

POLYMER COLLOIDS GROUP NEWSLETTER

Vol. 17 No. 1

15 May 1987

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Details of the programme for the 6th Biennial Gordon Research Conference at Tilton School, Tilton, New Hampshire 5-10 July, 1987 appear within. The Annual Business Meeting of the Group will be scheduled during this week. The fixed Conference Fee (inclusive of accommodation and meals) is \$ 310. The address for applications and further information is Dr Alexander M. Cruickshank, Gordon Research Conferences, Gordon Research Center, University of Rhode Island, Kingston, Rhode Island 02881-0801, U.S.A. (Telephone (401) 783-4011) or, after 15th June, Dr A.M.Cruickshank, Colby-Sawyer College, New London, New Hampshire 03257, U.S.A. (Telephone (603) 526-2870). For the convenience of those arriving at Logan International Airport, Boston chartered buses (for which advance booking is required) leave the Airport for conference sites at 4.00 p.m. on the Sunday and return after lunch on the Friday arriving about 3 p.m.

Other forthcoming events noted at the 1986 Annual Meeting were a proposal for a 3rd NATO Advanced Study Institute to be held at Strasbourg 8-15 July, 1988, a 7th Gordon Research Conference in 1989 with Irja Piirma in the chair, and an Emulsion Polymers Symposium to be held within the 64th A.C.S. Colloid and Surface Chemistry Symposium at Lehigh University in June 1990. A second 'Emulsion Copolymerisation and Colpolymers' symposium under the auspices of the C.N.R.S. is planned for Lyon in March 1989.

The Plastics and Rubber Institute is planning a 'Polymer Latex III' International Conference to be held in London in 1989. The emphasis in this meeting is intended to be on latex applications. The date is likely to be in June.

The 18th American and 10th European Short Courses on 'Advances in Emulsion Polymerization and Latex Technology' will be held, respectively, June 1-5, 1987 at Lehigh and August 17-21 at Davos, Switzerland. Information for the Lehigh course from Debra Nyby (215) 758-3590 or from Gary Poehlein (404) 894-4826 for the Swiss course.

Vivian Stannett is the recipient of this year's A.C.S. Award in Polymer Chemistry: a symposium on 'Radiation Chemistry of Vinyl Monomers and Polymers' in his honour was held at the Spring National Meeting in Denver. He writes that he will be retiring at the end of the 1987-88 Academic Year but plans to follow the example of H.Mark, C.S.Marvel and other senior polymer scientists and remain active in the field.

Stan Mason died on April 21 at the age of 73. A Memorial Service is to be held at McGill on a date to be arranged.

This issue will exhaust the funds available to pay for reproducing the Rest of the World Edition of the 'Newsletter' and the Annual Meeting will probably decide on alternative arrangements. Members should nevertheless get their material ready for despatch by mid-September and expect to receive instructions on where it should be sent before then.

The three-line whip sent to academic members last August has been effective in eliciting contributions for this issue or the previous one if not both from all except Watillon, Lin, and Healy.

A.S.D.

9 APR Recd

GORDON RESEARCH CONFERENCE ON POLYMER COLLOIDS

6th-10th July 1987

The Tilton School, Tilton, New Hampshire

Chairman, Ron H. Ottewill (University of Bristol)

Vice-Chairman, Irja Piirma (University of Akron)

PROGRAMME

Monday Morning: Ron Ottewill (University of Bristol), Discussion Leader

"Polymer Colloids Stabilized by Reactive Polymeric Surfactants" Dale Pickelman

"Polymeric Surfactants" Irja Piirma

Monday Evening: John Vanderhoff (Lehigh University), Discussion Leader

"Coagulative Processes in Latex Nucleation: What Really Determines Latex Polydispersity?" Don Napper

"Emulsifier-Polymer Complexation and its Influence on Particle Formation" Wim Donners

Tuesday Morning: Bob Rowell (University of Massachusetts), Discussion Leader

"Use of Nonaqueous Polymer Colloids in Reprographic Technologies" Melvin Croucher

"Polar and Apolar Interactions of Polymers" Carel van Oss

"The Adsorption of Diblock - Copolymer Stabilisers from Micellar Solutions" Alica Gast

Tuesday Evening: Sandy Dunn (UMIST), Discussion Leader

"Stability Conditions for Inverse Microlatexes" Francoise Candau

"Novel Poly(N-isopropylacrylamide) Latexes" Bob Pelton

continued over ...

GORDON RESEARCH CONFERENCE ON POLYMER COLLOIDS

Wednesday Morning: Jim Goodwin (University of Bristol) Discussion Leader

"The Electrical Control of Polymer Colloid Suspension Viscosity" Chip Zukowski

"Miniemulsion Copolymerisation" Mohamed El-Aasser

"Rheology of Aggregated and Aggregating Polymer Latexes" Paul Reynolds

Wednesday Evening: Ritchie Wessling (Dow Chemical), Discussion Leader

"Preparation and Characterization of Aqueous Nonionic Latexes" "Guru" Satgurunathan

"Non-Spherical Latex Particles" John Vanderhoff

Thursday Morning: Mohamed El-Aasser (Lehigh University), Discussion Leader

"Self-Stable Dispersions of Block Copolymers in Alkanes" Julian Waters

"Coalescence of Latex Particles in Film Formation" K. Hahn

Thursday Evening: Theo van de Ven (McGill University), Discussion Leader

"Viscoelastic Properties of Concentrated Polymer Latex Dispersions" Tharwat Tadros

"Comparative Studies of an Expandable-Layer Latex by Acoustic and Electro-phoretic Mobility" B. J. Marlow Bob Rowell

"Low Frequency Dielectric Spectral Shift due to Counterions at a Polystyrene Latex Interface" Bob Fitch L.S. Su S.L. Tsaur

Friday Morning: Irja Piirma (University of Akron), Discussion Leader

"Interactions of Colloids with Biological Systems" Karel Petrak

"Polymer Colloids in the Biosciences" John Ugelstad

D. C. Blackley, London School of Polymer Technology,  
The Polytechnic of North London, Holloway, London N7 8BB.

A few years ago, we completed an investigation into the preparation and properties of a novel series of non-ionic azo initiator/stabilisers which are suitable for the initiation of aqueous emulsion polymerisation reactions in the absence of other colloidal stabilisers. Being themselves surface active, these initiators are capable of functioning as colloid stabilisers for the latex which forms as the reaction proceeds.

Furthermore, they may facilitate particle nucleation by providing micelles whose constituent molecules are able to form free radicals by thermal decomposition. We are now in process of preparing this work for publication. Members of the group may be interested to have an advance indication of some of the salient findings of the programme of work which has been completed.

The initiators are prepared by reaction between the di-acid chloride of 4,4'-azobis-4-cyanopentanoic acid (4,4'-AB-4-CPA) and two mol-equivalents of various commercial fatty alcohol ethoxylates of a fixed fatty alcohol and varying average degrees of ethoxylation. They are thus the di-esters of 4,4'-AB-4-CPA formed from the acid groups of this compound and the terminal hydroxyl groups of the ethoxylate. The di-acid chloride of 4,4'-AB-4-CPA can be prepared by reacting 4,4'-AB-4-CPA with the appropriate amount of phosphorus pentachloride in benzene. The product of the reaction is worked up by standard procedures to give the di-acid chloride as a white solid. The initiators are then prepared by reacting 1 mol of the di-acid chloride

with 2 mols of the fatty-alcohol ethoxylate in toluene in the presence of 2 mols of triethylamine. Initiators have been prepared from a series of fatty-alcohol ethoxylates based upon a fixed fatty alcohol (a mixture of cetyl and oleyl alcohols) and having average mol ratios of ethylene oxide units to fatty-alcohol units which range from 2 to 60. They were all obtained as white waxy solids.

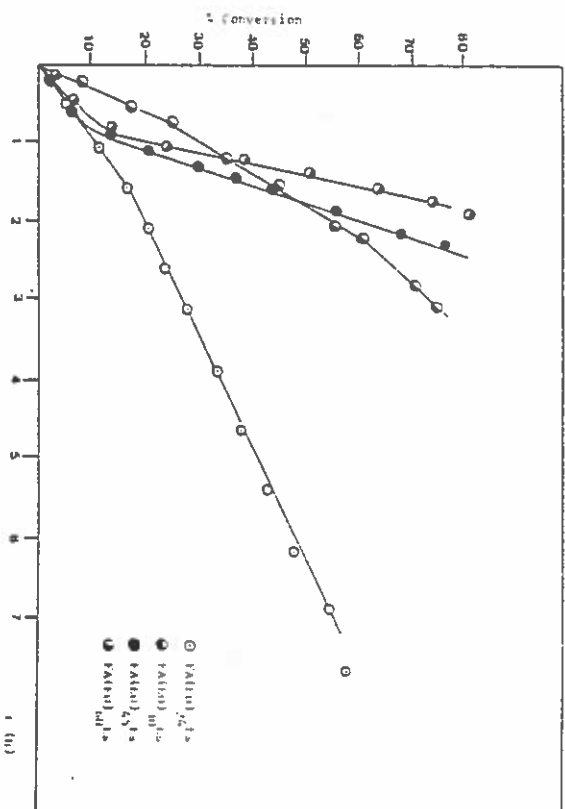
Initiators based upon ethoxylates which contain 10 mols of ethylene oxide or less appear to be at most only very sparingly soluble in water. Initiators based upon ethoxylates which contain 14 or more mols of ethylene oxide are soluble in water at ambient temperatures, although, as expected, they show a cloud-point transition as the temperature of the aqueous solution is raised. The temperature of the cloud point increases as the degree of ethoxylation increases. Although the initiators from the higher ethoxylates are able to reduce the surface free energy of water to approximately  $46 \text{ mJ cm}^{-2}$ , the curves of surface free energy v. concentration are not such that it is possible to estimate critical micelle concentrations from them. In this respect, they differ from the parent ethoxylates from which they are prepared.

The kinetics of the thermal decomposition of some of these initiators in water has been investigated. The decomposition of the azo group in the initiators was followed by ultraviolet spectroscopy. As expected, the kinetics of the thermal decomposition are accurately first-order. The variation of the values of the first-order rate coefficient for thermal decomposition at any given temperature with the degree of ethoxylation of

the initiator is rather more than can be accounted for by experimental error. However, all the values are within the expected range. Thus, for example,  $k_d$  for the initiator prepared from the 24-mol ethoxylate was found to be  $1.02 \times 10^{-5} \text{ sec}^{-1}$  at  $60^\circ\text{C}$ . Satisfactory Arrhenius plots were obtained for  $\log k_d \text{ v. } T^{-1}$ . The values obtained for activation energies again varied somewhat (probably again more than can be accounted for by experimental error) with the degree of ethoxylation of the initiator. However, all were again within the expected range. Thus the activation energy for the thermal decomposition of the 24-mol ethoxylate was found to be  $164 \text{ kJ mol}^{-1}$ .

All the initiators of this type which have been prepared have been found to be capable of initiating the bulk polymerisation of styrene, the aqueous emulsion polymerisation of styrene in the presence of a conventional surfactant such as sodium dodecyl sulphate, and the emulsion polymerisation of styrene in the absence of conventional surfactants. It is of interest that even the azo compounds of low degree of ethoxylation, which are at best very sparingly soluble in water, are effective as initiators for both types of emulsion polymerisation reaction.

