. H. Hashiya and T. Matsuo (Fukui Univ.) K. Makuuchi (JAERI, Takasaki)

Contribution to the Polymer Colloid

Group Newsletter

from The University of Akron

Submitted by: I. Piirma

30 SEP 1980

Experimental work done and report written by: S. Kincaid

The Importance of Branching in Styrene
Emulsion Polymerization

In a recent paper, Piirma and Kincaid¹ presented a study of the various kinetic parameters controlling the dependence of molecular weight on particle size in the emulsion polymerization of styrene. In this earlier work, an equation for the degree of polymerization (DP) formed the basis for calculating the rate of absorption of radicals into the latex particles, the time between entry of radicals, and the rate constant for termination of radicals within the particles. However, the DP equation is only applicable to linear polymers, while the results indicated the presence of branched molecules. The results are similar to those of Vanderhoff et al.², who first postulated that chain transfer to polymer could produce a significant degree of branching in the emulsion polymerization of styrene. The present paper first describes the derivation of a DP equation, which accounts for branching, and then demonstrates its use in recalculating the results of the authors' earlier work.

For linear polymer molecules formed by combination of radicals, the degree of polymerization is given by

$$\frac{1}{DP} = \frac{\rho_A}{2 R_p} + \frac{k_{tr}}{k_p} \quad (1)$$

where ρ_A is the overall rate of absorption of radicals into the particles ($\text{mol} \cdot \text{l}^{-1} \cdot \text{H}_2\text{O}^{-1} \cdot \text{sec}^{-1}$), R_p is the overall rate of polymerization ($\text{mol} \cdot \text{l}^{-1} \cdot \text{H}_2\text{O}^{-1} \cdot \text{sec}^{-1}$), k_p is the propagation rate constant ($\text{l} \cdot \text{mol}^{-1} \cdot \text{sec}^{-1}$), and k_{tr} is the rate constant for chain transfer

to monomer ($l\text{-mol}^{-1}\text{-sec}^{-1}$). In the earlier work, measurements of R_p and DP were used to calculate ρ_A .

According to Flory³, $1/DP$ equals the number of pairs of chain-ends per monomer unit, since each linear molecule has one pair of chain ends. In general, the number of pairs of chain ends per monomer unit is given by the number of pairs of chain ends per chain, N_p , divided by the DP. Thus, Equation (1) is a specific case of the general equation,

$$\frac{N_p}{DP} = \frac{\rho_A}{2 R_p} + \frac{k_{tr.}}{k_p} \quad (2)$$

Furthermore, since $N_p = N_e/2$, where N_e is the number of chain ends per chain, then

$$\frac{N_e}{2 DP} = \frac{\rho_A}{2 R_p} + \frac{k_{tr.}}{k_p} \quad (3)$$

For the combination of radicals, the number of chain ends per chain is given by

$$N_e = 2 + \beta DP, \quad (4)$$

where β is the mean number of branches per monomer unit in the polymer. Combining Equation (3) and (4) yields the final equation,

$$\frac{1}{DP} = \frac{\rho_A}{2 R_p} + \frac{k_{tr.}}{k_p} - \frac{\beta}{2} \quad (5)$$

For a bulk polymerization in which branching results from only chain transfer to polymer, Small⁴ has given an equation for the branching parameter, β , in terms of the fractional conversion. To adapt Small's equation to emulsion polymerization simply requires that the fractional conversion be replaced by the weight fraction of polymer in the particles, W_p . Thus, the mean number of branches per monomer unit is given by

$$\beta = C_{tp} \left[- (1/W_p) \ln (1-W_p) - 1 \right], \quad (6)$$

where C_{tp} is the transfer constant per monomer unit in the polymer. For an emulsion polymerization of styrene at 50°C, with a molecular weight of one million and $W_p = 0.40$, Equation (6) predicts that 55% of the polymer molecules have at least one branch.

