

POLYMER COLLOID GROUP NEWSLETTER

Vol. 12 No. 1

14 May 1982

Ron Ottewill was elected as a Fellow of the Royal Society of London on 18th March. The Royal Society was founded by King Charles II in 1660 and is the most select of British scientific societies - even more select than the Polymer Colloid Group! Election as an F.R.S. is a testimony to the reputation of the Fellow's scientific achievements. No doubt members of the Group will wish to congratulate Ron.

Evidently members of the Polymer Colloid Group depend completely on getting the reminders which Mrs Proctor sends out to stimulate them into preparing their Newsletter contributions. We had to postpone the deadline for the receipt of contributions for this issue by 3 weeks because we only remembered to send the reminders out at about the time when members should have been sending their copy in! Only one contribution and two notices arrived in time for the original deadline! For what good it may be the deadline for the receipt of copy for the Autumn issue will be Monday, 27th September 1982 assuming that we do remember to despatch the reminders in mid-August as usual.

The 1982 Annual Meeting of the Group will be held during the N.A.T.O. 'Polymer Colloids II' Advanced Study Institute at Bristol, Preparations in Bristol are in full swing. At the time of writing some places are still available (though perhaps not for potential participants from the U.K. and U.S.A.) but any one who has not yet arranged to go should contact the Director, Gary Poehlein by the quickest available means. His telephone number is (404) 894-2867 at the Georgia Institute of Technology. The dates are Monday 28th June with the first lecture at 2.15 p.m. until 5.45 p.m. on Thursday 8th July. The 28th IUPAC Macromolecular Symposium will be held at Amherst, Massachusetts during the following week but Polymer Colloids do not figure in the programme this year: there is a section on Rheology but this will probably concentrate on melt rheology.

The 1983 Annual Meeting will most probably be arranged during the Fourth Gordon Research Conference on 'Polymer Colloids' of which John Vanderhoff will be Chairman. This has now been scheduled for July 11-15, 1983 at Tilton School, Tilton, New Hampshire.

The title of the Plastics and Rubber Institute Conference to be held at The Institution of Electrical Engineers, Savoy Place, London on Tuesday and Wednesday, 16th and 17th June 1982 has been changed to 'Emulsion Polymers'. John Vanderhoff will open the programme (at 9 a.m.) with a Plenary Lecture 'New applications of emulsion polymer systems in the surface coating industry'. The Plenary Lecturer on the second day will be Tharwat Tadros on 'Factors governing the stability of polymer latices'. Ten Contributed Papers are scheduled for each day. These are being preprinted and the preprint book can be purchased from the PRI after the conference by those who could not attend. Registration Forms from the Plastics and Rubber Institute, 11 Hobart Place, London, SW1W 0HL. Telephone 01-245 9555. The PRI hopes to organise another Conference under the title 'Polymer Latex II' in 1984.

The 13th Lehigh Short Course on 'Advances in Emulsion Polymerization and Latex Technology' is scheduled for 7-11 June 1982. Details from Mohamed El-Aasser. The European Version at Davos, Switzerland (the 5th) on 16-20 August, 1982. Details from Gary Poehlein.

The Call for Papers for the 'Polymer Colloids' Symposium at the American Institute of Chemical Engineers at Houston, Texas, 27-31 March, 1983 appears on a following page.

Mamoru Nomura is organising the '2nd Polymer Microspheres Symposium, Japan' to be held at Fukui, 11-13 November 1982. The meeting is sponsored by the Division of Colloid and Surface Chemistry of the Chemical Society of Japan, the Society of Polymer Science of Japan and four other societies. It is intended that the Microspheres Symposium should be a biennial event. Group members may be invited as plenary lecturers. Offers of Contributed Papers (in English) would be welcome and should be made to Dr Nomura.

A Review Symposium on 'Commercial Water-Soluble Polymers: Properties and Applications' will be held at UMIST, 15-17 September 1982. Details are enclosed.

Academic Press published 'Emulsion Polymerization' (Ed. I. Piirma) as scheduled. ISBN 0-12-556420-1. Price is \$58 in the U.S.A. or £38-40 in the U.K. which is a premium of about £6 on the U.S. price. The authors include Blackley, Dunn, Force, Hamielec, Hansen, Napper, Nomura, Ottewill, Poehlein, Stannett, Ugelstad, and Yeliseyeva.

Plenum Press's long-heralded translation of 'Emulsion Polymerization and its Applications in Industry' by Eliseeva, Ivanchev, Kuchanov, and Lebedev has now been actually published. ISBN 0-306-10961-1. The price is \$49.50 within the U.S.. The U.K. price £31.19 represents a £2 discount on the export price of U.S. \$59.40.

The publisher for the proceedings of the N.A.T.O. 'Polymer Colloids II' A.S.I. is now to be Martinus Nijhoff of Holland but publication before early 1983 is unlikely.

Two of the 30 papers to be presented at the 6th European Plastics Conference in Paris, June 7-9 relate to emulsion polymerisation: 'Continuous emulsion polymerization: optimal start-up policies for a single continuous stirred tank reactor' by S.-A. Chen and G.F. Shen of Taiwan and 'Mathematical modelling of emulsion polymerisation processes' by M.P. Wilson, T.Y. Cao, and A.J. Merry of Great Britain. The Registration Fee includes a book of proceedings which might be available subsequently from Societe de Chimie Industrielle, 28, rue Saint Dominique, F 75007 Paris.

The A.C.S. Division of Organic Coatings and Plastics Chemistry has 'Advances in Emulsion Polymerization' in its list of proposed topics for future meetings i.e. meetings after the August 1984 Philadelphia Meeting. Symposia topics and chairmen have already been selected for this and the earlier meetings.

A.S.D.

February 18, 1982

3 MAR 1982

ANNOUNCEMENT

&

CALL FOR PAPERS

FIRST AICHE SYMPOSIUM

on

"POLYMER COLLOIDS"

(Four Sessions)

76th Annual Meeting
American Institute of Chemical Engineers
March 27-31, 1983
Houston, Texas

Please submit a letter of intention to participate in the symposium as soon as possible by writing to any of the following Session Chairmen:

1st Session

Kinetics Aspects and Reactor
Engineering

Dr. Gary W. Poehlein
School of Chemical Engineering
Georgia Institute of Technology
Atlanta, Georgia 30332
Phone: (404) 894-2865

2nd Session

Interfacial Aspects

Dr. Pranab Bagchi
Research Laboratories
Eastman Kodak Company
Kodak Park
Rochester, New York 14650
Phone: (716) 477-7148

3rd Session

Colloid Aspects

Dr. Mohamed S. El-Aasser
Department of Chemical Engineering
Emulsion Polymers Institute
Lehigh University
Bethlehem, Pennsylvania 18015
Phone: (215) 861-3598

4th Session

Process vs. Properties

Dr. Gordon P. Beirwagen
Sherwin-Williams Company
10909 S. Cottage Grove Ave.
Chicago, Illinois 60628
Phone: (312) 821-3571

For further information, please contact Symposium Chairman Dr. Mohamed S. El-Aasser at the above address.

EFFECT OF NATURE OF HYDROPHOBE MOIETY ON ABILITY OF ETHYLENE OXIDE ADDUCTS TO
MODIFY MECHANICAL STABILITY OF NATURAL RUBBER LATEX

D. C. Blackley, London School of Polymer Technology,
The Polytechnic of North London, Holloway, London N7 3DB.

4 MAY 1968

Before commencing this contribution proper, I draw attention to what should be evident from the heading, namely that the name of our College has recently changed. The change, which occurred on 1st January of this year, marks the merger at The Polytechnic of North London of the former National College of Rubber Technology with the Polymer School from The Polytechnic of the South Bank to form a single centre for polymer teaching in the London area. Our new name reflects a somewhat broader range of interests than hitherto. Whereas our previous emphasis was primarily, though not exclusively, upon rubber science and technology, we are now very much concerned with plastics as well.

We continue to accumulate interesting information concerning the process whereby natural rubber latex becomes destabilised when subjected to mechanical shearing, and concerning the effects of additives upon mechanical stability. We have previously published results for the effect of increasing additions of various fatty alcohol-ethylene oxide adducts upon the mechanical stability of natural rubber latex(1). In these earlier experiments, the adducts were all based upon a single fatty alcohol (a mixture of cetyl and oleyl alcohols), but the overall mole ratio of ethylene oxide to fatty alcohol was varied over the range 2 to 60. In most cases, the adduct initially caused the mechanical stability to fall sharply to a minimum and thereafter to rise. The initial reduction is attributed to displacement of proteinaceous substances adsorbed at the rubber-water interface. The magnitude of the subsequent increase in mechanical stability depends greatly upon the mole ratio of ethylene oxide to fatty alcohol, and is particularly marked when the ratio is high.