Our interest has, of course, been principally in the use of these compounds to initiate polymerisation reactions in the absence of conventional surfactants. The products of this type of reaction are stable latices of small particle size. Using this type of initiator in the absence of conventional surfactant, it is possible to prepare stable latices which are presumably non-ionic and of very low ionic strength. Various shapes of conversion-time curve for this type of reaction have been observed. The shape appears to depend upon factors such as the temperature of the reaction and the degree of ethoxylation of the initiator. A typical series of conversion-time curves is shown below. These curves are for the emulsion polymerisation of styrene at  $50^\circ\text{C}$  in reaction systems comprising monomer  $40 \text{ cm}^3$ , water  $100 \text{ cm}^3$  and initiator  $1.1 \times 10^{-3} \text{ mol}$ . It can be seen that, under these reaction conditions, whereas the 24-, 30-, 45- and 60-mol ethoxylate initiators give broadly similar conversion-time behaviour, the 14-mol ethoxylate initiator gives a reaction system which polymerises very much more slowly than do the other reaction systems in the series.



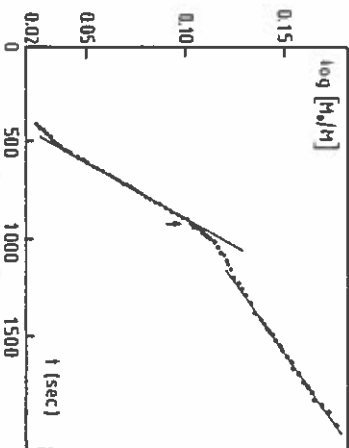
Contribution from the Institut Charles Sadron (CRM-EAHP) CNRS-ULP  
6, rue Bousingault, 67083 Strasbourg Cedex, France

by F. CANDAU

KINETICS OF PHOTOPOLYMERIZATION OF ACRYLAMIDE IN AOT REVERSE MICELLES  
(M. Carver, U. Dreyer, R. Knoesel, F. Candau, R.M. Fitch)

A rotating sector technique has been used to follow the polymerization of acrylamide (AM) in AOT/toluene/water inverse micelles, photo-initiated by azobisisobutyronitrile (AIBN) or by a water-soluble dye methylene/blue eosin. The rates of polymerization were determined by dilatometry, the data being corrected for the effect of reaction exothermicity. Rates of polymerizations were found to be proportional to the first power of the incident light intensity  $I$  and to the first power of the initiator concentration.

These results confirm that a monoradical termination occurs within the droplets. A possible mechanism for this termination involves transfer to AOT, followed by exo-diffusion of the new radical species into the toluene phase. A second possibility is that transfer to toluene forming a stable benzylic radical occurs at the oil-water interface. In either case, these radicals are apparently deactivated



Rates of acrylamide consumption by switching from steady light to intermittent light at the point indicated by the arrow. Dark to Light ratio of the rotating sector = 2.07. The ratio of the slopes gives  $R_p^{\text{Dark}}/R_p^{\text{Light}} = 1.07$ .

in the organic phase rather than undergoing reentry into other micelles. The molecular weight are independent of the rates of initiation and polymerization, which supports the degradation chain transfer mechanism. Furthermore, since a first order dependence of both the rate of initiation and the polymer molecular weights on the monomer concentration was found, the possibility of degradative chain transfer to monomer can be discounted.

Copolymerization of acrylamide and sodium acrylate in microemulsions  
(F. Candau, Z. Zekhnini and J.P. Durand, Progress in Colloid and Polymer Sci., in press)

We have investigated the thermal copolymerization of acrylamide and sodium acrylate in nonionic microemulsions. The formation of microemulsions is strongly related to the acrylate content in the comonomer feed due to a salting out effect of the ethoxylated surfactant. After polymerization, clear and stable inverse latexes are formed which contain high solid contents (up to 23%) dispersed in the oil-continuous medium. The dimensions of the particles determined by photon correlation spectroscopy are rather low ( $450 \text{ \AA} < d < 700 \text{ \AA}$ ) with a narrow distribution. They decrease with increasing emulsifier or sodium acrylate concentrations. The latter result was attributed to the combined effects of dehydration of the ethoxylated emulsifier together with a lowering of the water activity in the particles caused by the sodium acrylate salt.

Publication

"Copolymerization of water-soluble monomers in nonionic bicontinuous microemulsions". F. Candau, Z. Zekhnini, J.P. Durand, J. Colloid Int. Sci., 114, n°2, 398 (1986)



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Emulsion Polymerisation of Highly Water-insoluble Monomers

In his contribution to the Spring 1977 Polymer Colloids Group Newsletter

D.W.J. Osmond reported some results which Fred Waite had obtained at I.C.I. Paints Division to the effect that monomers - C<sub>12</sub> to C<sub>18</sub> methacrylates and tert-butyl styrene which are even less soluble in water than styrene could not be polymerised in emulsion using persulphate initiation unless their solubility in the aqueous phase was increased by addition of acetone or methanol or if a more water-soluble co-monomer - even styrene was added: highly water-soluble comonomers such as acrylic acid were ineffective merely undergoing homopolymerisation in the aqueous phase. I have always thought this was a most important observation and have often quoted it (with their permission) because it appears to show that sulphate radical ions cannot initiate the polymerisation of monomer which is presumably solubilised in emulsifier micelles until oligomer radicals have been formed by polymerisation of monomer dissolved in the aqueous phase despite the calculations of Fitch and Shih (Prog. Coll. Polym. Sci. 56 (1975) 1) which show that the energy barrier between a charged micelle and a singly charged radical would be too small to prevent the entry of the radicals. Subsequently Miss M. Westby of I.C.I. Paints Division mentioned in discussion at the P.R.I. Polymer Latex II Conference in London (May 1985) that it had now been found that these monomers could be polymerised in emulsion if non-ionic emulsifiers were used. This seemed to imply that the energy barrier between an ionic micelle and a sulphate ion radical was indeed sufficient to prevent entry of the radical unless the van der Waals' attraction was increased by the addition of a few monomer units to the radical. Unfortunately the authors could not be persuaded to publish the details of these observations which left many questions unanswered. Would oil-soluble initiators be effective? Would a hydrogen peroxide initiation system producing uncharged radicals work? What was the minimum monomer solubility required to permit persulphate initiated polymerisation? Dr Uma S. Satpathy who had obtained a Ph.D. from Burtman University in India with Professor Konar and had subsequently held a post-doctoral fellowship in Professor Nomura's Department in Japan was awarded a one-year Leverhulme Fellowship in this Department creating an opportunity to get some of these questions answered.

Preliminary experiments with octadecyl methacrylate appeared to confirm the I.C.I. observations. The monomer did not polymerise at 60 °C using persulphate initiation and sodium dodecyl sulphate as emulsifier although styrene, methyl methacrylate, and even vinyl acetate (which is completely inhibited by oxygen) did polymerise under similar conditions. Octadecyl methacrylate did polymerise when some without and a series of experiments at different methanol concentrations was undertaken to find the minimum concentration required to permit polymerisation. Then it was found that this concentration was zero! Octadecyl methacrylate does polymerise in emulsion when deoxygenation is sufficiently thorough. However it seems to be exceptionally effectively inhibited by traces of oxygen so that the usual industrial method of waiting for the reaction to start after the residual oxygen has been consumed does not work.

Contribution to the Polymer Colloids Group Newsletter

from  
W.A.H. Donners  
DSM Research  
P.O. Box 18  
6160 MB Geleen  
The Netherlands

F13 MAY Reed

The effect of emulsifier-polymer complex formation on particle nucleation in emulsion polymerisation (H. Midgley)

The first details of this study have appeared in *J. Polym. Sci. Polym. Lett. Ed.* 25 (1987) 29-35.

Since then our research efforts have been concentrated on kinetic measurements during preparation of latices with MAA/MMA ratios of 8/20, 5/95 and 0/100.

The results for the 80/20 latices confirm the picture given in the article cited above. Even small quantities of PEO 20,000 give retardation of the polymerisation. However after the retardation period polymerization rate is as high as found for PEO free latices right from the start.

Two hypotheses brought forward in our article have been disproven by recent measurements. First it was thought that the larger particle size of particle formed in the presence of PEO (MW 20,000) was caused by reduction of particle number because of interactions of oligomers with PEO chains. Kinetic measurements, however, show no influence of the presence of PEO on conversion vs. time curves for MMA. The first results of T<sub>g</sub> measurements on PMMA latices with and without PEO (after cleaning by serum replacement and drying) suggest that PEO is included in the polymer particles, possibly by grafting.

We also put forward in our article the hypothesis that in PEO-free latices electrostatic stabilization by initiator residues was the main stabilizing factor in latices with MAA/MMA ratios from 0/100 to about 50/50 and that at higher MAA/MMA ratios steric stabilization by acid-rich copolymer comes into play. Stability measurements by addition of Na<sub>2</sub>SO<sub>4</sub> to various latices, however, have proven that already in MAA/MMA = 5/95 latices steric stabilization dominates.

Kinetic measurements on the 5/95 latices show that MMA polymerizes faster than MAA, thereby forming polymers of which the acid content rises with time to about 25 % on average.

Further work is in progress.

Octadecyl methacrylate is presumably made by ester interchange from methyl methacrylate. Any residual methyl methacrylate, being a more water-soluble co-monomer, would account for the polymerisation if present. Residual methyl methacrylate could be detected in the octadecyl methacrylate used both by gas chromatography and infra-red spectroscopy. Extraction with water reduced the concentration of methyl methacrylate below the level detectable by these methods. Although the rate of polymerisation was also reduced, further extraction did not reduce the rate of polymerisation further. Variation of initiator and emulsifier concentration gave a 0.46 order in initiator and a 0.68 order in emulsifier in fair agreement with expectation on Smith-Ewart theory.

Tert-butyl styrene (95% para) was supplied by I.C.I. Paints Division from a batch test marketed by Dow who give its solubility in water at 25°C as 0.00053 g compared with 0.032 g for styrene. (The precise solubility of styrene in water does not seem to have been established unequivocally: other values are lower but still much higher than for tert-butyl styrene). This also proved to contain a little styrene which could be removed by distillation. The purified tert-butyl styrene still polymerised at a rate very similar to that of styrene under the same conditions. It has not yet been possible to get electron micrographs of these latices to see whether the number concentration of latex particles is also similar. If it is, this would seem to imply that the solubility of the monomer in the aqueous phase is not a critical factor in emulsion polymerisation and that direct entry of charged radicals into latices is possible.

Increasing the solubility of the monomer in the aqueous phase is known to increase the number of latex particles formed in the emulsifier-free emulsion polymerisation of styrene, no results for the effect of hydrotropes in the presence of emulsifier micelles have been published. Increasing methanol concentrations did increase the rate of polymerisation of octadecyl methacrylate somewhat but the latex obtained is not very suitable for particle size determination by electron microscopy.

Polymer Colloid Newsletter  
**MICROCALORIMETRIC STUDIES**

113 MAY 1964

Submitted by  
 D. S. Jayasuriya  
 Louis Laboratories, Johnson Wax  
 Racine, Wisconsin

Experimental work was initiated to study the energetics of interaction of surfactants and polymers with latex particles using a "Tronac" micro-calorimeter with enhanced software. Preliminary experiments carried out on a model system, sodium dodecyl sulfate on polystyrene latex, have given reproducible heats of adsorption profiles. An approximate analysis of the data assuming adsorption to involve an equilibrium between the surfactants in the absorbed and the solution state gives an enthalpy of adsorption of 100 cal mol<sup>-1</sup> and an equilibrium constant of 1x10<sup>4</sup> at 25°C. This study is being carried out in the Colloid Section of the Physical Research Labs.  
 (sent in by Bob Fitch)

by  
 Archie Hamielec 14 APR Recd

1. HIGH CONVERSION BATCH AND SEMI-BATCH SUSPENSION POLYMERIZATION OF VINYL CHLORIDE.

The kinetics of high conversion polymerization of VCM (Xp. 75) are being investigated to better understand the control of particle porosity, resin bulk density and PVC thermal stability.

A paper entitled:

"Experimental Investigation of Vinyl Chloride Polymerization at High Conversion - Temperature/Pressure/Conversion and Monomer Phase Distribution Relationships" by T.Y. Xie, A.E. Hamielec, P.E. Woods and D.R. Woods.

has been accepted for publication in J. Appl. Polym. Sci. (1987).