Using the styrene polymerization data reported earlier¹, Equations (5) and (6) were used to recalculate the previous results. The values of k_p and k_{tr} were the same as used previously, and the value of the transfer to polymer constant was that of Schulz et al.⁵, i.e. $C_{tp} = 2.0 \times 10^{-4}$ at 50°C. The weight fraction of polymer in the particles was calculated from the data on the monomer concentration in the particles. The data from the previous paper and the recalculated results are given in Table I.

Table I. Summary of Results

Percent Emulsifier	2.0	1.5	1.0	0.75
$R_p \times 10^4$ (mol-ℓH ₂ O ⁻¹ -sec ⁻¹)	8.01	6.11	4.58	2.90
$N \times 10^{-17}$ (ℓH ₂ O ⁻¹)	11.5	7.12	3.39	1.51
$DP \times 10^{-4}$	2.21	1.82	1.43	1.02
D (Å)	874	1040	1390	1910
[M]	5.27	5.44	5.84	6.20
W_p	0.430	0.410	0.362	0.319
$\beta \times 10^5$	6.1	5.7	4.8	4.1
\bar{n}	0.65	0.78	1.1	1.5
a	1.71	2.42	3.95	5.52
$\rho_A \times 10^8$ (mol-ℓH ₂ O ⁻¹ -sec ⁻¹)	6.5	5.9	5.4	4.8
$k_t \times 10^{-4}$ (ℓ-mol ⁻¹ -sec ⁻¹)	2.0	2.4	4.2	11.0
τ (sec)	29	20	10	5.2

note: N = number of particles/ℓH₂O

D = swollen particle diameter

[M] = monomer concentration in the particles

\bar{n} = average number of radicals/particle

The new results do not alter the major conclusions drawn in the previous paper, except for the observations concerning the dependence of ρ_A on particle size and number. Originally, the rate of absorption of radicals into the particles was found to increase as the number of particles decreased, but this trend could not be explained. However, the branching correction yields the expected result of ρ_A decreasing as the number of particles decreases, as shown in Figure 1. According to Fitch and Shih⁶ and also Ugelstad⁷, ρ_A should be directly proportional to the product of the number of particles and the particle radius, Nr , since the entry of radicals into the particles is diffusion controlled. The plot in Figure 2 confirms this proportionality predicted by diffusion theory.

Without the branching term in the DP equation, the values of τ , the time between successive radical entries into a particle, increase very rapidly at the lower particle sizes as shown in Figure 3. The parameter τ is given by $\tau = N/\rho_A N_A$, where N_A is Avogadro's number. For no branching, ρ_A is calculated from

$$\rho_A = 2 R_p \left(\frac{1}{DP} - \frac{k_{tr}}{k_p} \right). \quad (7)$$

Since $\tau \propto 1/\rho_A$, the rapid change in τ results from ρ_A approaching zero as $1/DP$ approaches k_{tr}/k_p in Equation (7). Figure 3 also shows that use of the branching term yields more realistic τ values, which do not increase asymptotically. However, the dependence of τ on the number of particles ($\tau \propto N \propto 1/r^3$) still remains the dominant factor controlling the dependence of molecular weight on particle size.

Since ρ_A is used in calculating the termination rate constant, k_t , the branching term should also influence the previous values of k_t . Figure 4 shows that the use of the branching parameter simply shifts the k_t values and does not alter the previous con-

clusions concerning the variation of k_t with particle size.