We have recently carried out experiments in which the overall mole ratio of ethylene oxide to hydroxy hydrophobe base has been kept constant at 30, but the nature of the hydrophobe base was varied. Four adducts have been used, based respectively upon lauryl alcohol (A), cetyl-oleyl alcohol (B), castor oil (C), and an octyl phenol (D). The results are summarised in the following table, the entries in which are the results for mechanical stability times expressed in seconds:

| <u>level of adduct</u> <u>(pphr of latex</u> <u>solids)</u> | <u>adduct A</u> | <u>adduct B</u> | <u>adduct C</u> | <u>adduct D</u> |
|---|-----------------|-----------------|-----------------|-----------------|
| 0 | 853 | 853 | 853 | 953 |
| 0.12 | 180 | 103 | 185 | 435 |
| 0.25 | 290 | 154 | 205 | 290 |
| 0.50 | 598 | 203 | 359 | 273 |
| 0.75 | 1250 | 313 | 410 | 700 |
| 1.00 | 1533 | 328 | 410 | 1175 |
| 1.50 | 3440 | 510 | 583 | 3370 |

These results show several interesting features, of which the most important are that

- i) all the adducts initially reduce the mechanical stability of natural rubber latex; and
- ii) the subsequent enhancement of the mechanical stability depends greatly upon the nature of the hydrophobe moiety of the adduct.

The second of these observations is particularly interesting, because it parallels observations which have been made concerning, for instance, the effect of added potassium n-alkanoates upon the mechanical stability of natural rubber latex(2). Furthermore, in the case of the potassium n-alkanoates, it was observed that, as the chain length of the alkanolate was increased, the ability to enhance mechanical stability passed through a maximum when the alkyl chain contained approximately 11 carbon atoms. Looking at the present results, it is particularly interesting to note that the adduct based upon lauryl alcohol conferred much higher mechanical stability at the higher levels of addition than did the adducts based upon cetyl-oleyl alcohol and upon castor oil. It is also interesting that the adduct based upon an octyl phenol gave enhancements of mechanical stability at the higher levels of addition similar to those given by the lauryl alcohol adduct. These generalisations remain true whether the levels of addition are considered on a weight basis (as in the above table) or upon a molal basis. They provide further evidence that the effect of an added surface-active substance upon the mechanical stability of natural rubber latex can depend greatly upon the nature of the hydrophobe moiety which anchors the molecule at the rubber-water interface, as well as upon the nature of the hydrophilic moiety.

References

1. D. C. Blackley, b. N.M. Salleh and R.Twaits, Plastics and Rubber: Materials and Applications, 1977, 2, 117
2. D. C. Blackley, bt. A.A. Nor Aisah and R.Twaits, Plastics and Rubber: Materials and Applications, 1979, 4, 77

Properties and Structure of Polyvinyl Alcohol

Mr R. B. Abdul Ghani from the University of Malaysia, Kuala Lumpur (N.B. this is a different - Malay medium - institution from the University of Malaya which also has a campus at Kuala Lumpur) expects to have his Ph.D. thesis ready before the end of the summer. He has been pursuing the question of the effect of the structure of the polyvinyl alcohol used on the properties of a polyvinyl acetate latex prepared with it. Large differences in latex viscosity are commonly observed. These seem to arise from differences in the tendency of different samples to associate. Although the presence of 12 mole % residual acetyl groups greatly reduces association, it does not eliminate it completely. Heublein et al. (University of Jena, East Germany) have shown [Acta Polymerica 31 (1980) 145 [2]] by g.p.c. that a small associated fraction remains even with a sample with 16 mol % acetyl prepared by alkaline methanolysis. Incidentally there is an error in the legend for Fig. 1 of this paper which relates to reacetvlated PVOH: Prof. Heublein confirms that the acetyl contents should be 301, 0; 302, 6; 303 11, and 304 17 mole %. Particle size would affect the rheology of concentrated latex but we found previously that when persulphate initiation was used any differences in particle size which might be attributable to differences in the extent of adsorption of the polyvinyl alcohol were evidently masked by the effect of electrostatic stabilisation by the sulphate end-groups. Therefore hydrogen peroxide-tartaric acid initiation has been used in recent experiments but the same latex particle size is obtained with different polyvinyl alcohols although the latex viscosities differ. The inference is that it is the associative tendencies of the thickeners which differ. In this connection it is interesting to see that Prof. J.E.Glass who is now at the Department of Polymers and Coatings of North Dakota State University has arranged a Symposium on 'The Influence of Associative Thickeners and Rheology on Coatings Performance' in Chicago on May 25. He is also giving a paper on this topic at the FATIPEC meeting in Liege, Belgium earlier in May. A further paper from the Jena group [Acta Polymerica 32 (1981) 559 [9]] concludes that although polyvinyl alcohol-acetates with different distributions of residual acetyl groups (alkaline methanolysis in different solvent mixtures or complete hydrolysis and partial homogeneous reacylation) differ in their ability to form the red ($\lambda_{\max} = 488 \text{ nm}$) PVOAc-I₂ complex, they do not differ in their dispersive ability e.g. in dispersing carbon black [Acta Polymerica 30 (1979) 637 [10]]. This is surprising but does also seem to be the conclusion from our experiments. Short-chain non-hydrolysable branching can probably be eliminated by polymerising vinyl acetate at a sufficiently low temperature (-30°C). This linear material has a much enhanced reaction with the iodine-boric acid reagent (green complex $\lambda_{\max} = 610 \text{ nm}$) after complete hydrolysis but this could also be attributable to reduction of the 1,2-glycol content. Some linear PVOH without a reduced 1,2-glycol content has been prepared by low temperature photoinitiated copolymerisation with vinylene carbonate to check this. Efforts to prepare the model comonomer 1,3,5-triacetoxy-5-hexene to enable the short-chain branch content to be varied failed probably because this material may cyclise very readily.

Polymer Colloids and Polymers at Interfaces
A Review of Current Research at The University of Connecticut

by
Robert M. Fitch

10 MAY Recd

An overview of research interests and work in progress Seven
related areas may be identified:

(1) Particle nucleation and growth kinetics in emulsion polymerization. The rates of appearance, growth and disappearance (by coagulation) of polymer particles is followed by Rayleigh light scattering. Homogeneous nucleation theory is applied to the results since surfactant micelles are absent.

(2) Synthesis of model polymer colloids with controlled surface chemistry. A variety of new initiators, comonomers, and chain transfer agents have been used to obtain monodisperse colloids in which particle size and surface chemistry can be varied independently.

(3) Surface analysis and characterization. In addition to conventional conductometric titration, ISS/SIMS is being investigated for quantitative surface chemical analysis. NMR and ESR relaxation techniques are being used to probe molecular motions at polymer/liquid interfaces.

(4) Chemical reactions at the interface in polymer colloids. Latex particles bearing surface sulfonic acid groups catalyze the hydrolysis of small molecules at rates which depend upon the surface acid concentration and the magnitude of the hydrophobic interaction between substrate and polymer particle. The surface chemistry of metallized latex particles is also being studied.

(5) Controlled release systems. Polyacrylate colloids with surface strong acid groups undergo autocatalyzed hydrolysis with the formation of polyacrylic acid and the release of alkanol. The kinetics have been studied, and controlled-release drug systems are being investigated.

(6) Interactions between planar surfaces and colloidal particles. Sticking kinetics of model polymer colloidal particles under purely Brownian diffusion conditions are being measured by a microscopic technique.

(7) Amphiphilic polymer monolayers at liquid interfaces. The dynamic behavior of surface-active block and graft copolymers at liquid/air and liquid/liquid interfaces is being studied by means of a Langmuir-type film balance. Other probes employed are diffusion rates of small molecules through polymer monolayers and intensity fluctuation light-scattering of colloids with adsorbed amphiphilic polymers.

30 APR Recd

COLLOID RESEARCH AT MCMASTER UNIVERSITY - RECENT DEVELOPMENTS

1) McMaster Institute of Polymer Production Technology

A large grant has been received from the Federal Government of Canada. This grant which applies for a three-year period is being used to develop the McMaster Institute of Polymer Production Technology. We are now seeking sponsor companies to provide guidance and financial stability for this new organization. Hardware for a miniplant with high-pressure stainless steel reactors has been ordered and its erection and startup is slated for September, 1982.

2) Semi-batch and continuous emulsion polymerization of vinyl acetate

Semi-batch reactor studies are being done to develop practical techniques to extend the nucleation time of polymer particles and permit online measurements of particle concentration. The aim of the study is to reduce batch-to-batch variability of the particle-size distribution.

Continuous reactor studies are being done to develop novel operating techniques for stable reactor configurations.

3) Semi-batch and continuous emulsion polymerization of styrene/butadiene

Dynamic reactor models are being developed for the design, operation and control of latex reactors for the production of hot and cold styrene/butadiene latices.

A kinetic model for the copolymerization which accounts for long chain branching and crosslinking has been developed.

The work reported herein is being done in collaboration with Dr. J.F. MacGregor, McMaster University.

Polymer Colloid Group Newsletter

Contribution from The University of Akron

by

I. PIIRMA

Polymerization of Acrylamide in Water-in-Oil Microemulsion Mu-Yen Wu

Stable polyacrylamide microlatices were obtained from the polymerization of acrylamide in water-hexadecane mixture. The microemulsion was stabilized by potassium oleate as surfactant and hexanol (octanol, decanol) as cosurfactant. The polyacrylamide molecular weights under these experimental conditions were as high as 1.5×10^6 . A study of the kinetics of the polymerization by dilatometric technique seems to indicate that the reactions follow bulk rather than emulsion kinetics. We are in the process of evaluating the chain transfer constants of hexanol, octanol and decanol from this microemulsion system.