Work is continuing.

2. MICROSUSPENSION COPOLYMERIZATION OF ACRYLAMIDE WITH ANIONIC AND CATIONIC MONOMERS USING BATCH, SEMI-BATCH AND CONTINUOUS PROCESSES.

(a) Nonionic polyacrylamides have been fractionated (solvent/non solvent precipitation) to give narrow MWD samples which were carefully characterized by viscometry, light scattering photometry and aqueous size exclusion chromatography, to provide molecular weight standards. These narrow MWD samples are being hydrolyzed to form anionic polyelectrolyte standards and cationic polyelectrolyte standards are being made using Mannich reaction. These polyelectrolyte standards are being used to develop valid analytical methods for the molecular weight characterization of anionic and cationic polyelectrolytes.

(b) Solution copolymerizations in a CSTR are being done to measure reactivity ratios for various cationic monomers with acrylamide.

3. EMULSION POLYMERIZATION OF VINYL ACETATE AND VINYL ACRYLATE/ACRYLIC ACID COPOLYMERS.

A manuscript is being prepared for publication.

4. PRODUCTION OF CROSS-LINKED POLYELECTROLYTES

A model which describes the growth and structure of cross-linked gel formed during the copolymerization of vinyl and divinyl monomers is being developed.

\* These studies are being done in collaboration with C.M. Crowe, J.F. MacGregor, P. Wood and D.R. Woods.

BASF Aktiengesellschaft D-6700 Ludwigshafen

16 MAY Recd

Contribution to Polymer Colloids Newsletter

The following papers have been published recently by colleagues of BASF Aktiengesellschaft.

COPOLYMERIZATION IN EMULSION (H. SCHULLER)

Abstract - Mayo's copolymerization equation must be modified in the case of copolymerization in emulsion because of the varying solubility of the monomers in the water phase. By introduction of the distribution-coefficients of the monomers in oil and water as well as the monomer/water-ratio it can be shown, that the composition of the copolymer can be changed drastically in the emulsion copolymerization compared to the homogeneous copolymerization.

Thus for the more water soluble monomers the polymerization in the water phase must be taken into account. If a polymer chain grows partly in the water phase and partly in the latex particle it will have a block-copolymer-like structure. This can be demonstrated by a Monte Carlo-simulation and proven by special titration methods of the latex. In the latex particles we usually have a high concentration of polymers dissolved in the monomer. If the copolymer produced at the beginning differs from that at the end of the reaction, phase separation inside the latex particle makes still more difficult the calculation of copolymer composition. In this case practically every structure of the latex particles can be observed: raspberry structures, half-in-half structures, core-shell-structures.

In: Polymer Reaction Engineering, p. 137-145, Hüthig & Weyf, Basel 1987.  
 K.H. Reicherter ed.

ON PARTICLE COALESCENCE IN LATEX FILMS

(K. HAHN, G. LEY, H. SCHULLER, K. OBERTHÜR)

The Small Angle Neutron Scattering (SANS)-measurements discussed in this paper were a first attempt to investigate the molecular mechanism of the coalescence. These preliminary results clearly show that the coalescence is due to a massive interdiffusion of material of different latex particles - at least in our material. They also demonstrate that SANS is a valuable tool for latex film research.

In: Colloid & Polymer Science 264, p. 1092-1096 (1986)

114 APR 1980

Aggregation of polystyrene particles studied by single particle laser light scattering

Introduction

In order to gain detailed information about the aggregation state of a colloid system, particle size distributions are measured. We developed a modified ultramicroscope, in which the particles are individual sized by a light scattering method (see appendix). The apparatus is an improved version of an instrument described in the literature (1,2). It is possible to distinguish aggregates up to seven singlet units (figure 1). It is found that the kinetics of coagulation (induced by salt) and flocculation (induced by polymer) are different.

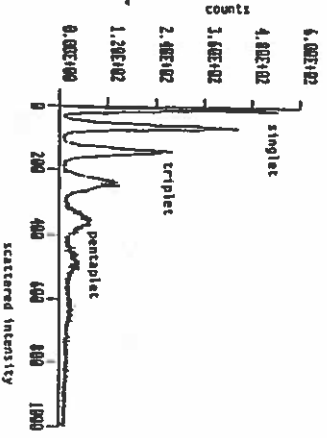


Figure 1. Size distribution of a coagulating polystyrene latex.  $10^3$  concentration  $0.2 \text{ ml/l}$ , latexial particle concentration  $2 \cdot 10^{10} \text{ particles/cm}^3$ , time after mixing 200 seconds.

Experimental

Polystyrene latices were prepared according to the method of Goodwin (3). We obtained monodisperse particles with a diameter of 680 nm and a surface charge density of  $-5.6 \text{ } \mu\text{C/cm}^2$ .

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Polyethylene oxide (BDH Laboratory reagent) was used without further purification. Potassium nitrate solutions (Merck p.a.) were filtered through a  $0.22 \text{ } \mu\text{m}$  Millipore filter.

Rapid coagulation was induced by mixing 10 ml latex with 10 ml salt solution in a T-shaped cell. Size distributions were measured by detecting a small amount of the mixed solution at different times and inject this in the single particle sizer. Initially we used a stopped flow as mixing device but by the forceful mixing some pressure induced aggregation occurs. In the flocculation experiments, a certain latex volume was injected in a same volume of polymer solution. The solution was agitated for 1.5 hours, diluted and measured in the single particle sizer.

Results

Coagulation.

The concentrations of singlets, doublets and triplets as a function of time are presented in figure 2. With the help of the differential equations 1-3 it is possible to calculate numerically the coagulation rate constants from the experimental results.

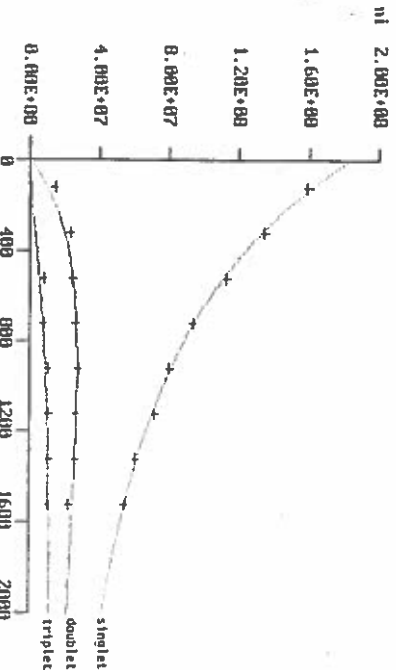


Figure 2. Numbers of singlets, doublets and triplets as a function of time. Initial particle concentration  $2 \cdot 10^8 \text{ particles/cm}^3$ ,  $10^3$  concentration  $0.5 \text{ ml/l}$ , temperature 293 Kelvin.

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$$\frac{dN_1}{dt} = -k_{11}N_1^2 - k_{12}N_1N_2 - k_{13}N_1N_3 \quad (1)$$

$$\frac{dN_2}{dt} = \frac{1}{2}k_{11}N_1^2 - k_{12}N_1N_2 - k_{23}N_2N_3 - k_{22}N_2^2 \quad (2)$$

$$\frac{dN_3}{dt} = k_{12}N_1N_2 - k_{13}N_1N_3 - k_{23}N_2N_3 - k_{33}N_3^2 \quad (3)$$

where  $N_1, N_2, N_3$  are the singlet, doublet and triplet concentrations at time  $t$  and  $k_{ij}$  the rate constant of the formation of aggregates of  $i+j$  singlets out of  $i$ -multiplets and  $j$ -multiplets.

The results are given in table 1.

Table 1  
 $k_{ij}$  ( $10^{12} \text{ cm}^3 \text{ s}^{-1}$ )

$k_{11}$	$k_{12}$	$k_{13}$
$6.0 \pm 0.1$	$7.2 \pm 0.6$	$10 \pm 2$

#### Flocculation.

The results are presented in three figures; an adsorption-isotherm (figure 3), stability versus polymer coverage (figure 4) and stability versus initial particle concentration (figure 5). The stability is expressed as the percentage of the singlets left in the system. No salt is added.

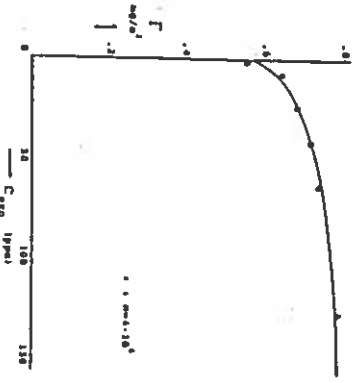


Figure 3. Adsorption-isotherm of Polyethylene oxide on polystyrene latex. Molecular weight  $4 \times 10^6$  g/mole.

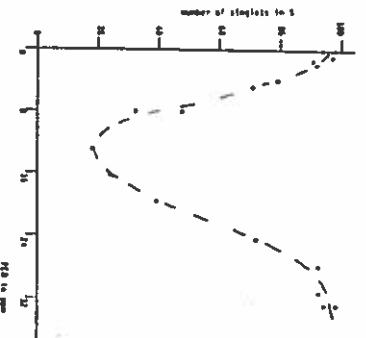


Figure 4. Stability versus polymer coverage. Initial particle concentration  $3 \times 10^{10}$  particles/cm<sup>3</sup>.

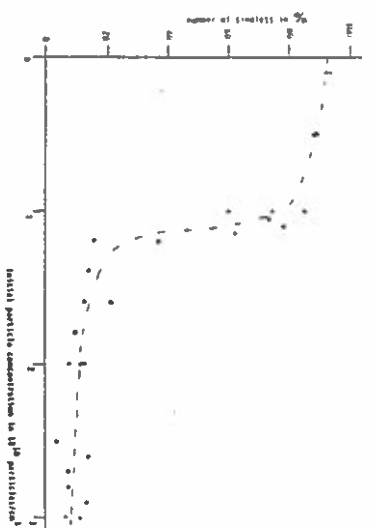


Figure 5. Stability versus initial particle concentration. Polymer/latex ratio is constant. Initial polymer concentration 13 ppm at  $3 \times 10^{10}$  particles/cm<sup>3</sup>.

#### Discussion

For diffusion controlled coagulation, the theory of Smoluchowski predicts a rate constant of doublet formation  $k_{11} = 12.2 \times 10^{-12} \text{ cm}^3 \text{ s}^{-1}$  at  $T=293$  Kelvin. Experimentally one finds  $k_{11} = (3.2-6.8) \times 10^{-12} \text{ cm}^3 \text{ s}^{-1}$  (1,2,4). Honig and Spielman have pointed out that hydrodynamic effects incorporated in the Smoluchowski theory reduce the rate constant by approximately a factor of two (5). Hence our results for the coagulation seem quite reasonable.

The flocculation experiments were focussed on mixing effects, in a later stadium we will concentrate on rate constants. The adsorption-isotherm is in agreement with results of Cowell and Vincent (6). The general features of the stability as function of polymer concentration is well known (7,8). At low polymer coverages, polymer chains can adsorb simultaneously on two particles and give rise to bridging flocculation. At high coverages, bridging is prevented because no free surface is available; steric stabilization is achieved.

The critical dependence of the stability on the initial particle concentration is rather surprising. Possibly the kinetics of bridging, in which two latex particles and one polymer coil are involved, is responsible for this effect. At low particle concentrations mainly encounters of one particle and one

# A NEW APPARATUS FOR SINGLE PARTICLE COUNTING

## OBJECTIVES

The development of an instrument for counting and sizing colloids. The technique is based on low angle light scattering by single particles as they pass through the laser illuminated volume. The method provides a sensitive measurement of the onset of aggregation and the initial kinetics.

## MODEL SYSTEM

Homodisperse aqueous polystyrene latex in the presence of electrolytes and polyethylene oxide.