References

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- (3) P. J. Flory, *Principles of Polymer Chemistry*, p. 137, Cornell University Press, Ithaca, New York, 1953.
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- (5) G. V. Schulz, G. Henrici-Olivé, S. Olivé, *J. Polym. Sci.*, 17, 45 (1955).
- (6) R. M. Fitch and L. Shih, *Prog. Colloid and Polym. Sci.*, 56, 1 (1975).
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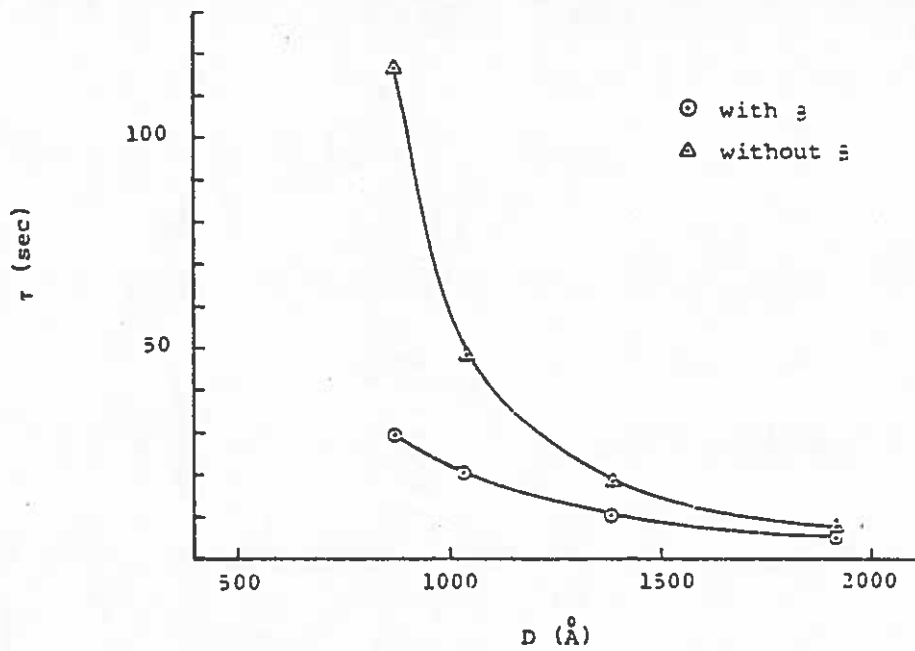