PSD in Styrene Polymerization Sam Kincaid

The use of a nonionic-ionic surfactant mixture has been known to yield monodisperse latexes. Currently, we are studying the emulsion polymerization of styrene with potassium persulfate initiation at 60°C. The emulsifier system consists of sodium dodecyl sulfate and a tridecyloxy-poly(ethyleneoxy)ethanol. The mole percent of SDS is 10%.

Using hydrodynamic chromatography (HDC) to measure particle size, the number concentration of particles was monitored throughout the polymerizations. Figure 1 shows the number of particles per $\mu\text{H}_2\text{O}$ versus conversion for three polymerizations with 3.0, 1.67, and 1.0% (w/w H_2O) emulsifier. The crosses at about 20% conversion in the plots from the 1.67 and 1.0% emulsifier concentrations indicate where extra SDS was added to keep the latex stable.

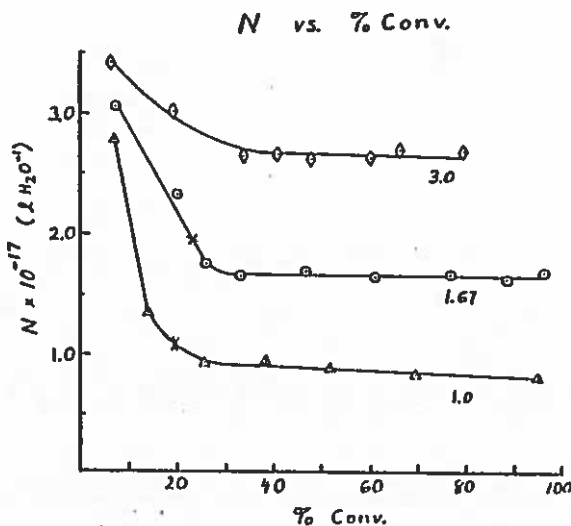


Figure 1

In each polymerization the number of particles reaches a maximum at low conversion and then decreases until it becomes constant at about 30% conversion. Thus particle flocculation is significant in determining the number of particles. With the lower emulsifier concentrations, this agglomeration of particles produces a lower number of particles.

In addition, the particle flocculation influences also the particle size distribution (PSD). Figure 2 shows some PSD's as determined by electron microscopy of samples from the polymerization with 1.67% emulsifier. The numbers accompanying the distributions are the percent conversion and the ratio of the weight to number average diameters. From 2.7 to 7.9% conversion, the distribution broadens as the number of particles increases. However, by 20% conversion the particle agglomeration leads to a more narrow PSD with a large particle size tail. By about 40% conversion, the number of particles has become constant (see Figure 1) and the PSD is very narrow with $D_w/D_n = 1.012$. Thus, the particle flocculation occurring in this mixed emulsifier system is an important factor in obtaining a monodisperse latex.

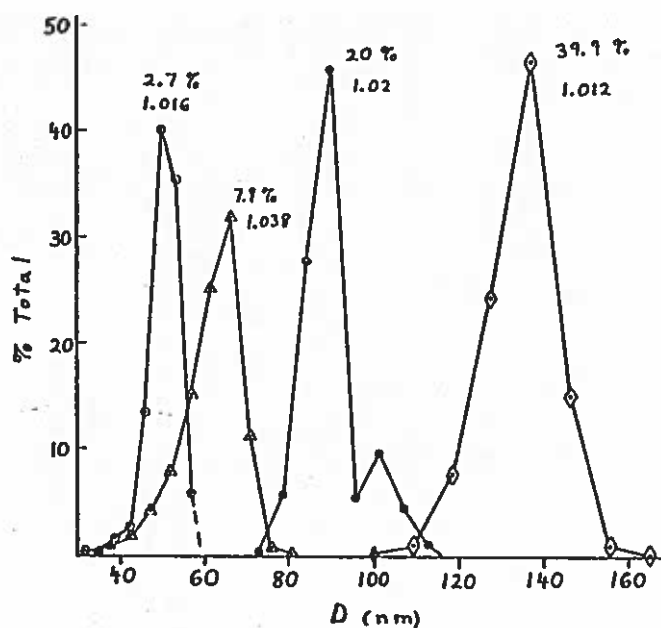


Figure 2

Contribution to the Polymer Colloid Group

A.A. Robertson, T.G.M. van de Ven and S.G. Mason
Pulp and Paper Research Institute of Canada
and
Department of Chemistry, McGill University

28 APR 1966

1. Kinetics of coating by colloidal particles (T. Dąbroś & T.G.M. van de Ven)

The kinetics of coating of solid walls (collectors) by colloidal particles has been studied theoretically and experimentally taking into account the influence of (i) the time dependence of the escape rate (aging), (ii) the already deposited particles (blocking or masking effects), and (iii) the coagulation of the colloidal particles prior to deposition.

A detailed discussion is presented of the escape velocity due to the thermal motion of the particles and of the influence of hydrodynamic forces, especially under turbulent flow conditions. It is shown that particle detachment, masking and coagulation cause deviation from the linear relationship between coating density and time. Experimental data obtained from a direct visual observation of the deposition process are interpreted on the basis of the presented theory.

2. Transfer of Brownian particles to continuous moving surfaces (Z. Adamczyk, T. Dąbroś and T.G.M. van de Ven)

A theoretical analysis of particle deposition from a dilute suspension (or aerosol) subject to laminar flow onto moving continuous plates (sheets) and cylinders (wires) is presented. Complete transport equations have been formulated, taking into account specific surface interactions such as London-van der Waals and electrical double-layer forces. By solving these equations numerically the dimensionless mass transfer Sherwood number has been determined for a variety of conditions characteristic for suspensions and aerosols. It has been found that the effects of attractive double-layer forces are very important, especially for thin double-layers, increasing mass transfer rates by more than an order of magnitude for larger particles (at distances close to the entrance point). For Péclet numbers $Pe < 10^{-6}$ (small particles) the specific interactions play a less important role and the Sherwood number can be accurately approximated by an analytical expression derived for negligible particle dimensions (ions).

The major finding of this study is that compared to deposition on a stationary surface, deposition on moving continuous surfaces is larger by at least one order of magnitude, both in the presence or absence of specific surface forces.

3. An optical method for studying the properties of ordered lattices
(M. Tomita, K. Takano and T.G.M. van de Ven)

A method is described to study the properties of ordered lattices, which consists of normally illuminating and observing a latex dispersion covered by a flat glass plate. In this way a hexagonal pattern of diffraction spots, a ring-shaped halo, and a dark ring in the halo region are observed. The size of the hexagonal pattern of the diffraction spots depends on the volume fraction of the latex and on the particle size. Observed diffraction angles agree within experimental error with those calculated from the Laue theory. Also the dependence of the hexagon size on the volume fraction of the latex is in agreement with theory. It is found, both experimentally and by numerical calculations, that the thickness of the latex sample does not significantly affect the angle and intensity of the diffraction spots, and thus the diffraction spots contain no information about the three dimensional structure of the latex. From the inner and outer radius of the ring-shaped halo, the mean refractive index of the latex can be determined. This new method is much simpler than the Bragg diffraction method which has been employed by other workers. The volume fraction dependence of the refractive index of the latex was found to be in good agreement with literature results. The dark ring occurs at a radial distance corresponding to an angle which satisfies the Bragg condition. From the radius of the dark ring and the refractive index of the latex, the size of the latex particles can be determined and is found to be in good agreement with the size determined by electronmicroscopy. Although this darkening effect has not been observed in other materials, it seems to be a general optical phenomenon associated with crystal structure.

MEASUREMENT OF MACROMOLECULAR SHAPE BY WIDE ANGLE
LIGHT SCATTERING

by

Kevin M. Kidnie and Robert L. Rowell
Department of Chemistry
University of Massachusetts
Amherst, Massachusetts 01003

12 May 1982

Introduction

The theory of Rayleigh scattering is examined and a new parameter called the ellipticity is defined. A direct relationship between the depolarization ratio and the ellipticity is developed. In certain special cases the ellipticity is equivalent to the ratio of the major and minor axes of the scattering ellipsoid.

General Theory

In the theory of Rayleigh scattering, where the particles are small in comparison to the wavelength of the incident radiation, the depolarization ratio is related to the optical anisotropy of the scatterer (1). The depolarization ratio for vertically polarized incident light, ρ_v , is defined as the ratio of the horizontally polarized component H_v to the vertically polarized component V_v of the scattered radiation

$$\rho_v = H_v/V_v \quad (1)$$

In terms of molecular properties,

$$\rho_v = 3\Delta/(5+4\Delta) \quad (2)$$

where Δ is the square of the fractional anisotropy,

$$\Delta = \delta^2/9\alpha^2 \quad (3)$$

The quantity δ is the difference in the principal polarizability components of the scattering ellipsoid,

$$\delta = \alpha_1 - \alpha_2 \quad (4)$$

The quantity α is the average of the polarizability components; assuming a rotational ellipsoid

$$\alpha = (\alpha_1 + 2\alpha_2)/3 \quad (5)$$

If a new quantity, the ellipticity ϵ , is defined as $\epsilon = \alpha_1/\alpha_2$ then equation (3) may be combined with (4) and (5) to give a quadratic relationship between Δ and ϵ .

$$\Delta = (\epsilon - 1)^2/(\epsilon + 2)^2 \quad (6)$$

The average polarizability is a measurement of the electronic volume that is put into oscillation under the driving force of the incident radiation.