## DESIGN

A dispersion beam is hydrodynamically focused and flows through a laser focus. With accurate focusing and low dispersion concentrations, there are only single particles in the laser beam. Each particle will generate a light flash which is detected, at small angle, by a photomultiplier. The peak-heights of these pulses are collected by a multichannel analyser. Up to 20,000 particles/pulse can be detected.

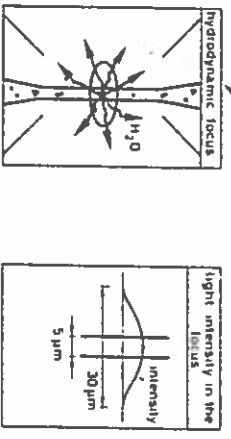
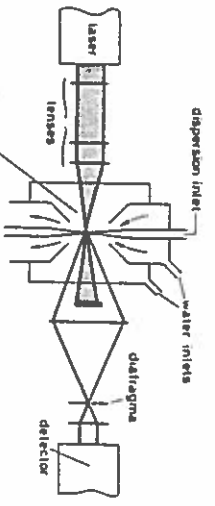


Fig. 1 An elliptical laser focus is used in order to have a homogeneous intensity across the hydrodynamic focus.

## LIGHT SCATTERING

At angle  $\theta = 0$  with respect to the laser beam, the scattering intensity is independent of the orientation and structure of the particles.

Relation for aggregates:

$$\theta = 0^\circ : I_1 = I_1^0 \cdot I_1^2$$

$$\theta = 8^\circ - 10^\circ : I_1 = I_1^0 \cdot I_1^2$$

(polystyrene/water)

## EXPERIMENTAL RESULTS

Particle size distribution of a latex (650 nm in diameter) calculating in 0.5 M KNO<sub>3</sub>.

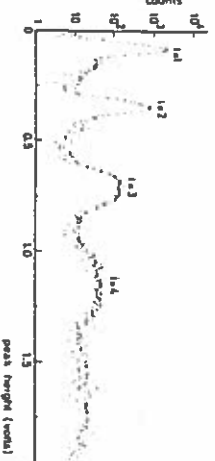


Fig. 2

## DISCUSSION

- Sensitive monitoring of the onset of aggregation. Detection limit 1 doublet on 200 singlets.
- Aggregation Kinetics: until now, up to triplets can be counted accurately.
- Shear forces in the instrument are small; aggregate break-up does not occur. If it would occur for weak aggregation, it is detected.
- Problems:
  - 1) For particles with high contrast:  $I_1$  is not only determined by  $I_1$  but also by the structure and orientation of the floc.
  - 2) For very wide size distributions the range of the detector is too small. A laser feedback system could be used.

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 2. J. Collin, P. C. Commins, S. J. Stapleton and S. Thompson, "Colloids and Interfaces", in press.

polymer molecule will occur. Before another singlet comes near, the polymer will adapt a rather flat conformation. No tails will protrude through the double layer and no bridging flocculation will occur. At high particle concentrations one polymer chain may adsorb with both ends on different particles at the same time. The radius of gyration of the polymer is of the same order as the double layer thickness. Therefore the polymer can adsorb on two particles at the same time. Because no salt is added, the double layer is rather thick.

We also used a smaller polyethylene oxide (molecular weight  $6 \times 10^5$  g/mole), the radius of gyration of this polymer is smaller than the double layer thickness. No flocculation could be induced without using a small amount of salt. For this polymer we could separate the adsorption process and the bridging process by adding the salt after the adsorption is established.

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 The Netherlands

Eduard Peeters  
 Gerard Fleer

by  
Mamoru Nomura,  
Fukui University, Fukui, Japan

6 MAY Read

We held the biennial three days Symposium, "4th Polymer Microspheres Symposium, Japan" in Fukui in November 6-8, 1986. It was very successful gathering 58 presentations and 254 participants. Dr. Fitch was invited as a plenary lecturer. The titles presented in this meeting are listed below for reference. Preprints are available, although written in Japanese. Please write me for preprints, if needed.

- A-01 Preparation of Fine Polymer Particles in W/O Micro-emulsions: K.Kono and A.Kitahara (Science University of Tokyo, Tokyo, Japan)
- A-02 On the Processes of Particle Formation and Growth in NMD Synthesis: M.Yabuta, S.Sugitara, K.Murata, Y.Sasaki(Technical R&D Department, Kansai Paint Co., Ltd, Hirakata City, Kanagawa, Japan)
- A-03 Emulsion Polymerization of Vinyl Acetate in the Presence of Modified Poly(vinyl alcohol): K.Yuki, T.Sato, J.Yamuchi, T.Okaya(Kuraray Co.,Ltd)
- A-04 Emulsion Polymerization of Methylmethacrylate with Graftcopolymer: F.Takeuchi, Y.Takizawa, T.Takeuchi, K.Kawase(Soken Chemical & Engineering Company Ltd.)
- A-05 Preparation of Amphoteric Polymers by Dispersion Polymerization: H.Kawaguchi, N.Nojiri, and Y.Ohtsuka(Faculty of Sci. & Technol., Keio University, Hi-yoshi, Yokohama)
- A-06 The Decomposition of Potassium Persulfate in Emulsion Polymerization Systems: M.Okubo and T.Mori(Department of Industrial Chemistry Faculty of Engineering, Kobe University, Kobe, Japan)
- A-07 A Study on the Locus of Particle Formation in Emulsion Copolymerization of Styrene and Methyl Methacrylate: M.Nomura, U.S.Satpathy, Y.Kono and K.Fujita (Dept. of Industrial Chemistry, Fukui Univ. Fukui)
- A-08 Seeding Reactor and Its Operation in Continuous Emulsion Polymerization: M.Nomura, B.D.Nguyen, and K.Fujita(Department of Industrial Chemistry, Fukui University, Fukui, Japan)
- A-09 Synthesis of Core/Shell Latex Employing PVC and Copolymers as Core Particles: M.Sakaya, M.Matsumoto, M.Iso and S.Omi(Tokyo University of Agriculture and Technology, Koganei, Tokyo, Japan)
- A-10 Kinetic Analysis of Vinylidene Chloride-Acrylonitrile Emulsion Copolymerization Reaction and Its Simulation: S.Omi, K.Kushibiki, M.Sato and M.Iso(Tokyo University of Agriculture and Technology, Koganei, Tokyo, Japan)
- A-11 Localization of Carboxyl Groups at Surface Layer of Carboxylated Polymer Emulsion Particles by Alkali Treatment: M.Okubo, K.Kanaiida and T.Matsumoto (Kobe University, Kobe, Japan)
- A-12 Production of Anomalous Carboxylated Polymer Microspheres: M.Okubo, K.Kanaiida and T.Matsumoto (Kobe University, Kobe)
- A-13 Film Formation from Alkali Thickened Polymer Emulsion: M.Okubo, A.Takamatsu, T.Wamura and T.Matsumoto (Kobe University, Kobe, Japan)
- A-14 Investigation of Poly(Vinyl Acetate) Latex Particles by Color Reaction with Iodine-Iodide: S. Hayashi, K.Suyama, and T.Hizatsi(Faculty of Textile Science and Technology, Shinshu University, Ueda, Japan)
- A-15 Structure and Temperature-Sensitive Stability of Latices Containing N-substituted Acrylamides: F.Hoshino, T.Fujimoto, H.Kawaguchi, and Y.Ohtsuka (Faculty of Science & Technology, Keio University, Yokohama, Japan)
- A-16 Characterization of Latexes by SCM NMR: J.Hasegawa, H.Inaki, M.Ogawa, M.Sekiya(Research & Development Center, Nippon Zeon Co.,Ltd)
- A-17 New Detection System of the Rapid Angular Scanning Light Scattering Photometer: S.Hashiya, T.Matsuo(Faculty of Engineering, Fukui University, Fukui, Japan)
- A-18 Heterocoagulation Between Polymer Latices and Inorganic Particles: K.Furusawa(Department of Chemistry, University of Yukuha, Ibaraki, Japan)
- A-19 Colloid Chemical Property of Hematite Particle Covered with Latex Particles: M.Ozaki(Yokohama City University, Yokohama, Japan)
- Silica in Sedimentation Equilibrium, and the Important Role of Length: T.Okubo

(Department of Polymer Chemistry, Kyoto University, Kyoto, Japan)

A-21 Dynamic Properties of Ordered Structure of Monodispersed Polymer Spheres: T.Okubo(Department of Polymer Chemistry, Kyoto University, Kyoto, Japan)

A-22 Structure of Colloidal Silica Dispersions as Studied by Small-angle X-ray Scattering: H.Matsuo and N.Ise.(Department of Polymer Chemistry, Kyoto University)

A-23 "Ordered" Structure in Dilute Latex Suspensions as Studied by Quasielastic Light Scattering: Y.Ueno, H.Okumura, K.Ito, H.Matsuo, N.Ise(Department of Polymer Chemistry, Kyoto University, Kyoto)

A-24 "Ordered" Structure in Polymer Latex Suspension. Analysis of lattice vibration by Using Image Processing System: H.Nakamura, K.Ito, and N.Ise(Department of Polymer Chemistry, Kyoto University, Kyoto)

A-25 "Ordered" Structure in Polymer Latex Suspensions Studied by Microscope-Image Processing System: K.Ito, and N.Ise (Department of Polymer Chemistry, Kyoto University, Kyoto, Japan)

A-26 Deposition of Polymer Latices on the Surface of Hollow Fiber: H.Tamai, Y.Nishida and T.Suzawa (Hiroshima University, Higashi-Hiroshima 2, Japan)

A-27 Adsorption of Blood Proteins onto Polymer Latices: T.Suzawa, H.Shirahama, S.Mori and K.Suzuki(Hiroshima University, Higashi-Hiroshima, Japan)

A-28 Adsorption of Biomolecules onto Polymer Microspheres Having Hydrophilic/Hydrophobic Heterogeneous Surface Structure: M.Okubo, S.Kamei, Y.Aoki, and T.Matsumoto(Kobe University, Kobe, Japan)

A-29 Preparation of the latex immobilized lectin in order to carry the function of lipid recognition: T.Arai, T.Asaba, T.Ando, H.Kitamura (College of Indus. Tech., Nihon University, Narashino, Japan)

A-30 Attachment of Antibody Fragments onto Latex Particles: H.Kawaguchi, K.Sakamoto, Y.Ohtsuka(Faculty of Sci. & Technol., Keio University, Hi-yoshi, Yokohama, Japan) T.Ohtake, H.Sekiyauchi, and H.Irifi(Faculty of Medicine, Keio University, Shinanomachi, Shinjuku, Japan)

A-31 Water Retention of Latex Coatings: A.Koyama, M.Tsurumi, S.Muroi(Asahi Chemical Industry, Kawasaki, Japan)

A-32 Binder Migration in Paper Coating: K.Naoi, M.Tsurumi and S.Muroi (Asahi Chemical Industry, Kawasaki, Japan)

A-33 Study of Gly-reactive Latex Distribution in Coated Paper: T. Kolke, Y.Oikawa, T.Tezuka, M.Sekiya(Nippon Zeon Co.,Ltd.)