Figure 3. Time Between Radical Entries vs. Swollen Particle Diameter

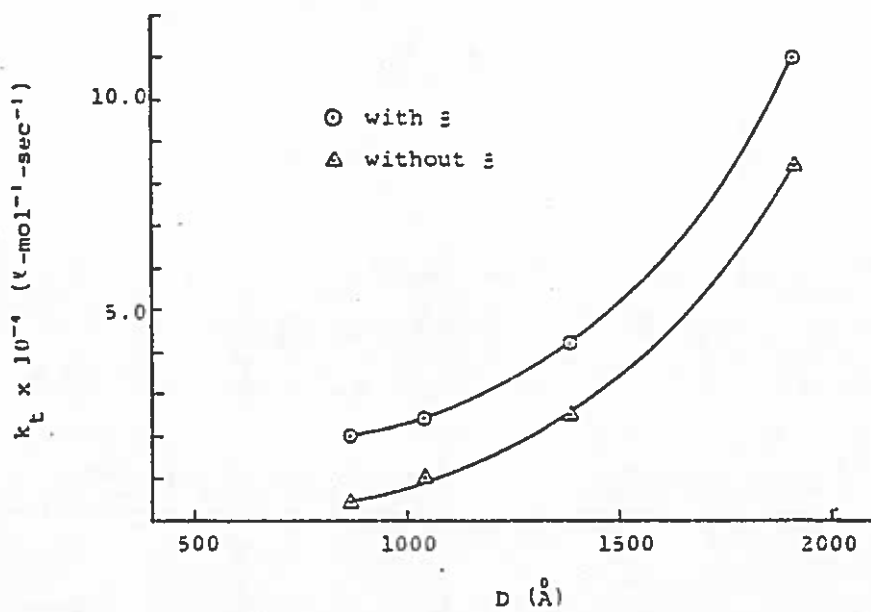


Figure 4. Termination Rate Constant vs. Swollen Particle Diameter

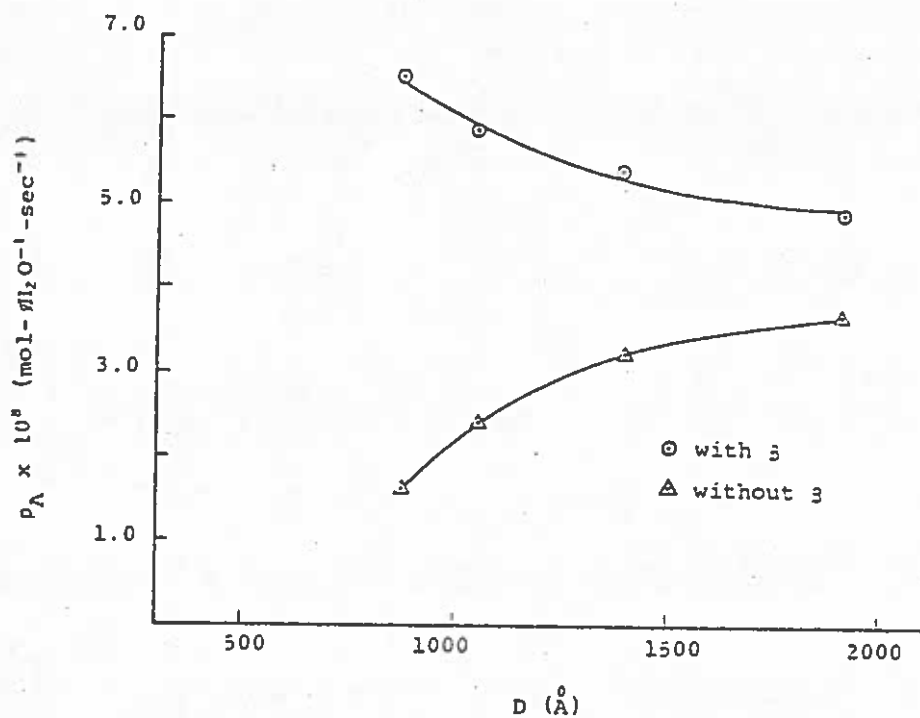


Figure 1. Rate of Absorption of Radicals vs. Swollen Particle Diameter

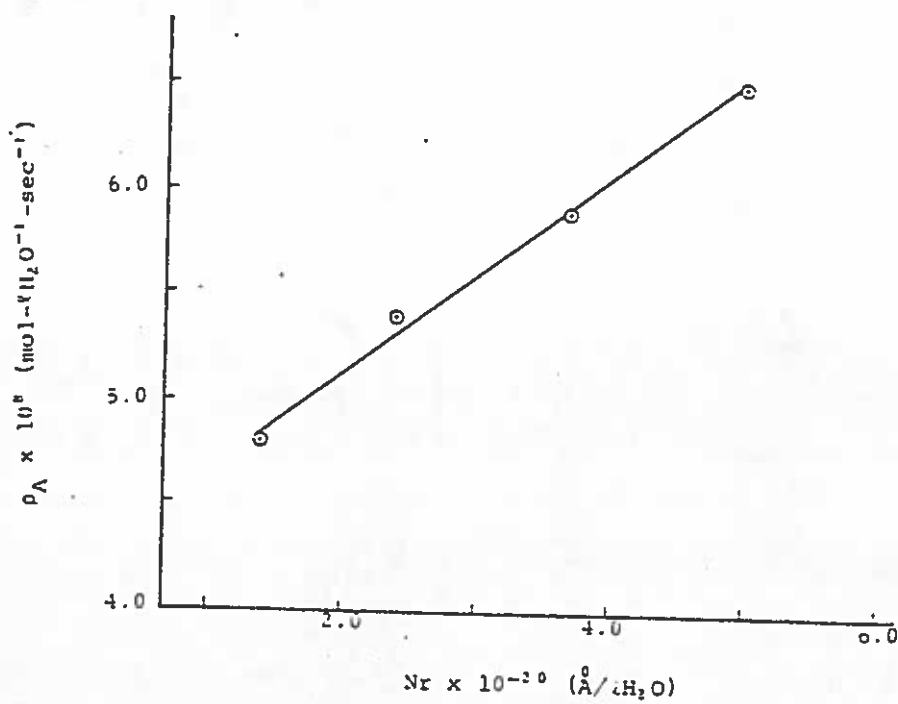


Figure 2. Rate of Absorption of Radicals vs. Nr

Contribution to the Polymer Colloid Group Newsletter

from

Dr D G Rance
ICI Limited, Plastics Division
Welwyn Garden City
Hertfordshire
England

Firstly I would like to thank the Group for electing me to its ranks at the 1979 Annual Meeting, and apologise for not writing a contribution sooner! Although we sell very few polymer colloids in the market place, nevertheless many of our products start life as emulsion polymers and so I thought you would like to know something of our polymer colloid interests at Plastics Division.

We sell as polymer colloids Polytetrafluoroethylene ('Fluon') dispersions and vinylidene chloride copolymer dispersions ('Viclan') with methyl acrylate or acrylonitrile as secondary monomers for coating application, the former for glass-cloth coating and fibre impregnation, the latter primarily for coating polymer films to give good oxygen and water barrier for food packaging applications. We also produce both of these materials as free-flowing powders from coagulated dispersions. The largest outlet for polymer colloids is in the PVC paste area, where dispersions are prepared by both seeded emulsion and microsuspension processes. These materials are spray dried and used extensively in the vinyl wall covering and floor tile areas. Another product is 'Diakon', an acrylic copolymer which is prepared as a latex, but subsequently coagulated and sold as a moulding powder principally to the automotive industry.

You can see that polymer colloids loom large in our commercial interests and at present I am involved with process research associated with the PVC seeded emulsion polymerisation process. However at this time I would like to report some work which I have been doing together with Ernest Zichy on some fundamental aspects of precipitation polymerisation which occurs in the early stages of the vinyl chloride suspension and bulk processes. PVC is insoluble in its monomer and phase separates in the early stages of polymerisation to form polymer gel particles which are heavily swollen by monomer. Our objective was to determine what was responsible for stabilising precipitated polymer and to proposing a mechanism for the particle growth and aggregation steps which result in the intergrown contiguous networks which make up PVC granules.