Our contribution to the Polymer Colloid Group Newsletter is this preprint prepared for IUPAC MACRO 82. We have uncovered a new relationship between the depolarization ratio and shape and find a number of interesting applications to polymers, polymer colloids and surfactants.

R. L. Rowell

The light scattering determinations of the average polarizability and anisotropy are optical measurements which have contributions from the overall shape of the scatterer as well as the overall electronic mobility within the scatterer. The combinations of the shape or form contribution and the electronic mobility or intrinsic contribution are not separated in the light scattering experiment. In electronically isotropic particles, the principal polarizabilities will coincide with the principal geometric axes of the molecular or particulate scatterer. Under such conditions the polarizability will be proportional to the volume of the scattering species and the ellipticity will be equivalent to the ratio of the geometric major and minor axes of the corresponding ellipse. The actual molecular or particle shape would be determined if a single value of the ellipticity could be obtained but since the intensity is proportional to the square of the volume of the scatterer, a unique value for the ellipticity cannot be obtained in many cases as discussed below.

Use of the ellipticity ϵ opens up new insight into the interpretation of light scattering data since Δ may be eliminated between equations (2) and (6) and an analytical relationship may be obtained between ρ_v and ϵ .

$$\epsilon = \{-(4\rho_v+2) \pm [(4\rho_v+2)^2 - 4(3\rho_v-1)(8\rho_v-1)]^{1/2}\} / 2(3\rho_v-1) \quad (7)$$

Equation (7) is a direct route between an experimental depolarization ratio and the characteristic optical anisotropy of an ellipsoidal scatterer. The relationship of Equation (7) gives a critical value at $\rho_v = 1/8$. For $\rho_v < 1/8$, equivalent pairs of oblate and prolate spheroids exist. For $\rho_v = 1/8$, the equivalent pairs become the infinitely thin disc with $\epsilon=0$ and a prolate spheroid with $\epsilon=4$. For $\rho_v > 1/8$, the function is single valued and the depolarization must arise from rod-like scatterers. From this point of view we may take $\epsilon=4$ as the definition of a rod-like structure. See Figure 1.

Application

Depolarization values above 1/8 have been rarely reported. A notable exception is the light scattering study of poly(vinyl acetate) solutions in methyl ethyl ketone reported by Kapalgam and Rao (2). The depolarization results on three separate polymer fractions are summarized in Table 1 along with calculated values of the ellipticity using equation (7) and the assumption of rod shape since most of the data are clearly in the rod-like domain.

Table 1. Depolarization Ratios on Poly(vinyl acetate) in Methyl Ethyl Ketone.

| Fraction (Mol. Wt.) | Conc. g/l | ρ_v | ϵ |
|---|-----------|----------|------------|
| F ₅ (1.06x10 ⁶) | 0.83 | 0.283 | 21.15 |
| | 0.98 | 0.161 | 5.22 |
| | 1.12 | 0.151 | 4.84 |
| F _{4a} (1.49x10 ⁶) | 0.40 | 0.204 | 7.48 |
| | 0.80 | 0.086 | 3.02 |
| F ₃ (1.53x10 ⁶) | 0.33 | 0.140 | 4.40 |
| | 0.46 | 0.106 | 3.49 |

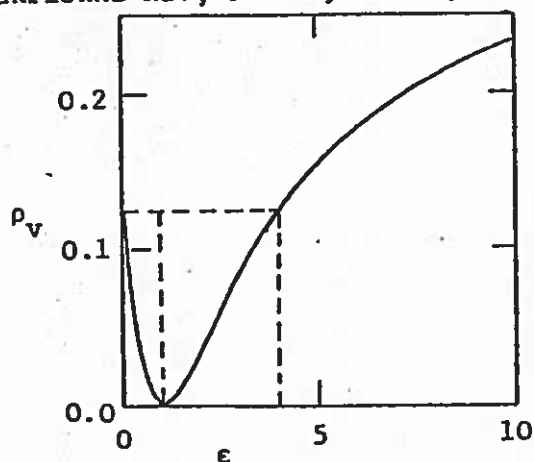
Conclusion

The results of Table 1 support the concept that poly(vinyl acetate) uncoils in the good solvent methyl ethyl ketone to an appreciable extent and can be unambiguously assigned a rod-like structure with an ellipticity greater than 3 at all concentrations for each of the fractions studied.

References

1. M. Kerker, The Scattering of Light and Other Electromagnetic Radiation, (Academic Press, New York, N.Y., 1969).
2. V. Kapalgam and M. Ramakrishna Rao, *J. Poly. Sci.*, Pt. A, 1, 517 (1963).

Figure 1. Graphical representation of Equation (7) giving $\rho_v(\epsilon)$. The relationship is single-valued above $\epsilon=4$.



CONTRIBUTION TO THE POLYMER COLLOID GROUP NEWSLETTER

M.S. El-Aasser, A. Klein & J.W. Vanderhoff
Emulsion Polymers Institute
Lehigh University

27 APR Recd

We, currently, have 32 active projects, the titles are included in the attached index of our Graduate Research Progress Reports, Issue No. 17, which was published on January 1982. We have some copies of the reports available for distribution to the members of The Polymer Colloid Group on the first come first serve basis. You can request a copy by writing to M.S. El-Aasser, Emulsion Polymers Institute, Bldg. #5, Lehigh University, Bethlehem, Pa. 18015.

The major event in our activity during this period was the first seeded emulsion polymerization conducted under microgravity aboard the shuttle Columbia STS-3 on March 22-March 29, 1982. The experimental package comprised of two units: one unit containing the four stainless steel dilatometers reactors and the second unit containing the electronic supports and the data acquisition system. Four seeded emulsion polymerization recipes were used; one, as control, with 0.19μ particle as seed, and the other three recipes with a starting seed of 2.5μ - diameter. The monomer/polymer ratio was the variable in the last three recipes, with values of 2/1, 4/1 and 10/1 on a volume basis. Kinetic data (change in volume vs time) as well as temperatures at four different locations in each reactor were recorded on a tape deck. After landing of the shuttle Columbia, the package was retrieved and inspected. The four polymerizations were completed successfully, latexes were found to be stable, and the data on the tape were properly recorded. All three large-size latexes look good with respect to size uniformity under the optical microscope. A complete and thorough analysis of particle size and size distribution and the kinetic data are currently underway and will be published in due time. This program is scheduled to go on the next three STS flights, with the next anticipated launch date for STS-4 on June 27, 1982.

Three of our graduate students have completed their Ph.D. Thesis: Ahmed M. Kamel (1981) "The Preparation and Characterization of Polystyrene Latexes as Model Colloids"; Trisno Makgawinata (1981) "Kinetic Studies of Semi-Continuous Emulsion Copolymerization"; and Yen-Jer Shih, "Colored Latexes: Preparation, Characterization & Application". Kamel is currently working for Tektronix (Beaverton, Oregon); Makgawinata is on a post graduate appointment at Lehigh for completing papers from his thesis; and Shih is currently working for National Starch and Chemical Corporation, Bridgewater, New Jersey). A copy of Makgawinata's abstract is included. Shih's thesis is being withheld for a patent application and Kamel's abstract was included in the previous newsletter.

Dr. Victoria Dimonie, of the Chemical Research Institute in

Bucharest, Romania has joined our group as a visiting research scientist. She is currently studying the core-shell emulsion polymerization of styrene and acrylonitrile in seeded system. Her studies involve the influence of the various parameters in batch and semi-continuous processes (monomer/polymer ratio, emulsifier and initiator concentration, monomer feed rate and temperature) on the degree of grafting, copolymer composition and morphology of the copolymer latex.

Our 13th Annual Short Course on "Advances in Emulsion Polymerization and Latex Technology will be held at Lehigh University on June 7-11, 1982.

All members in the Polymer Colloid Group are invited to participate (give papers or attend) in the forthcoming AIChE Symposium on Polymer Colloids which will be held in Houston, Texas U.S.A., on March 27-31, 1983. Please see enclosed announcement and call for papers and write to the appropriate session chairman promptly.