A-34 Lowering of Internal Stress of Epoxy Resin by the Modification with Core-shell Polymer Microsphere Containing Functional Groups: Y.Nakamura, H.Tabata, H.Suzuki, K.Iko(Nitto Electric Industrial Co., Ltd.)M.Okubo and T.Matsumoto (Faculty of Engineering, Kobe University, Kobe, Japan)

A-35 The Application of Microgels for Radiation Curing Systems: K.Kanda, Y.Ninomiya, K.Ishii, S.Ishikura, R.Mizuguchi(Nippon Paint Co. Ltd., Technical Center, Neyagawa, Osaka, Japan)

A-36 Chemical Deposition from Anionic Polymer Emulsion of which pH was Adjusted with Various Acids onto Anodized Aluminum Plate: M.Okubo, Y.Mizushima, Y.Fujiwara, T.Matsumoto(Kobe University, Kobe, Japan)

A-37 Contact Electrification of Ultrafine Spherical Polymethyl Methacrylate Particles: T.Takeuchi, Y.Takizawa, S.Kawase (Soken Chemical & Engineering Company Ltd.) T.Oguchi (Toshiba Research and Development Center) M.Kohishi(Faculty of Pharmaceutical sciences, Science University of Tokyo, Tokyo, Japan)

A-38 Kinetic Analysis of Association of Latex Particles Modified with Antigens and Antibodies: H.Kitano, S.Iwai, T.Okubo, and N.Ise (Department of Polymer Chemistry, Kyoto University, Kyoto, Japan)

A-39 Application of Fluorine-containing Polymer Latices to Immunolateral Reagents: M.Sugimura, T.Shimizu(Daikin Industries, Ltd., Osaka, Japan)

T.Suzuta(Tokyo Medical College, Tokyo)

A-40 Determination of Blood Group Antigens in Uroepithelial Tissue with High Specific Gravity Type Soup-Free-Latex: M.Nakagawa, T.Kuge and S.Ohata(Sekisui Chemical Co., Ltd., Shimanoto, Osaka, Japan) R.Abe, T.Kato and M.Moriyama (Department of Urology, Akita University, Akita, Japan)

A-41 Assessment of a Latex Agglutination Inhibition Test for Quantitative Analysis of Serum Amikacin: J.Shinoda and T.Kuge (Medical Division, Sekisui Chemical Co., Ltd. Osaka, Japan.)

- A-42 Function of Proteins Immobilized on Albumin Microspheres: Y. Chang-hong, H. Kitano, N. Ise (Department of Polymer Chemistry, Kyoto University, Kyoto, Japan)
- A-43 Covalently Immobilization of Trypsin Enzyme Molecules onto Composite Polymer Microspheres Having Hydrophilic/Hydrophobic Heterogeneous Surface Structure by CNBR Method: M. Okubo, Y. Tosakai, S. Kamel, K. Fukunaga, and T. Matsumoto (Kobe University, Kobe, Japan)
- A-44 Immunoactive Reaction on Composite Polymer Microspheres Having Hydrophilic/Hydrophobic Heterogeneous Surface Structure: M. Okubo, Y. Yamamoto, M. Uno, S. Kamel, and T. Matsumoto (Kobe University, Kobe)
- A-45 Preparation of Latices Immobilizing Hemin and Their Catalytic Function: H. Matsumoto, H. Kawaguchi, and Y. Ohtsuka (Faculty of Science and Technology, Keio University, Hiyoshi, Kohoku-ku, Yokohama)
- A-46 Microencapsulation of Magnetic Ultra-Fine Particle-Biological Application: H. Kikuta (Ultra-Fine Particle Project, Research Development Corp. of Japan, Ibaraki-Ken, Japan)
- A-47 Preparation of Capsule Containing Drug with Porus Particles: K. Saito, M. Koike (Faculty of Pharmaceutical Science, Science University of Tokyo, Japan)
- F. Hosoi, K. Makiuchi (Takasaki Radiation Chemistry Research Establishment, JAERI, Gunma)
- A-48 Slow Release of Anti-Cancer Drug from Poly-Lactic Acid Microspheres: R. Wada, Y. Tabata, S.-H. Hyon and Y. Ikada (Research Center for Medical Polymers and Biomaterials, Kyoto University, Sakyo-ku, Kyoto)
- Invited Lecture: Dielectric Spectroscopy of Model Polymer Colloids.  
(S.C. Johnson & Son Inc., U.S.A.) R. M. Fitch
- B-01 Synthesis of Latex using Phospholipid as Emulsifier: K. Yamaguchi, S. Watanabe and S. Nakahama (Department of Polymer Science, Tokyo Institute of Technology, Chokkayama, Meguro-ku, Tokyo, Japan)
- B-02 Hybrid Rubber Latexes Polymerized by Transition Metal Catalyst in water: K. Kasai, N. Itho, H. Ono and H. Hixai (Japan Synthetic Rubber Co., Ltd, Yokkaichi, Mie, Japan)
- B-03 GRIM (Gradient-Index) Sphere Lens with Low Spherical Aberration and Non-destructive Method of Measuring composition-Distribution: Y. Koike, Y. Sumi, and Y. Ohno (Fukaya Faculty of Sci. and Techn., Keio University)
- B-04 Synthesis and Application of Magnetic and Fluorescent Immunolater Particles: I Synthesis: K. Furusawa, N. Tobori (University of Tsukuba, Ibaraki, Japan) M. Sales (Fundacio Gaspar de portia, Barcelona-Espana) H. Noguchi, Y. Uchida (University of Tokyo, Tokyo, Japan) T. Suzuta (Tokyo Medical College, Tokyo, Japan)
- B-05 Synthesis and Application of Magnetic and Fluorescent Immunolater Particles II Application: T. Suzuta, N. Yanase, H. Asakura (Tokyo Medical College, Tokyo, Japan) M. Sales (Fundacio Gaspar de portia Barcelona, Espana) H. Noguchi, Y. Uchida (University of Tokyo, Tokyo, Japan) K. Furusawa (University of Tsukuba, Ibaraki, Japan)
- B-06 Phagocytosis of Latex Particles Having Different Hydrophilicity: H. Kawaguchi, T. Ozawa, Y. Ohtsuka (Faculty of Science and Technology, Keio University, Hiyoshi, Yokohama, Japan) M. Miyamoto and S. Sasakawa (Central Blood Center, Japanese Red Cross, Hiroo, Shibuya-ku, Japan)
- B-07 Phagocytosis of Polymeric Microspheres by Macrophages: Y. Tabata, Y. Ikada (Research Center for Medical Polymers and Biomaterials, Kyoto University, Kyoto, Japan)
- B-08 Applicability of Labeled Latex particles as a Tracer in Living Bodies: T. Arai, U. Moriya (College of Industrial Technology, Nihon University, Narashino, Chiba, Japan)
- B-09 Preparation and Function of Latex for Controlled Release of Drugs: H. Kawaguchi, T. Mita, Y. Ohtsuka (Faculty of Science and Technology, Keio University, Hiyoshi, Yokohama, Japan)
- B-10 Preparation of Latex Particles Immobilizing two Enzymes and Their Function (Faculty of Science and Technology, Keio University, Hiyoshi, Yokohama, Japan)

CONTRIBUTION TO THE POLYMER COLLOIDS GROUP NEWSLETTER  
FROM LABORATOIRE DES MATERIAUX ORGANIQUES (CMRS)

Submitted by J. GUILLOT / C. PICHOT

29 APR 1982

1 / Study of the water phase polymerization in emulsion copolymerization of systems containing polar or functional monomers

Accurate kinetic investigation (GC, FTIR, NMR) at low conversion have shown the occurrence of a water copolymerization for systems of comonomers with various polarity (S-AN, S-MEA, EtA, BuA-VAc...). Its importance increases with relative amount and propagation rate constant of the more hydrophilic monomer. The water polymerization can be quite well estimated from comparison of experiments and simulation programs taking into account monomer partition and computing, at any conversion (time), the overall propagation rate constants in particle and water phases, which are complex functions of homopolymerization rate constants, monomer feed and concentrations.

Experiments were also compared with simulation for carboxylic acids, methylolacrylamide (NMA), sulfonated functional monomers in terpolymerization with the basic S/BuA comonomer system. For instance, the huge  $k_p$  for NMA and carboxylic acids (at low pH) make the overall  $k_p$  to vary in a complex way and can explain the formation at a high rate of hydro-soluble polymers, the effect of which playing a role on colloid stability. This approach also appears very useful to investigate the location of functional monomers.

2 / Preparation of hydrogel polymers by micro-suspension polymerization (M. LEPAIS)

After selecting experimental conditions to provide stable water in cyclohexane emulsions, polymerizations are carried out at 40°C, using a water soluble initiator ( $K_2S_2O_8$ ), with

mixtures of acrylic acid and acryloyloxyethyltrimethylammonium chloride, varying the comonomer composition, degree of neutralization and the concentration of a crosslinking agent. Kinetics are followed by recording the exotherm as a function of time. Final products are characterized by their water soluble polymers content, swelling behavior and mechanical properties. Kinetics of water adsorption of the corresponding hydrogel polymers are currently investigated by microwave spectroscopy (giving the dielectric constants  $\epsilon'$ ,  $\epsilon''$ ) as a function of reaction parameters, morphology of materials, etc.

3/ Recent publications and thesis

. Kinetics of batch emulsion copolymerization of vinyl acetate-butyl acrylate system (submitted to European Polymer Jol)

. Characterization of particle surface and morphology in vinylacetate-butyl acrylate emulsion copolymers  
(In press - Colloid and Polymer Science)

by X.Z. KONG, C. PICHOT, J. GUILLOT

. Kinetics of Batch emulsion copolymerization of styrene and methyl acrylate

I. With  $K_2S_2O_8$  as initiator

II. With  $K_2S_2O_8/Na_2 S_2O_8$  system as initiator submitted. Die Mak. Chemie

by W. RAMIREZ-MARQUEZ; J. GUILLOT

. Emulsion copolymerization of vinyl acetate and butyl acrylate. Relations ships process - structure - thermomechanical properties

Thesis X.Z. KONG Mars 1987 - LYON

Synthesis - structure - properties in methyl acrylate - styrene emulsion copolymers

Thesis W. RAMIREZ-MARQUEZ Mai 1987 - LYON

Polymer Colloid Group Newsletter  
Contribution from the University of Akron  
by Dr. Irja Pirmo  
MAY 1987

THE EFFECT OF HYDROPHILIC LENGTH  
IN ELECTROSTATIC SURFACTANTS IN EMULSION POLYMERIZATIONS

Carlo B. Diltman McBain

The hydrophilic content of nonionic stabilizers has been studied in this group (1,2) as well as in others (3,4 for example). It has been observed that as the percent of polyethylene oxide content is increased in nonionic surfactants, the overall rate of polymerization increased in styrene emulsion polymerizations. The particle size decreased and the number of particles per cubic centimeter increased with increasing polyethylene oxide content as well. As of yet there has been no systematic study of the effect of increasing ethylene oxide content in electrostatic surfactants.

Currently we are studying this effect by using the Avoncel Series S<sub>90</sub> surfactants from PPG Industries (S). The surfactant series is a sodium alkyl polyether sulfonate of the chemical structure  $C_{12-14}H_{25-27}O_3CH_2CH_2SO_3Na^+$  where n is 3, 7, 9 and 15. All polymerizations were done by the bottle technique. Rates were determined by gravimetric analysis of timed aliquots of solution. Particles were determined by photon correlation on a Malvern 11c particle-sizer. Several different initiation systems were used: potassium persulfate, iron (III)/benzoyl peroxide, and diisopropylbenzene hydroperoxide/tetraethylene amine.

We found that in the potassium persulfate initiated systems little or no effect was observed in the rate of polymerization of styrene. The particle size was  $64 \pm 2$  nm which corresponds to approximately  $10 E^{14}$  particles/cm<sup>3</sup> for the case of styrene at 45°C. Increasing the temperature to 55°C increased the rate by approximately a factor of 2.5, and decreased the particle size by 10nm. Using MMA and vinyl acetate, little or no effect due to steric length was observed at 45°C, although it was noted that the vinyl acetate system appears to be retarded by the surfactant in comparison to styrene or MMA. As a general trend, an increase in overall rate was observed with increasing water solubility of the monomer, due to the ease with which the monomer can diffuse into the growing polymer particles. The lack of an effect due to steric length can be explained by the repelling of the radical anion initiator species by the surfactants' head-group negative charge. The radical anion must stay in the aqueous phase and initiate the dissolved monomer forming oligomers, which are then able to enter the particle.