Our most recent views were presented as an invited lecture at the 3rd International Symposium on PVC held in Cleveland, Ohio in August and I enclose a prepublication copy of this work. We studied the initial stages of polymerisation by photon correlation spectroscopy (PCS). Using this technique we could not study the first precipitated particles ('basic' particles of size 15-20nm), since they aggregate within seconds of formation to form the nuclei of 'primary' particles. We were able to follow the growth of 'primary' particles by PCS up to the conversion at which they begin to aggregate further into the clusters which can be identified in high conversion polymer. The stability of 'primary' particles to aggregation has been attributed by us to electrostatic stabilisation, and recently quantified by Martin Speirs (he carried out postgraduate collaborative work with us at Edinburg University) who demonstrated that PVC particles in liquid vinyl chloride monomer show

normal electrophoresis behaviour Speirs showed that electrostatic stabilisation could account for the sharp onset of flocculation of 'primary' particles at a given critical size if the particles grew at constant particle number (constant total charge in the system). This was subsequently supported by PCS measurements where for a system with a low polymerisation rate, particle growth at constant particle number was clearly observed. The paper presents a model which describes the aggregation of 'basic' particles to form 'primary' particles, and shows that the 'primary' particle size first observed by PCS is when approaching a constant particle number, is completely predicted simply by considering the ratio of collision cross-sections of 'basic' particles to 'primary' particles. The paper concludes with the description of a mechanism of suspension polymerisation of PVC which pools all our experimental observations at low and intermediate conversions to describe the life-cycle of the two phase system (polymer gel/monomer) from the time the first gel particles precipitate to the time when the contiguous gel network loses all its free monomer, leading inevitably to pressure drop.