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Kinetic Studies of Semi-Continuous Emulsion Copolymerization

T. Makgawinata
Ph.D. Thesis (1981)

ABSTRACT

The semi-continuous emulsion polymerizations of 80:20 vinyl acetate-butyl acrylate and 40:60 methyl methacrylate-butyl acrylate are carried out separately with different monomer addition rates under the same recipes and isothermal conditions. The main experimental procedure is to grow the seed latex particles, which are prepared in a separate formation step, to a larger size by adding the monomer to the reactor mixture at constant rates. The overall conversion, the instantaneous conversion, the conversion at time t , the polymer particle size and the compositions of the copolymer as a function of reaction time are determined experimentally. A mathematical model of this copolymerization system, in which the polymerization reactivities are very different from each other, has been derived based on the mass balances around the system and the assumptions that the overall rates of monomer addition are much smaller than the overall rates of polymerization in the batch reactor. The major locus of polymerization is mainly in the outer zone of the monomer-polymer particles (seeded) and the number of particles is constant in the whole system. In the theoretical treatment, the derivation of overall conversion is based on the curve-fitting method; the instantaneous conversion and the conversion at time t are based on mass balances around the system which are related to the overall conversion. The average particle size is a function of the volume of latex particles formed at time t which is related to the conversion at time t . The average and instantaneous copolymer compositions are also based on mass balances around the system. The instantaneous copolymer

composition is equal to the initial mole fraction of comonomer. The average copolymer composition is a function of initial mole fractions of comonomer, the instantaneous mole fractions of comonomer in latex particles and the conversion at time t .

The reactions are run under the controlled region (overall rates of monomer addition are much smaller than overall rates of polymerization in the batch reactor) and are referred to as monomer-starved reaction. The overall rates of polymerization are a function of time and are controlled by the rate of monomer addition, i.e., controlled only by the amount of monomer added to the reactor at that time in the controlled region. The ratios between the overall rates of monomer addition are a function of time or feed rates and not fixed constant values as described in the literature. The instantaneous conversion is a function of time and cannot reach higher conversion at the beginning of the reaction. It is suggested that this phenomenon may be due to the effect of the mass transfer resistance, interfacial resistance, the reactivity of monomer radicals or the idiosyncrasies of the monomer activity, as well as the "monomer solvent" plasticizing the latex particles. Owing to the monomer-starved reaction, the swelling of the seed particles is less than the "saturation-swelling" equilibrium condition. Meanwhile, the surface of the seed latex particles becomes the locus for propagation, with the particle size increasing with time and feed rates. The average number of free radicals per particle in the seeding system deviates from the Smith-Ewart Case 2 kinetics. Using the semi-continuous techniques, the average copolymer compositions are maintained at

nearly the same composition as the original monomer ratios.

A comparison is made between the theoretical results and the experimental data. The predicted values according to the derived equations agreed well with the experimental data.

Fundamental Studies of the Effect of Particle Size and Particle Stability on Critical Pigment Volume Concentration in a Model Latex Coating

(A.I. Ranka, M.S. El-Aasser, J.W. Vanderhoff).

Objective:

Development of model latex coating and quantitative determination of effect of particle size and stability of binder and pigment on critical pigment volume concentration (CPVC).

Progress:

The model latex coating comprised of poly(styrene-butadiene) (60:40) latex (PSB) as the binder and poly(styrene) latex (PS) as the pigment particles, was developed and optimized [GRPR No. 16, p. 127]. This model coating was used for determination of effect of particle sizes of binder and pigment on CPVC. The following particle size range given in the Table I was chosen for the study.

TABLE I

PHYSICAL PROPERTIES OF LATEX SYSTEMS USED IN THE PREPARATION OF MODEL LATEX COATING FILMS

| <u>S.N.</u> | <u>Designation</u> | <u>Chemical Name</u> | <u>Particle size nm</u> | <u>Solid content (fraction)</u> | <u>Density gms/cm³</u> |
|-------------|--------------------|----------------------|-------------------------|---------------------------------|-----------------------------------|
| 1 | LS-162-B | PSB | 165 | 0.3996 | 1.02 |
| 2 | 1177B | PSB | 314 | 0.4256 | 1.02 |
| 3 | 1102A | PS | 190 | 0.4330 | 1.05 |
| 4 | 1019E | PS | 280 | 0.3826 | 1.05 |
| 5 | 1121B | PS | 310 | 0.2659 | 1.05 |
| 6 | 1103 | PS | 400 | 0.4194 | 1.05 |
| 7 | 1115B | PS | 600 | 0.1485 | 1.05 |

The following range of pigment volume concentration (PVC) was studied for the determination of the CPVC: 0.2; 0.4; 0.45; 0.50; 0.55; 0.60; 0.65; 0.70. The ingredients used for the preparation of the model latex coating systems are: poly(styrene) latex (T_g=100°C); poly(styrene-butadiene) (60:40) latex (T_g=-6°C); solution of SLS 25%; 2% methyl cellulose solution; solution containing a mixture of 0.2% methyl cellulose and 0.5% SLS. The procedure to make a model latex coating is as follows: (1) The surface tension of the latexes are adjusted to 37-40 dynes/cm by adding 25% solution of SLS. (2) lcc solution of methyl cellulose and SLS mixture containing 0.2% and 0.5% respectively is added to ten cc of latex, irrespective of the latex type (3) polystyrene latexes are slightly thickened by adding 2% methyl cellulose solution and then the poly(styrene-butadiene)

latex binder is slowly added under stirring conditions. Precaution is taken not to trap air in the mixture. (4) The latex is thickened to the desired level by adding 2% methyl cellulose solution. (5) Films are applied from the above mixture by K-coater to a desired thickness. Generally for tensile strength measurements 10 to 15 mil thick wet films are applied.

Testing of Latex Coatings: (1) Mechanical property - the tensile strength of free latex coating films were determined by ASTM D-2370 test using the instron. (2) Optical property - contrast ratio was determined using KCS-40 spectrophotometer. (3) Permeability property - standard ASTM-D-3258 test was used to measure porosity of the films using K&N ink as a penetrating medium.

One should note that the loosest type of packing of uniform, non deformable spheres is cubical packing with a theoretical packing factor of 0.5236 and the densest type of packing is tetrahedral packing with a packing factor of 0.7405. Average values of packing factors reported in the literature for loose and dense packings are 0.589 and 0.639 respectively. These values could represent the highest CPVC achievable for a uniform size pigment particle, which is the case in our model latex coating.

Figures 1-3 show typical graphs for coating films of B-2 series (see Table II). Tensile strength, contrast ratio and porosity are plotted against PVC. The point at which a sharp transition occurs for the property measured is taken as the CPVC.

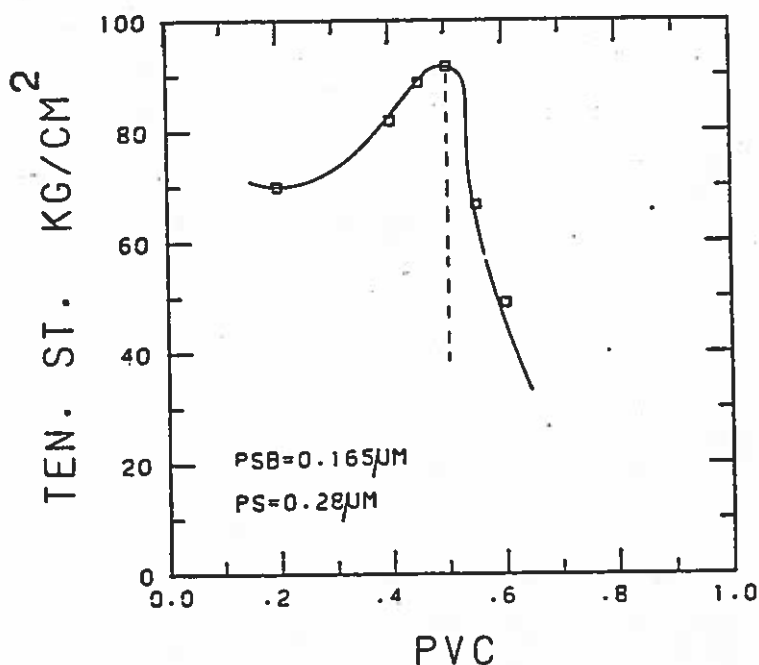


Figure 1: Plot of tensile strength vs. pigment volume concentration for latex coating films of B-2 series, See Table II.

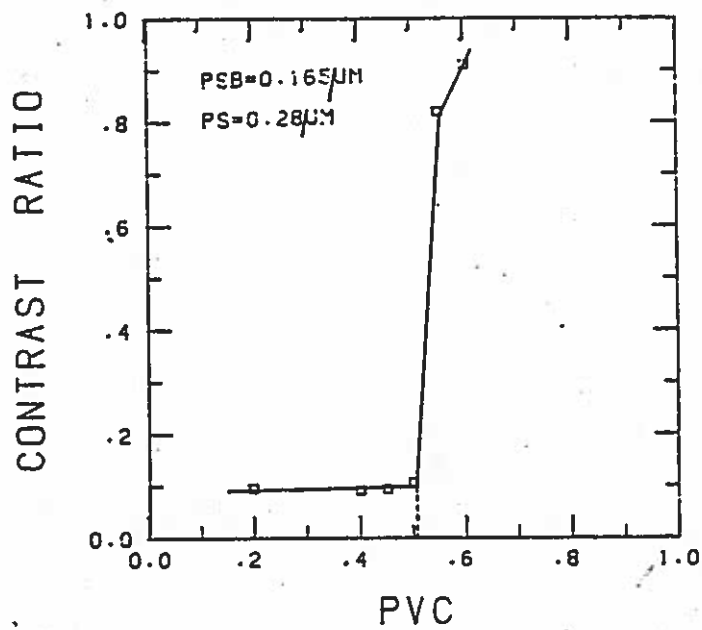


Figure 2: Plot of contrast ratio vs. pigment volume concentration for latex coating films of B-2 Series, see Table II.