Using a redox system of iron (III) (0.3g)/benzoyl peroxide (0.1g), an increase in the number of ethylene oxide units in the surfactant gave a decrease in the overall rate of polymerization in styrene at 25°, 35°, and 45°C. A slight curvature in a plot of rate of polymerization versus ethylene oxide content was noticed, especially as temperature increased. Particle size and the number of particles correspond as expected to the rate of

polymerization data. Upon going to a more water soluble monomer, such as butyl acrylate or MMA, the curvature of the plot becomes more pronounced. An actual minimum in the overall rate of polymerization is observed in the case where n equals nine, whereas the rate increases again as n equals fifteen. Also we observed that the number of particles did not correspond directly to the rate. Further investigations using the amine/hydroperoxide initiating system with styrene monomer gave the same trend as the butyl acrylate and MMA monomers in the iron (II)/benzoyl peroxide system.

We have postulated that for the case of n equal to three, the surfactant acts more like an electrostatic stabilizer, and is able to both stabilize the ongoing polymerization system as well as the resulting polymer particles. However, in the case where n equals seven or nine we see that the ability to stabilize the particles is decreased relative to n equals 3, even though the polymerization rate is not proportionately decreased. For the case where n equals 15, we again see an improved effectiveness of the surfactant, attributed to the increased steric length.

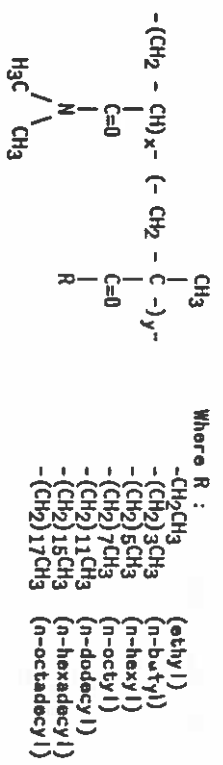
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5. Surfactants provided by PPG Industries.

**Steric Stabilization of Aqueous Polymerizing Systems  
Utilizing Copolymers of  
N,N Dimethyl Acrylamide and Esters of Methacrylic Acid**

Author : Raymond J. Weinert Jr.

The body of knowledge for the stability of sterically stabilized systems is large, but most investigators have concentrated on nonaqueous systems to avoid the complications associated with the polar character of water and its ability to form hydrogen bonds. This lack of knowledge in aqueous systems has made the thermodynamic description of aqueous polymeric systems difficult. [1] The lack of knowledge about colloidal aqueous systems of polymers has made the mechanism of nonionic steric stabilization in aqueous emulsion and dispersion polymerizations not well understood. Recent studies have focused on the use of water soluble polymeric units extending from water insoluble backbones. In this study the use of random copolymers of N,N dimethyl acrylamide (NDMA), a water soluble monomer, and water insoluble methacrylic esters will be studied as polymerization stabilizers.

Poly (N,N dimethyl acrylamide), P(NDMA), is a water soluble polymer which does not form any strong hydrogen bridges. [2] The polymer has low chain flexibility with few, if any molecules in an actual coil, it forms few aggregates [3] while still remaining water soluble. The reactivity of N,N dimethyl acrylamide with many comonomers, combined with its hydrophilic nature, allows one to prepare a wide range of copolymers possessing intriguing hydrodynamic and surfactant properties through copolymerization with many hydrophobic monomers. This will provide a unique way to explore (1) the loop effect of a hydrophilic polymer anchored to a polymer surface and (2) the effects that changing the length of the hydrophobic anchor and the stabilizer molecular weight have on the surfactant properties of the system. The following class of copolymers were synthesized:



The NDMA-methacrylic ester copolymers will be studied to elucidate their interfacial and solution properties in aqueous systems, and the results applied to the emulsion or dispersion polymerization of acrylonitrile, butyl acrylate and styrene.

NDMA and its copolymers were polymerized in benzene, toluene, hexane, and heptane. The benzene and toluene systems permitted the polymerization to be carried out in solution, while the alkane systems caused the (co)polymers to precipitate as a fine powder. The copolymers were analyzed by  $^{1}H$ -NMR for the determination of their composition. Initial experiments were prepared from recipes for the preparation of copolymer from Alfrey-Price Q-e values; these were found to be far from satisfactory. A Fineman-Ross experiment was conducted for the ethyl methacrylate - NDMA copolymer system. The reactivity ratios of the two monomers were found to be 1.40 and 0.62. These experimentally determined reactivity ratios indicate a blocking of the methacrylate monomer and a need to increase the feed ratio of the methacrylic esters in the copolymer feed. The addition of  $t$ -dodecyl mercaptan to the polymerizations gave three distinctive molecular weight regions for the (co)polymers with intrinsic viscosities in the 0.1, 0.6 and  $> 1$  dl/g region.

The surface tension and interfacial tension of aqueous solutions of the NDMA copolymers were determined using the Wilhelmy plate method with a roughen platinum substrate. The effect of ester carbon length on the surface tension of water was determined for NDMA copolymers at constant weight percent composition (6 wts) and high molecular weights ( $[M] > 1.5$  dl/g) at a concentration of 5 g/liter. The homopolymer reduced the surface tension to about 50 dynes/cm. The effect of the carbon length shows a minimum, with the butyl and hexyl methacrylic ester (4 to 6 carbon length). Using the same copolymers at various concentrations in water yields an order of effectiveness at lowering the surface tension of water to be in the following order:



The butyl, hexyl and octyl methacrylate containing copolymers exhibit surface tensions of water which appear concentration dependent, suggesting a critical micellar concentration at about 0.1 g/l. The dodecyl (lauryl) methacrylate/NDMA copolymer shows some concentration dependence suggestive of some particle aggregation which was discernible concentration dependence. The lack of a sharp critical micelle concentration can be attributed to the polydispersity of the surfactant systems.

The effect of molecular weight (as measured by intrinsic viscosity at constant temperature) of the hexyl methacrylate in the NDMA copolymer shows an increase in the surface tension with increasing molecular

weight. The hexyl methacrylate/NDMA copolymers show an apparent minimum at an intrinsic viscosity of 0.5 to 0.6 dl/g.

The surface activity of the NDMA copolymer was found to increase with increasing weight percent of hexyl methacrylic ester. The decrease in the surface tension (increasing surface activity) will be somewhat limited, because the increase in ester content will decrease the water solubility of the copolymers. Surface tension measurements indicate the best surfactant will be a copolymer of NDMA with over 10 weight percent butyl or hexyl methacrylate at an intrinsic viscosity of about 0.5-0.6 dl/g in water at 25°C.

The interfacial tension (IFT) measurements with water and monomers were made with P(NDMA) and 6 weight percent ester copolymers with intrinsic viscosity greater than 1.5 dl/g at 5.0 g/l concentrations against distilled acrylonitrile, styrene, and butyl acrylate. The effect of the methacrylate ester carbon length appear to be less pronounced in its effect on the interfacial tension of the monomer/water systems, than on the surface tensions. All three monomer/water systems exhibit interfacial tension values which reach a minimum at  $C_4$  to  $C_6$  ester chain lengths. The overall interfacial tensions of styrene/water systems being the most hydrophobic and hence the highest. The butyl acrylate, a polar molecule, which is largely water insoluble, had the next lowest interfacial tension. The minimization of the interfacial tension at the same point for each of the monomer systems was surprising. This indicates that the decrease in the interfacial tension with monomer was structurally dependent on the nonionic surfactant systems utilized in the experiments.

There is no apparent effect of molecular weight of the copolymers on the interfacial tension in any of the monomer/water systems. The increasing of the methacrylic ester content in the copolymers exhibit a slight decrease in the interfacial tension of the system. The interfacial tension data indicates a butyl, hexyl, or octyl methacrylate copolymers at higher weight percentages of methacrylic ester content to be the most active surface agents for the aqueous polymerization systems of styrene, butyl acrylate and acrylonitrile.

The polymerization of acrylonitrile with the hexylmethacrylate-NDMA copolymers show a dependence of stability on molecular weight of the surfactant. A surfactant with an intrinsic viscosity of 0.1 dl/g or greater than 1.0 dl/g is ineffective while a surfactant with an intrinsic viscosity of 0.6 dl/g was effective as a stabilizing agent. The aqueous polymerization of acrylonitrile using this particular surfactant system appears to proceed by dispersion polymerization in that there is little rate dependence on the amount of surfactant present, with an actual decrease in molecular weight of the resulting polyacrylonitrile polymer with increasing rates of polymerizations.

Table 13 : Aqueous Polymerization of Acrylonitrile With 13 Wt% Hexylmethacrylate-NDMA Surfactant

Sample Number	[ $\eta$ ] (dl/g)	AN/Water (phm)	S (phm)	Rpx10 <sup>4</sup> (ml-sec)	M <sub>v</sub> (g/mol)	M <sub>w</sub> ( $\sigma$ )
1504801	0.6	100/900	10	6.78	67000	2000
1504804	0.6	100/900	5	4.77	135000	4000
1504807	0.6	100/900	1**	2.34	219000	1000
1504803	none	100/900	0**	2.43	217000	5000

\* The rates of polymerization have an error associated with them of about 10 %  
\*\* Unstable dispersion

The polymerization of styrene was found to require a surfactant with a intrinsic viscosity of 0.1 dl/g, with the 0.6 and 1.0 dl/g surfactants being ineffective. Initial studies show a rate of polymerization with its ester side group dependent with increase ester side chain increasing the rate and the size of the styrene homopolymers.

#### References:

1. Napper, D.H., Polymeric Stabilization of Colloidal Dispersions. Academic Press, N.Y. (1983).
2. Brandrup, J.E., H. Immergut; Polymer Handbook Second Edition. III-147 (1975).
3. Trossarelli, L., M. Meirone; J. Polymer Science. 57, 445-52 (1962).
4. Periard, J. G. Riess, Kolloid Z.-Z. Polym. 24801-20 (1971). C.A. 76: 127905.



School of Chemistry

Polymer Colloids at Sydney University

16 APR 1981

Reporter:

D H Napper

#### Termination Events in Polystyrene Emulsion Polymerizations

Ms H Adams has been determining the termination rate coefficient for styrene as a function of the weight fraction of polymer using  $\gamma$ -initiated relaxation methods. For small styrene seed latex particles (size  $\leq 50$ nm), the kinetics of the relaxation process when irradiation ceases are determined primarily by the exit rate constant  $k$  since  $\bar{n} < 0.5$ , even in the  $\gamma$ -field. When the size of the particles is increased substantially, the value of  $k$  becomes small and  $\bar{n} > 0.5$  in the irradiation field; relaxation is then determined by bimolecular termination events rather than exit. At relatively low weight fractions of polystyrene ( $w_p \leq 0.6$ , say), the relaxation appears to follow a single exponential decay and the value of  $k_t$  is of order  $10^{-10}$  dm<sup>3</sup> mol<sup>-1</sup> s<sup>-1</sup>. These values, as expected theoretically, are several orders of magnitude smaller than the value reported for bulk styrene polymerizations at  $w_p = 0$ . The reduction reflects the influence of entanglements on the diffusion of polymeric free radicals through the latex particles. At higher weight fractions of polymer, however, multiple exponential relaxations appear to occur. The reasons for this are not yet clear but the observations appear to be consistent with the occurrence of more than one type of bimolecular termination mechanism.