Polymer Colloids at the Institute for Surface Chemistry

Per Stenius and Bengt Kronberg
Institute for Surface Chemistry
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118 SEP 1980

The Polymer Colloid work at the Institute for Surface Chemistry in Stockholm concerns the adsorption of surfactants on latexes and the formation of colloids by association between cationic and anionic polymers. The work on adsorption is subdivided into three closely related areas. They are (i) adsorption of nonionic surfactants and polymers on latexes, (ii) competitive adsorption, either with two surfactants (e.g. nonionic + anionic) on one surface or one surfactant on two surfaces (e.g. latex + pigment) and (iii) effects of adsorbed surfactants on the stability of latex dispersions i.e. mechanical stability, freeze-thaw stability and salt stability.

The work on association between cationic and anionic polymers is aimed at an understanding of the conditions for the formation of stable colloidal particles, their coagulation kinetics and their adhesion to solid surfaces.

Abstracts of papers, recently submitted for publication, concerning work on polymer colloids done at the Institute for Surface Chemistry and Abo Akademi:

ADSORPTION OF NONIONIC SURFACTANTS ON LATEXES

Bengt Kronberg, Lena Käll and Per Stenius

Adsorption isotherms of ethoxylated nonylphenols on poly(styrene) and poly(vinyl chloride) latexes have been measured. The isotherms all reach a limiting adsorption at concentrations somewhat higher than the critical micellar concentrations of the surfactants. The relative affinity of the surfactants to the latex surfaces was found to decrease with increased ethylene oxide chain length. Analysis of the isotherms indicates some affinity of the ethylene oxide chain to the latex surface. This affinity may possibly be attributed to the presence of surface carboxylic groups.

Some of the isotherms were obtained using the serum replacement technique developed by S.M. Ahmed et al (S.M. Ahmed, M.S. El-Aasser, G.H. Pauli, G.W. Poehlein and J.W. Vanderhoff, *J. Coll. Interface Sci.*, 73 388 (1980)). In the application of this technique to the adsorption of nonionic surfactants it was found that polydispersity of the surfactant plays an important role since surfactant species with high affinity to the latex surface will continuously replace other species with lower affinity.

FORMATION OF COMPLEXES, COLLOIDS AND PRECIPITATES IN
AQUEOUS MIXTURES OF LIGNIN SULPHONATE AND SOME CATIONIC
POLYMERS

Göran Ström and Per Stenius

A quantitative study has been carried out of the formation of polyelectrolyte complexes between calcium lignin sulphonate (LS) and three cationic polyelectrolytes, two polytrimethylaminoethylmethacrylates (I and II) with different molecular weight and one acrylamide copolymer. The parameters studied were the weight ratio of the oppositely charged polymers, the concentration of NaCl and the temperature. Separated molecular weight fractions of LS were studied in combination with I. The interactions were found to result in soluble complexes, colloids or macroscopic precipitates, mainly depending on the polymer weight ratio and the molecular weight of LS. For fractions with $M_w > 1000$ the complexation between I and LS was stoichiometric when LS was present in excess of charge equivalence, resulting in formation of only macroscopic precipitate and quantitative precipitation. Soluble polyelectrolyte complexes were formed with LS if the M_w was < 1000 and I was in excess. Very stable colloids were formed with this LS fraction and I. In unfractionated LS, these soluble complexes are probably adsorbed on precipitating particles containing high molecular weight LS and I.