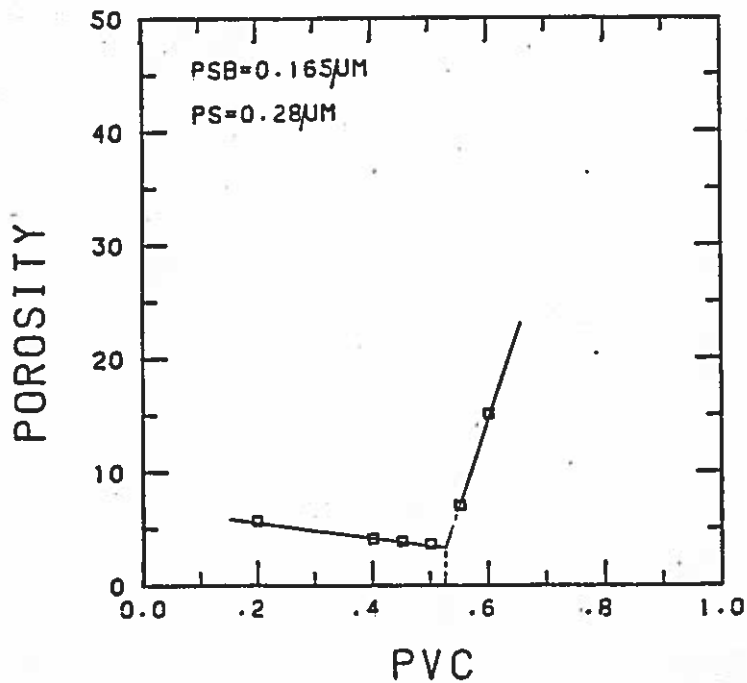


Figure 3: Plot of porosity vs. pigment volume concentration for latex coating films of B-2 Series, see Table II.

Table II contains a summary of the values of the CPVC for two series of model coating films, measured by the different technique described above. Series A, comprises of films made from PSB latex binder with particle diameter of 314nm. Series B comprises of films made from PSB latex binder with particle diameter of 165nm. In both series A and B several different particle size PS pigment particles were used.

TABLE II
CPVC OF MODEL LATEX COATING FILMS

| Designation | Particle Dia. PSB nm (DB) | Particle Dia. PS nm (DP) | CPVC | | |
|-------------|---------------------------------|--------------------------------|---------------------|-------------------|----------|
| | | | Tensile Strength | Contrast Ratio | Porosity |
| A-1 | 314 | 190 | 0.30 | 0.130 | 0.40 |
| A-2 | 314 | 280 | 0.27 | 0.290 | 0.34 |
| A-3 | 314 | 310 | 0.40 | 0.400 | 0.41 |
| A-4 | 314 | 400 | 0.45 | 0.450 | 0.45 |
| A-5 | 314 | 600 | 0.55 | 0.480 | 0.45 |
| B-1 | 165 | 190 | 0.40 | 0.250 | 0.40 |
| B-2 | 165 | 280 | 0.50 | 0.510 | 0.53 |
| B-3 | 165 | 310 | 0.50 | 0.525 | 0.58 |
| B-4 | 165 | 400 | 0.50 | 0.550 | 0.55 |
| B-5 | 165 | 600 | 0.56 | 0.590 | 0.58 |

Figures 4-6 show how the CPVC is affected by the ratio of pigment to binder particle diameter (DP/DB). It is seen from the graphs that the CPVC increases rapidly up to the ratio of DP/DB of 2, followed by a much slower increase and almost levels off at a value of 4. At DP/DB value of 4, CPVC value 0.59 of model latex coating is surprisingly close to the maximum random packing factor, which indicates that we are indeed getting ideal dispersion i.e., poly(styrene) particles exist as singlets or doublets. Figure 5 shows that for DP/DB ratio less than one, the value of CPVC is very low i.e., 0.13 from the contrast ratio measurements. The probable reason is that due to localized distribution of bulk binder discrete air pockets exist in the film. Air has a refractive index of 1.0, which lowers the refractive index of the medium, resulting in enhanced hiding power of the model latex coating film.

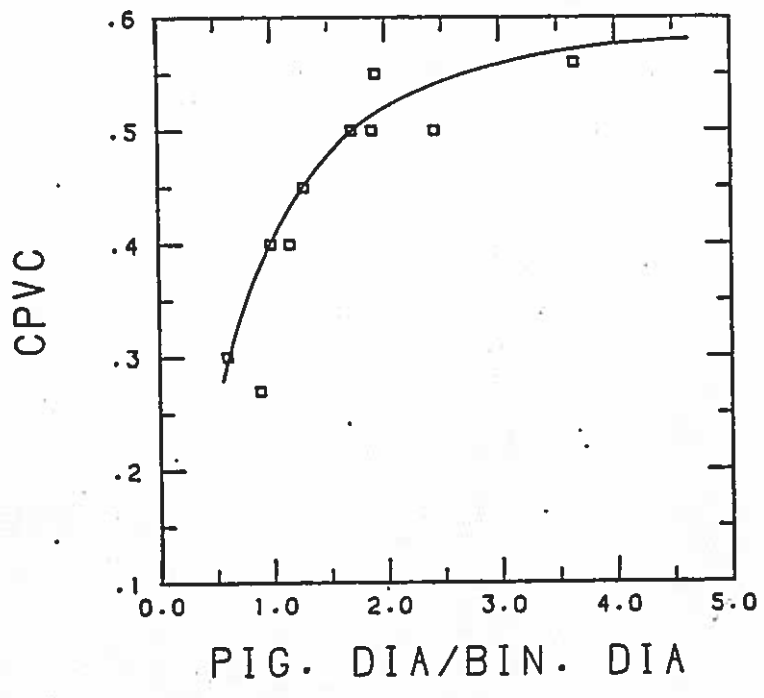


Figure 4: Plot CPVC from tensile strength data vs. DP/DB.

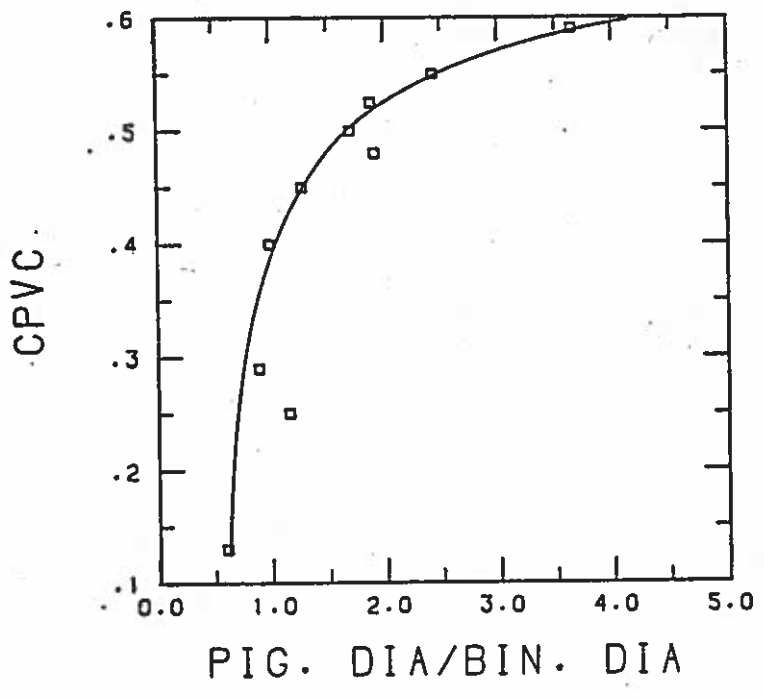


Figure 5: Plot of CPVC from contrast ratio data vs. DP/DB.

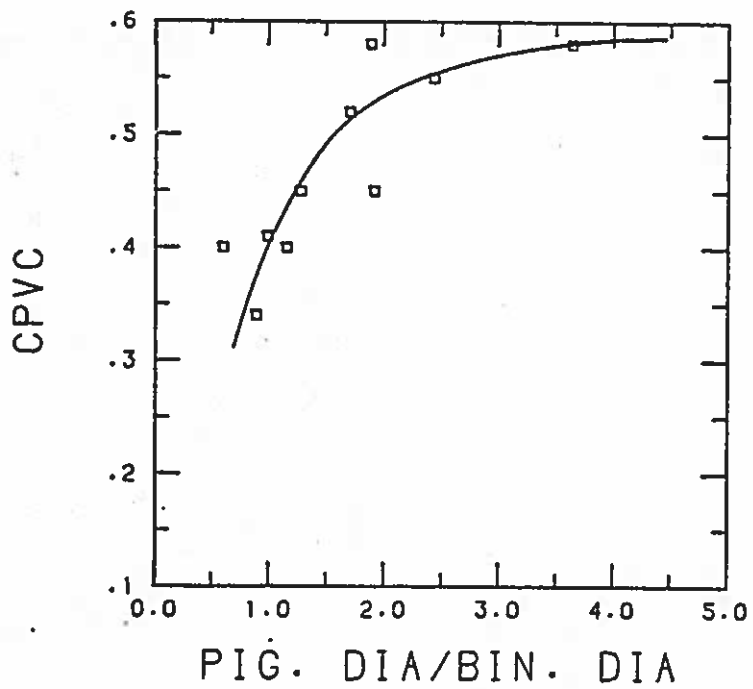


Figure 6: Plot of CPVC from porosity data vs. DP/DB.