#### Possible Roles of Surfactants in Determining Latex Monodispersity

Aerosol MA appears to be the surfactant of choice in preparing monodisperse polystyrene latices. It is not at all clear why this should be so and why, for example, sodium dodecyl sulfate, under comparable conditions, produces latices that are significantly more polydisperse. One simple explanation for the relative effectiveness of Aerosol MA could lie in a relatively short nucleation period and this may well be a factor determining the narrow polydispersity of samples taken at the end of interval 1. It can be shown, however, that the long-time (final) polydispersity is determined primarily by factors other than the length of the nucleation period. Of prime importance is the free radical entry rate into the particles. Aerosol MA generates latices with relatively few latex particles compared with, say, SDS so that the entry rate is very high. The coefficient of variation of particle volume at long times can be shown theoretically to be given by  $CV = (2/\bar{v})^2$ , where  $\bar{v}$  = entry rate coefficient. This formula predicts quantitatively the observed CVs of latices prepared using different types of surfactants.



Grafting Reactions/Emulsion and Solution Systems

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Grafting reactions are important in a number of free radical polymerization systems. Such reactions normally occur via chain transfer or by propagation reactions with residual unsaturated bonds in the polymer chain. Grafting can involve polymer molecules which were formed earlier in the reaction or polymers that are added to the reaction mixture. A number of free radical species could conceivably be involved in grafting reactions as indicated below.

- (1) Reaction of initiator free radical with a polymer molecule.
 
$$I \cdot + P \longrightarrow P \cdot + ?$$
- (2) Reaction of an oligomeric free radical with a polymer molecule.
 
$$R_n \cdot + P \longrightarrow P_n + P \cdot$$
- (3) Reaction of a free radical generated by a transfer reaction with a polymer molecule.
 
$$M \cdot \text{ or } T \cdot + P \longrightarrow P \cdot + ?$$

where  $M \cdot$  and  $T \cdot$  are radicals formed from monomer or chain transfer agent.

Most work reported in the literature on grafting studies provide measurements of grafting efficiencies as a function of various recipe and reaction parameters. Our recent work has involved some experiments but most of the effort has been devoted to developing kinetic models to quantify grafting reactions.

Our initial work has been with emulsion systems in which a seed latex of one material is grafted with polymer formed from another monomer. The model is based on an assumption that the water-soluble initiator free radicals in emulsion polymerization will not penetrate the monomer-swollen latex particles. The hydrophilic end groups of the oligomeric radicals formed from these initiators are presumed to remain on the surface of the particle with radical penetration

taking place via the propagation reaction. Hence, the model includes the concept of non-uniform distribution of free radicals and the different polymer materials within the particles. Reaction 1, involving the initiator free radical, is excluded from the model because the  $I \cdot$  radical cannot contact the polymer to be grafted.

Model simulation of experimental data reported in the literature for several systems and of data obtained in our laboratories has been reasonably successful. We can predict the influence of polymer concentration, initiator concentration, added chain transfer agent and conversion on measured grafting efficiencies.

Grafting in solution polymerization is different because, among other things, the free radicals generated from the initiator can come in contact with polymer molecules. Some workers claim that this provides the major mechanism for grafting -- i.e. via Reaction 1. In addition, different initiators are reported to be more or less effective in promoting grafting.

We have modeled the grafting data reported by Brydon, Burnett and Cameron (*J. Polym. Sci., Polym. Chem. Ed.*, 11, 3255 (1973)) for the polymerization of styrene in benzene solutions of polybutadiene in order to examine probable mechanisms and model effectiveness in simulation of the experimental results. Brydon et al., used benzoyl peroxide, an initiator that is reported to promote grafting.

Reaction rate constants for Reactions 2 and 3 had been previously estimated from experimental results in emulsion systems with polybutadiene seed latex and styrene monomer. Persulfate initiator was used in these runs so Reaction 1 was not considered to be functional. Hence, only one new kinetic parameter, the rate constant for Reaction 1, needed to be fitted with the solution grafting data.

Brydon et al varied rubber, monomer and initiator concentrations. They measured polymerization rates and grafting efficiencies. In summary, the model calculations were quite successful in simulating all the experimental results. The rate constant for Reaction 1 that was required to achieve the good fit was of the same order of magnitude as free radical propagation rate constants. This is quite in contrast to the lower rate constants which were determined for Reactions 2 and 3. Both the magnitudes and the temperature dependence of the rate constants for Reactions 2 and 3 suggest grafting by chain transfer---transfer with hydrogen atoms in the allyl position. Hence,



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Department of Chemistry

6 MAY 1968

PCD Newsletter Contribution from R. L. Howell

Below are abstracts of three papers presented at the ACS Meeting in Denver covering earlier work on electrophoresis, acoustophoresis and NMR. We are shifting from studies on coal to more fundamental characterization of the solid/liquid interface.

THE ELECTROPHORETIC MOBILITY AS A PROBE OF THE SURFACE CHEMISTRY OF COAL DISPERSIONS. Robert L. Howell and Robert E. Marganakis, Department of Chemistry, University of Massachusetts, Amherst, MA 01003.

A procedure was devised for obtaining reproducible measurements of the electrophoretic mobility of aqueous coal dispersions in dilute concentrations at low ionic strength without added surfactant. Under such conditions, the ionic strength is defined by the measured aqueous conductance and is termed system limited ionic strength (SLIS). Several bituminous coals were examined and compared using the SLIS mean mobility as a function of pH. Pronounced similarities were obtained when the data were displayed as a function of pH shift from the isoelectric point. We also report a comparison of the dependence of the distribution of the electrophoretic mobility on pH and show the importance of the electrophoretic mobility distribution as a characteristic fingerprint of a particular coal sample. The general properties obtained in our work are compared with recent reports from other laboratories.

\*Presently at E. I. DuPont De Nemours & Co., P.O. Box 430, Pass Christian, MS 39571

A COMPARISON OF THE ACOUSTIC MOBILITY AND THE ELECTROPHORETIC MOBILITY OF COAL DISPERSIONS. Bruce J. Harlow, Fenken, Inc., 341 Adams, St., Bedford Hills, NY 10607 and Robert L. Howell, Department of Chemistry, University of Massachusetts, Amherst, MA 01003.

The general characterization of colloidal concentrates by acoustic mobility is briefly reviewed. The acoustic mobility is proportional to the zeta potential in much the same way as the electrophoretic mobility is proportional to the zeta potential. However, acoustic mobility measurements may be extended to very high concentration and the theoretical analysis, originally derived for dilute colloidal systems, can be extended to 50% by volume using the cell model theory of Levine et al. In this work we report the dependence of the acoustic mobility on pH and concentration and a comparison with the mean electrophoretic mobility on pH for several aqueous dispersions of bituminous coal.

133Xe AND 131Xe NMR STUDIES OF XENON AS A PROBE OF ASSOCIATED POLYETHYLENE OXIDE POLYMER-SURFACTANT MIXTURES. S.M. Hasselid and R. L. Howell, Department of Chemistry, University of Massachusetts, Amherst, MA 01003

The associated polymer used is a long chain polyethylene oxide which is end-capped with saturated hydrocarbons (C<sub>12</sub> or C<sub>18</sub>). The molecular weight varies between 53,000 - 106,000 based on the length of polyethylene oxide. In previous work we have shown that the chemical shift of Xenon in solution is especially sensitive to the environment; the shift arises mostly from Van der Waals interactions. Natural Xenon gas contains two isotopes suitable for NMR studies: 133Xe (28%) with I = 1/2 and 131Xe (23%) with I = 3/2. 133Xe shift and 131Xe relaxation time T<sub>1</sub> vs. concentration of aqueous solutions of polymer-surfactant are presented. The 133Xe shift is strongly affected as micelles form. This makes Xenon an excellent probe for observing any possible polymer-surfactant interaction by focusing on the effect of polymer concentration on the CMO.

Recent Publications:

"Structure and breakup of flocs subjected to fluid stresses: I. Shear experiments", Journal of Colloid and Interface Science 113, 399 (1986) [with R. C. Sonntag].

"Structure and breakup of flocs subjected to fluid stresses: II. Theory", Journal of Colloid and Interface Science 115, 378 (1987) [with R. C. Sonntag].

"Structure and breakup of flocs subjected to fluid stresses: III. Converging flow experiments", Journal of Colloid and Interface Science 115, 390 (1987) [with R. C. Sonntag].

"The intrinsic viscosity and Huggins coefficient for potassium polystyrene sulfonate solutions", Macromolecules 20, 518 (1987) [with R. H. Davis].

"Theoretical approaches to the rheology of concentrated dispersions", Powder Technology 51, 15 (1987).

Current Research:

1. Non-equilibrium statistical mechanics of concentrated colloidal dispersions

Low shear rates or small amplitude oscillations perturb the structure of stable dispersions only slightly from their equilibrium rest state. Nonetheless this non-equilibrium structure generates stresses in concentrated systems comparable to or substantially larger than the viscous contribution. This weak flow limit contrasts sharply with strong flows in which viscous stresses dominate. Data for several well-characterized dispersions, e.g., hard spheres, and polymerically stabilized spheres, indicate clearly the importance of these non-hydrodynamic stresses.

Our approach to the construction of theories for the low shear limiting viscosity and the dynamic viscosity and modulus begins with fundamental descriptions of the microstructure in terms of the interparticle forces and the macroscopic stresses in terms of the microstructure and the forces. With well-defined approximations, e.g.,

- (1) pairwise additive hydrodynamic interactions
- (2) superposition of the pair distribution functions,

we close in a physically reasonable manner the hierarchy of many body interactions. The non-equilibrium microstructure and the rheological functions are calculated numerically as functions of the volume fraction of particles and the nature of the pair potential.

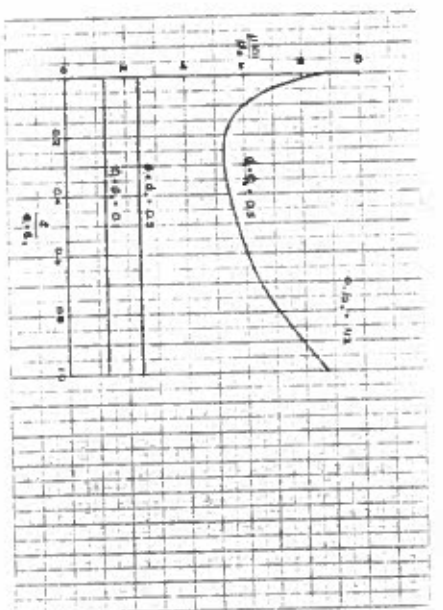


Figure 1. Variation of low shear viscosity with composition for bimodal mixture of hard spheres with  $a_1/a_2 = 0.5$ .