THE MECHANISM OF SOAP-FREE EMULSION POLYMERISATION OF STYRENE IN METHANOL/WATER SOLVENTS

Juhani Laaksonen and Per Stenius

The polymerisation reaction before particle formation in soap-free emulsion polymerisation of styrene in mixtures of methanol and water has been studied by using the method of initial rates to determine the order of the reaction with respect to the different reacting species. The polymerisation was carried out in homogeneous solution containing methanol up to 50 vol-%. The polymerisation was initiated with potassium persulfate. It was found that in the presence of methanol the polymerisation rate decreases in the first steps of polymerisation. The increasing polymerisation rate with increasing concentration of methanol in the heterogeneous system (after particle formation) can be explained by the increased solubility of the monomer and the increase in particle radius. The mechanism has been studied also by determination of the surface groups on the latexes by conductometric titration. In this case the latexes were synthesized under heterogeneous conditions (10 weight-% styrene) in order to obtain sufficient latex for determination of the change density on the particles. The particle diameter was determined by electron microscopy. The results indicate that particle formation is governed by electrostatic stabilization of the aggregates that are formed when the primary particles coagulate.



The Commonwealth of Massachusetts

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9-8-80

DEPARTMENT OF CHEMISTRY

111 SEP 1980

Two papers, presented at the Las Vegas ACS Meeting (August, 1980) summarize our current interest and progress. R. L. Rowell

CHARACTERIZATION OF LATEX PARTICLES BY LIGHT SCATTERING. R. L. Rowell and J. R. Ford. Department of Chemistry, University of Massachusetts, Amherst, Massachusetts 01003.

The exact electromagnetic wave theory of angular light scattering is reviewed and represented in graphical form in order to illustrate the regularity and simplicity of the three most pronounced general features: (1) the increase in forward scattering with increased particle size, (2) the increase in the number and magnitude of angular maxima and minima with increased particle size and (3) the dependence of intensity level and angular structure on refractive index. The angular method is used to illustrate the concept that structure or variation in the data is the key to the determination of particle size distribution and refractive index by light scattering. The inter-relationship between polydispersity in size and refractive index is discussed in relationship to the inversion of light scattering data. The wave theory for spheres is compared with particles of other shapes. The determination of size distribution and refractive index from angular light scattering is compared with the turbidity spectra method and with recently developed techniques using photon correlation spectroscopy.

LIGHT SCATTERING STUDIES OF THE INTERNAL STRUCTURE OF EMULSION POLYMER PARTICLES.

J. R. Ford and R. L. Rowell, Department of Chemistry, University of Massachusetts, Amherst, Massachusetts 01003 and D. R. Bassett, Union Carbide Corporation, Technical Center 720-130, South Charleston, West Virginia 25303. Work done at the University of Massachusetts.

Carboxylic emulsion copolymer particles prepared from acrylic ester-acrylic acid (2%) monomer have been examined previously by sedimentation and light scattering and presented in terms of a model with a hydrated acid-rich shell surrounding a compact polymer core. The sedimentation method has been used to characterize particle expansion with increasing pH but the technique cannot differentiate between uniform and surface layer expansion. The present study employs wide angle light scattering measurements and the exact electromagnetic wave theory of light scattering by a core-shell model to probe the internal structure of emulsion particles as a function of pH. Theoretical calculations show the feasibility of the light scattering method in the 130°-150° angular range. The solution to the principal experimental problems of dust particles and pH stability of the latexes on dilution is discussed. Wide angle light scattering measurements by single photon counting using a laser source have been carried out as a function of dilution of the latex with sufficient sensitivity to distinguish two distinct ranges of linear scattering: one dominated by scattering from latex particles and one dominated by the background molecular scattering from monomer, oligomer and emulsifier.