Future Work:

1. Determination of effect of stability of pigment and binder on CPVC.
2. To study the morphology of latex coatings.

Inverse Emulsion Polymerization of Acrylamide
(F.V. DiStefano, M.S. El-Aasser, J.W. Vanderhoff).

Objective:

To study the kinetics of inverse emulsion polymerization of acrylamide and the stability of the inverse latex.

Progress:

During this period a M.S. Report was completed and accepted in fulfillment of the requirement for M.S. degree. The abstract is as follows:

"Polyacrylamide inverse latexes were prepared using a Tetronic 1102 surfactant, with an oil-soluble initiator, benzoyl peroxide, present in the continuous o-xylene phase. The effects of initiator, [I], and emulsifier, [E], concentration upon the particle size and distribution, polymerization rate, R_p , degree of polymerization, and coagulum were examined. Morphology of the monomer emulsion and latex droplets was also investigated, as was the influence of emulsifier structure upon the sedimentation rate and viscosity of the latex.

The following relationships were found:

$$R_p \propto [E]^{1.0}$$

$$R_p \propto [I]^{2.0}$$

$$R_p \propto v^{0.7}$$

$$N \propto [E]^{3.7}$$

$$N \propto [I]^{0.3}$$

$$[\eta] \propto [E]^{-0.5}$$

$$[\eta] \propto [I]^{-0.3}$$

where $[\eta]$ is the specific viscosity, and N number of droplets per unit volume.

A liquid nitrogen freezing technique was used to study the soft latex droplets by transmission electron microscopy. The number-average particle diameter of the latex was 40-100 nm. Oil-in-water-in-oil (o/w/o) multiple droplets were found in the monomer emulsion and latex. The morphology of

these droplets was a function of agitation rate. A strong correlation between the droplet size, distribution, and morphology, in the monomer emulsion and corresponding latex at 212 and 425 rpm, indicates that aqueous monomer droplets are the dominant site of initiation. The strong dependence of particle number upon emulsifier concentration supports this conclusion.

The sensitivity of R_p to initiator concentration, polymerization of aqueous acrylamide with benzoyl peroxide in the presence of an oil-phase radical inhibitor, and other indirect evidence suggests that benzoyl peroxide dissolved in the aqueous phase of the latex plays an important role in initiation.

Coagulum formation was associated with auto-acceleration. Increasing the initiator concentration was found to decrease coagulum formation. Changing the surfactant did not appear to affect coagulum but an oligomeric surfactant greatly reduced the sedimentation rate of the latex and lowered the viscosity, both in accord with steric stabilization theory."

An Investigation into the Effects of Prepolymer on Flocculation
During Emulsion Polymerization
(V. Lowry, M.S. Al-Aasser, J.W. Vanderhoff).

Objectives:

To study the effect of prepolymer on the amount of coagulation that occurs during an emulsion polymerization of styrene.

Progress:

During the past six-month period, a final report on this subject was submitted to the Emulsion Polymer Institute and Department of Chemical Engineering. The Abstract of this report is as follows:

"The extent of coagulation during the emulsion polymerization of styrene was observed using two types of batch reactors. The primary reactor employed was a 3-oz. bottle in which the reactants were charged and polymerized. Also, a 500 ml round bottom flask was used in a few trials. The basic intent was to observe the effect of prepolymer contamination on coagulum formation, both high (10^5) and low (10^3) molecular weight polystyrene were used as the prepolymer.

In the bottle reactors, two types of coagulum were produced which were initially characterized by their physical appearance. In other words, one type of coagulum appeared as a hard and glossy polymer, whereas the other coagulum appeared as a finely divided powder when dried. The two types of coagulum also differed based on a microscopic point of view. The hard coagulum seems to be primarily composed of the original prepolymer contaminant whereas the powder seems to be composed of the latex polymer. This last statement was based on both electronmicrograph and molecular weight distributions of the coagulum.

The amount of each type of coagulum produced was found to be a function of prepolymer concentration, prepolymer molecular weight and emulsifier concentration. The powdery type of coagulum seems to be independent of prepolymer molecular weight, whereas the hard coagulum is directly related to the molecular weight of the prepolymer. Also, in the low molecular weight prepolymer trials, the

amount of hard coagulum produced was independent of emulsifier concentration, whereas the powdered coagulum was a strong function of the emulsifier concentration.

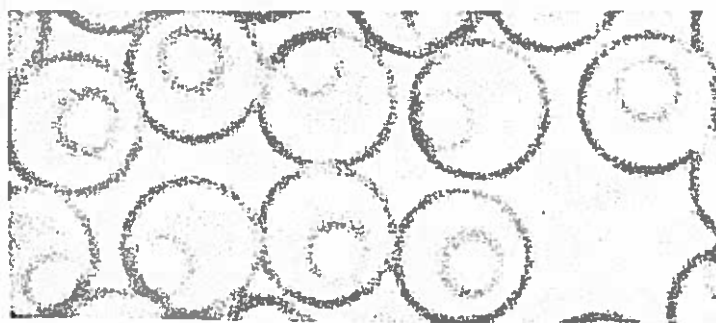
Some data obtained using the bottle reactors was somewhat erratic. Therefore, a round bottom flask was used in order to develop a more consistent method. The primary indication is that the round bottom polymerization yields more consistent results".

Report on work in Trondheim, by John Ugelstad.

The work on monodisperse particles has continued in Trondheim (A. Berge and T. Ellingsen at SINTEF) and at Dyno Industries A.S., who has got the rights to the patents. (F.K. Hansen, A. Jørgedal and S. Ramstad). The work in Trondheim has been centered around development of new types of particles for special applications. At Dyno they have mainly worked on improvements, scaling up and automatization of the processes.

1. Swelling of cross linked particles.

The principles which we have applied for preparing swelling particles also apply for particles which are relatively highly cross linked. In this case we get formation of monodisperse core and shell particles. The unusual behaviour is again that we have an extremely high swelling degree, that is we get a very thick shell. The thermodynamical consideration of this case follows the same lines as the one with a homogenous system, only we have in the swelling shell no polymer only the water insoluble low molecular compound (2) and the slightly water soluble compound (1). The rate of swelling is as expected relatively high. The picture shows an example of swelling in two step of a cross linked styren divinylbenzene particles.



2. Our highly monodisperse porous particles have been introduced on the market by Pharmacia, Uppsala; Sweden, in this Fast Protein Liquid Chromatography, FPLC System.

The system includes anionic, cationic and polybuffer exchanges. It is claimed that the monodispersity leads to a very drastic increase in both speed and resolution.

ON THE MORPHOLOGY CONTROL OF COMPOSITE LATEX POLYMERS
OF A GIVEN FORMULATION

V.I.Eliseeva, N.V.Titova

Institute of Physical Chemistry
of the USSR Academy of Sciences,
Moscow, USSR

It was reported^{1,2} that by varying emulsion polymerization techniques for a monomer composition it is possible to strongly affect mechanical properties of films formed from polymer lattices (Fig.1). In particular, it was demonstrated that on the basis of the same monomer composition there can be obtained not only lattices of statistical copolymers but also lattices of microcomposite polymers with a variable topographic location of polymer components in individual particles and transition layers of intermediate composition between particles. Thus, the influence mentioned above was explained by the variation of polymer structure in individual latex particles with size between 100-200 nm.

The control of polymer morphology on this ultramicroscopic level is only possible by employing emulsion polymerization technique.

The present work shows, with carboxylated lattices of styrene-acrylic polymers taken as an example, that the factor affecting the morphology of particles and hence the properties of latex films is the mechanism of particles formation and growth. In addition to that, this mechanism exerts its influence on the

topographic location of carboxyl groups in the particles. It can be seen on electron photomicrographs of latex particles obtained from the St-BA-MAA system by the two-stage polymerization method (Fig. 2a,b) that the particles are formed as a result of flocculation of newly emerged particles of the St-BA-MAA copolymer with the particles of the seeding polystyrene latex (conversion 90%). It seems that the cause of the formation of new particle is that the rate of diffusion of hydrophobic monomers (St-BA) into "old" particles of the seeding latex is lower than the rate of formation of polymer radicals in aqueous phase since the system contains a water-soluble initiator and one of the components of the monomer system (MAA) possesses a high solubility in water. On the other hand, hydrophobic monomers will be distributed among "old" and flocculating new particles thus giving rise to a transition layer of the copolymer enriched with styrene as compared with the mixture of monomers introduced into the reaction. Thus, the structure of an individual latex particle obtained by two-stage polymerization can be represented by the scheme given in Fig. 3. On the contrary, the mixture of latices of polystyrene and the St-BA-MAA copolymer consists of individual particles containing different polymers; hence, the copolymer film contains a mixture of individual particles of different polymers directly (with no intermediate layer) bordering on each other.

at 60°C

The difference in morphology between films obtained from the latex synthesized by two-stage polymerization and films prepared from the mixture of latices has been confirmed by the results of dielectric relaxation measurements³.