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MORPHOLOGY OF TWO STAGE LATEX PARTICLES I. POLYSTYRENE AND STYRENE-BUTADIENE COPOLYMER PAIR SYSTEMS. Do Ik Lee, Designed Latex & Resins, 1604 Building, Dow Chemical USA, Midland, Michigan 48640

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The morphology of two-stage (styrene//styrene-butadiene) latex particles was studied with respect to variations in stage ratio, molecular weights, styrene-butadiene (S/B) copolymer composition, polymerization sequence, and polymerization conditions. The characterization methods included electron microscopy with the osmium tetroxide staining method as well as various chemical, physical, thermal, and mechanical analyses. The morphological features observed were mainly structures resulting from phase separation rather than the core-shell morphology expected from surface polymerization with no interpenetration. At intermediate chain transfer agent levels the second-stage polymer phase-separated as microdomains within the first-stage polymer particles, then underwent phase inversion to become a continuous phase as the amount of the second-stage polymer increased. At high CTA levels, polymers were completely separated, resulting in a hemispherical morphology at the equal stage ratio. Upon further increase in the amount of the second-stage polymer, asymmetric encapsulation occurred. Phase domain sizes decreased with decreasing butadiene in the S/B copolymers, as expected from better compatibility. This study strongly suggests that the morphology of two-stage latex particles greatly depends on the thermodynamic nature of polymerizing latex systems, polymerization conditions and the order of polymerization.

CATIONIC POLYMERIC SURFACTANTS. D. M. Pickelman and R. A. Wessling, Polymer Research Lab, 1712 Building, Dow Chemical USA, Midland, Michigan 48640

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Polymeric surfactants are water-soluble polyelectrolytes that exhibit enhanced surface activity. Those considered in this work were random addition copolymers in which one of the components was substituted with cationic groups, such as the quaternary ammonium group. The surface activity of a water-soluble ionic copolymer is determined primarily by charge density and molecular weight. Maximum activity is observed in polymers with a charge density and degree of polymerization in the ranges 1-4 meq/g and 10-100, respectively. But behavior is also markedly influenced by other structural features such as backbone polarity, chain

stiffness, hydrogen bonding sites, pendant hydrophobes, and certain structure. The effect of some of these variables on the surface activity of copolymers made up of vinylbenzyl onium units and various nonionic hydrophobic units like styrene and methyl methacrylate was investigated. Activity was characterized by the surface tension of aqueous solutions. CMC's were measured by a variety of physical techniques and the results interpreted in terms of polymer structure. Polymers with the proper balance of properties make excellent stabilizers for both monomer emulsions and polymer colloids.

PARTICLE SWELLING CHARACTERISTICS OF EMULSION POLYMERS CONTAINING ACRYLIC ACID AND HYDROXYETHYL ACRYLATE. F. L. Saunders, L. L. Killat & R. E. Gunderman, Polymer Research Lab, 1712 Building, Dow Chemical USA, Midland, Michigan 48640

Particle swelling characteristics were measured by hydrodynamic chromatography (HDC) on acrylic latex compositions containing acrylic acid (AA) and hydroxyethyl acrylate (HEA) in which these functional monomers were incorporated into the latex polymer in different stages of the polymerization. HEA serves to impart hydrophilicity to the polymer while AA provides alkali sensitivity. Latexes with a composition of methyl methacrylate/butyl acrylate/HEA/AA (52.5/41/5/1.5) were prepared by a continuous monomer addition process. The polymerization was divided into two stages, stage 1 being the first half of the monomer feed and stage 2 the last half of the feed. Acrylic acid and HEA were added in either of the two stages or equally divided between the stages. MMA and BA were added continuously during both stages. Thus the latexes prepared have the same overall composition but with three different modes of monomer addition.

HDC particle size measurements were made at pH of 5.5, 7.0 and 9 to indicate the effective particle size as a function of pH. An estimate of the distribution of AA in the latex was made by potentiometric titration on the latex before and after treatment with ion exchange resin. A summary of these data are given below:

AA & HEA Monomer in Stage	HDC Particle Size, Å			% of AA Charged		
	pH	pH	pH	Surface	Soluble	Buried
	5.5	7.0	9.0			
1 & 2	1160	1580	1770	73	8	19
1	1230	2150	2330	83	2	12
2	1350	2220	2520	80	20	<1

These results suggest that the acid rich polymer formed in Stage 1 process migrates to the surface region of the latex particle. Latex viscosity follows the pH dependence of particle swelling.