There were studied α transitions caused by segmental mobility of macro chains. Fig.4 presents temperature dependences of $\text{tg } \delta$ for samples 1 and 2 (see Fig.1) and a sample obtained after the dissolution of film 1 in toluene and casting a new film from the solution. Peak asymmetry and its shift towards higher temperatures disclosed for the film made of latex obtained by seeding polymerization make it possible to arrive at a conclusion about the presence of a certain transition layer enriched with styrene; this layer could have been formed on the seeding St latex during the synthesis of the composite latex, at the beginning of introduction of the plasticizing St-BA-MAA mixture. No peak asymmetry was observed for films obtained from solution or from the mixture of latices.

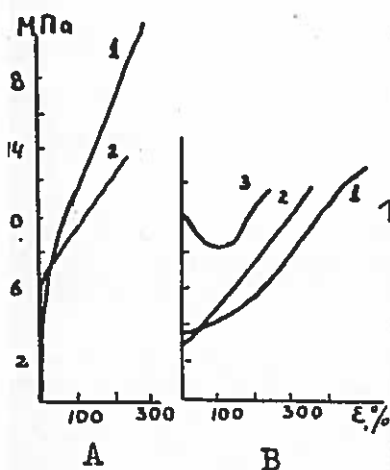
The peculiarity of location of carboxyl groups in individual particles of latex obtained by seeding polymerization can be judged upon from electron photomicrographs taken at pH 9.5 when carboxyl groups convert into a dissociated form and electrostatic repulsion develops between them. As it can be seen from Fig.5a, under these conditions there appears in a ready latex a new fraction of rod-shaped particles peculiar to a highly carboxylated acrylic polymer in a dissociated form⁴. The copolymer fraction enriched with methacrylic acid is formed during synthesis after the introduction of a mixture of monomers (St-BA-MAA) into the reaction system containing the seeding polystyrene latex. At higher pH, electrostatic repulsion leads to the redispersion of particles flocculated during polymerization (see above); the particles are enriched with MAA and since the content of MAA in the copolymer is high, they acquire the shape

characteristic of sodium polyacrylate⁴. The enrichment of the external zone of individual particles with carboxyl groups leads to a more oriented location ^{them in} the particles and can favour the formation of a greater number of intermolecular hydrogen bonds between particles and hence to the growth of polymer strength. As it can be seen from Fig.5b, no deaggregation of latex particles of a statistical polymer of the same composition occurs thus indicating a more uniform distribution of MAA in the bulk of particles.

References

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Figures



1 Unit elongation vs. stress for films obtained: 1 - by drying the latex synthesized by two-stage polymerization; 2 - from the mixture of latices; 3 - from the latex of a statistical copolymer; A - MMA-BA-MAA composition (57.4 : 39.3 : 3.3) with pMMA as seeding latex; B - St-BA-MAA composition (45 : 50.4 : 4.6) with pSt as seeding latex.

Fig.1

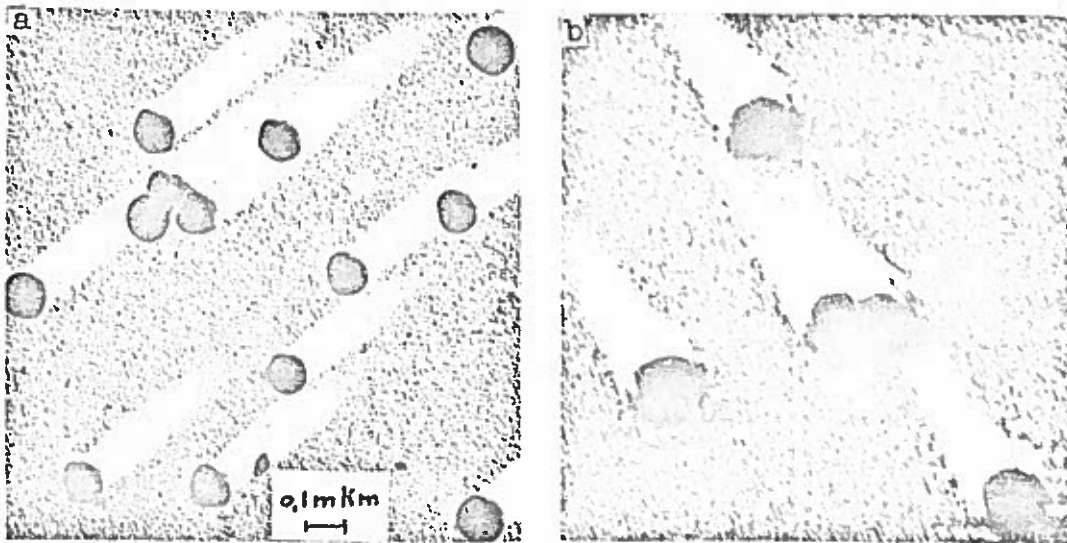
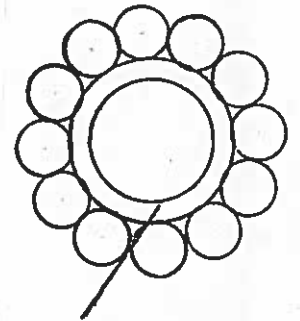


Fig.2 2. Electron photomicrographs of particles of latex synthesized by two-stage polymerization, series B (sampling in the course of synthesis; latex dry residue: a - 13.0%, pSt; b - 32.5%); pH 5.5.

3. Structure scheme of particles of latex obtained by two-stage polymerization.



transition layer:
Fig.3

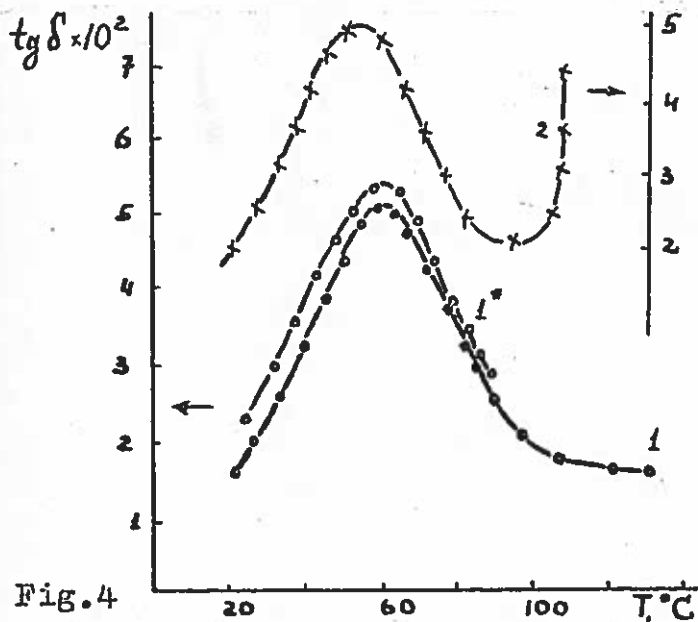


Fig.4

4. Temperature dependence of $\text{tg } \delta$ for samples of films obtained:
1 - by drying the latex synthesized by two-stage polymerization;
2 - from the mixture of polystyrene latex and St-BA-MAA; 1* - film 1 after dissolution in toluene.

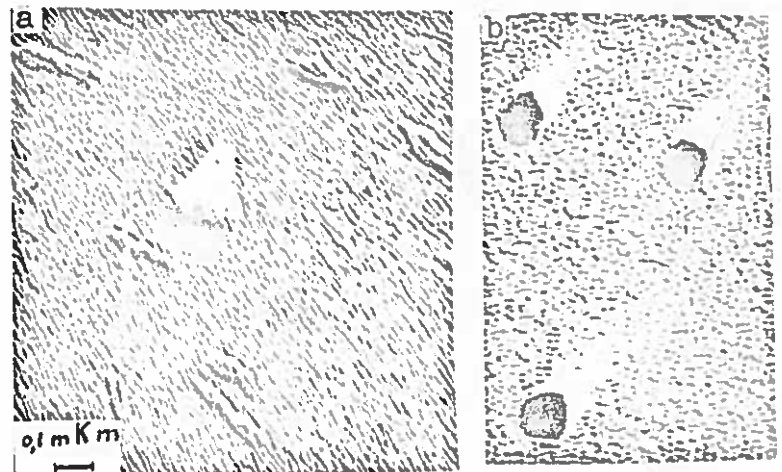


Fig.5

5. Electron photomicrographs of latices: a - synthesized by two-stage polymerization, pH 9.5; b - statistical copolymer, pH 9.5.