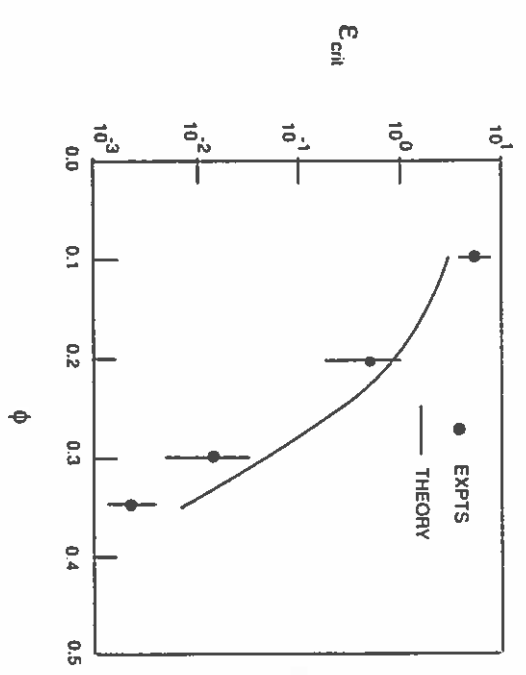
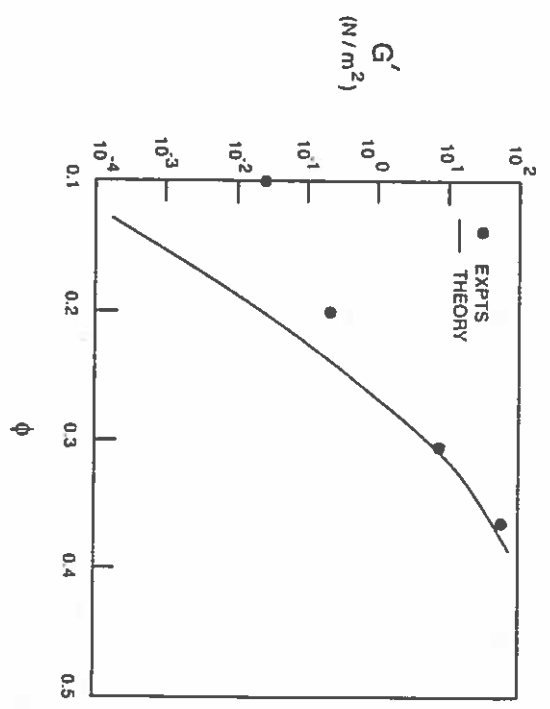
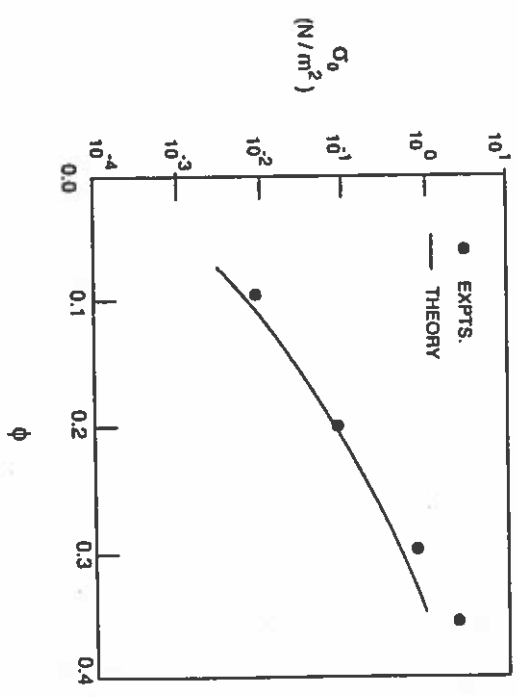
### 2. Rheology of flocculated dispersions

For flocculated dispersions the rest state represents a non-equilibrium configuration which often depends on the history of the sample. In many cases the particles form a volume filling network or gel producing a rheological response characteristic of a pseudoplastic solid with a finite zero frequency modulus  $G'(0)$ ; a critical strain  $\epsilon_{crit}$  beyond which the modulus decreases; a yield stress; and a shear rate dependent viscosity at higher stresses.

Electrostatically stabilized lattices flocculated through the volume exclusion mechanism by the addition of non-adsorbing soluble polymer, Dextran, provide a model system for studying these phenomena. Our measurements define the dependence of  $\sigma_0/G'$ , and  $\epsilon_{crit}$  on volume fraction and ultimately will explore the effects of particle size and attractive potential.

To interpret these measurements we have constructed a mean field theory describing the effect of mechanical stresses on floc size or network structure for both steady and oscillatory shear. The model contains several parameters characterizing the structure of the individual flocs:  $D$  the fractal dimension;  $n$  the power law index relating elasticity to volume fraction;  $S_0$  a critical stress. Once these are specified the theory predicts floc size as a function of shear rate and the rheological response. Figure 2 illustrates the predictions for  $D = 2.5$  from independent measurements and  $n$  and  $S_0$  chosen to fit the data. Though far from perfect, the general correspondence with the data gives some support for the conceptual basis of the model.

Figure 2. Comparison of predictions from mean field theory (—) with data for polystyrene lattices with dissolved Dextran (o)



# POLYMER COLLOID GROUP NEWSLETTER

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Contribution from Vivian T. Stannett  
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6 MAY 1986

September 1986

13 OCT

A small program has been started on radiation induced polymerization of N-vinyl pyrrolidone

in an inverse emulsion system. Excellent conversions to very high molecular weight polymer are being obtained. The Ph.D. student Mr. M. B. Taylor (Fiber and Polymer Sciences Program) is now well underway with his experimental program. Professors R. D. Gilbert, J. L. Williams, and myself are looking after the work which we hope will soon be extended with additional students. The next newsletter should have details of the results. Considerable effort has been made to develop gel permeation chromatography for quantifying the conversion. In the more conventional practice with gravimetric methods, the hydrocarbon oil that is present during the reaction presents a significant separation problem when determining percent conversion.

Fractional factorial design experiments are currently being conducted to study the kinetics of this reaction. The variables of interest include:

1. Emulsifier type and concentration
2. Dose rate
3. Loading of the emulsion
4. Monomer to water ratio
5. Temperature of reaction
6. Stirring rate

## Contribution to the Polymer Group Newsletter

Donald C. Sundberg  
Polymer Research Laboratory  
University of New Hampshire

The current activities center around the following projects:

- 1.) The effect of fillers (carbon black, glass, etc.) on the diffusion controlled polymerization kinetics of highly crosslinked systems (e.g. styrene cross-linked polyester).
  - 2.) The effect of phase separation of polymeric additives (e.g. low profile additives such as PVAc) during the curing of crosslinked polyesters. Interest in the effects upon polymerization kinetics and morphological structure of the dispersed phase.
  - 3.) The swelling of polymer gels by organic solvents dissolved in water at low concentrations.
  - 4.) Morphology control in polymeric microparticles.
- The morphology work is an extension of the microencapsulation work that I reported in collaboration with Bengt Kronberg and Johan Berg from the Swedish Institute of Surface Chemistry. Presently the New Hampshire group is studying the morphological structures created when an immiscible oil/polymer system is dissolved in a common solvent, this single phase 3-component system emulsified in water with the use of a surfactant, and followed by solvent removal via evaporation. Our emphasis is upon the influence of the surfactant (type and concentration) on the thermodynamic driving force which controls the resultant morphology. The polymer/oil system represents one in which the diffusional resistance to establishing the preferred thermodynamic morphology is low due to the fluidity of the oil. We plan to extend these studies to include polymer/polymer systems where the diffusional resistance may be significant or even dominant.

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Morphological Structure Control in Polymeric Microparticles

Berg, Kronberg and Sundberg had suggested earlier (Poly. Mat. Sci. & Engr., 54, 367 (1986)) that the morphology of polymer microparticles should be strongly dependent upon the interfacial tensions involved. In keeping with this idea they found that the choice of surfactant was critical in forming core-shell particles as evidenced by the results they obtained while trying to encapsulate emulsified oil droplets with PMMA by in-situ polymerization. At UNH, our polymer research group has been using these ideas to study the morphology of polymer encapsulated oil droplets derived by physical, rather than chemical, processing routes. The current work involves the dissolution of polymer and oil in a common solvent, emulsification in water containing a surfactant, followed by solvent removal. Our objective is to follow the morphological development of the resulting two phase particle as the solvent is removed and as it is dependent upon the type and concentration of surfactant. Figures 1 and 2 show results for a PMMA/mineral oil system which utilizes a natural pectin (Meypectin - a Grindsted product) and sodium lauryl sulphate, respectively. Figure 1 shows a core-shell arrangement (the top of the particle has been torn off and the oil inside is exposed) while figure 2 shows a hemispherical arrangement. These results are in keeping with the inequality

$$\gamma_{ow} > (\gamma_{ow} + \gamma_{ob}) \quad \text{for core-shell}$$

$$\gamma_{ow} < (\gamma_{ow} + \gamma_{ob}) \quad \text{for hemisphere}$$

as put forth by Torza and Mason (J. Coll. & Interf. Sci., 33, 67 (1970)) and applied by Berg et al (op. cit.). In our work the approximate values of the interfacial tensions between the water phase and the oil were 32 mN/m for a 0.5% Meypectin aqueous solution and 8 mN/m for a 0.5% SLS aqueous solution. The  $\gamma_{ob}$  values were in the 8 to 12 mN/m range and the  $\gamma_{oo}$  were estimated to be between 1 and 2 mN/m.

Our concept for morphology control involves thinking of interfacial energy (through interfacial tensions) as the driving force and polymer chain mobility as the resistance. The systems we are presently using display large differences in interfacial tensions while having reasonably high chain mobility (i.e. the low molecular weight oil provides for rapid diffusion). These systems should show the largest influence of interfacial tensions upon the resultant morphology. In our studies we are using polymer and oils of various polarities (e.g. PMMA, polystyrene, styrene-acrylonitrile copolymer, decane, decanol). Our future efforts will be directed towards studying the role of chain mobility by replacing the oils first with low molecular weight polymers and then by high molecular weight polymers.

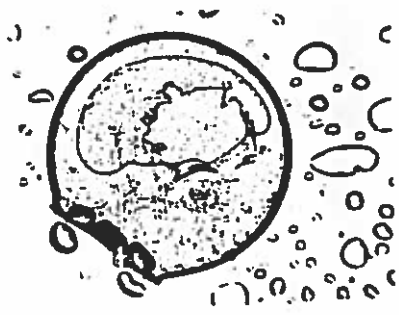


FIG. 1

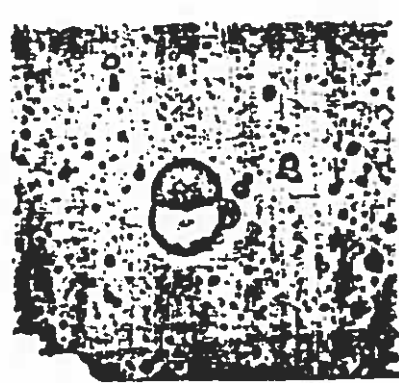


FIG. 2

Diffusion Controlled Polymerization Studies

1. The Effect of fillers on the kinetics of Free-Radical Polymerization
2. The Effect of Phase Separation During Curing on the Polymerization Kinetics of Highly Crosslinked Polymers

Materials such as poly(vinyl acetate) are commonly added to styrene/polyester resins in order to reduce the degree of shrinking during the crosslinking of the polyester. The PVC phase separates early in the reaction and forms droplets having interesting morphology. The purpose of this work is to determine the effect of this phase separation upon the polymerization kinetics and to investigate the types of morphologies produced. As a reference point, the phase separation of PVC or PSty from a solution of MMA monomer during bulk polymerization is being studied in order to contrast the effect of phase separation in thermoplastic systems with thermosetting systems.

Contribution to the Polymer Group Newsletter

M. S. El-Aasser, A. Klein, F. J. Micalé,  
C. A. Silabi and J. W. Vanderhoff

28 APR Recd

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There are currently 26 active projects which cover different aspects of the preparation, characterization, modification and application of polymer latexes. The titles of the different projects are included in the enclosed Index of our Graduate Research Progress Report Issue No. 27, January 1987. Request for any of the reports should be directed to Ms. Debra Nyby at the above address.

In addition to the above mentioned ongoing projects four new research projects have been started:

"Preparation of Rocket Propellants by Emulsification": In this research project the emulsification parameters are studied to prepare cheap rocket fuels by emulsifying eutectic salts in low molecular weight oligomers which are cure in place once the fuel is in its containers.

"Modification of Latex Rheology by Associative Thickeners": Associative thickeners are hydrophobically modified water-soluble polymers which interact to form a structure that improves the rheological profile of a latex paint or coating. The objective of this research is to understand the association and thickening mechanisms by using well characterized model thickeners.

"Phase Behavior of Mixed Emulsifier Liquid-Crystals": The identification of liquid crystals in aqueous solutions of mixed emulsifier systems (ionic surfactant/fatty alcohol) used in the preparation of miniemulsions, has led research toward the characterization of the crystalline structure and to study the role on the miniemulsion formation and stabilization.

"Miniemulsion Copolymerization in a Tubular Continuous Reactor": Following the series of studies carried in the Institute over the past years on the homopolymerization and copolymerization of miniemulsion, a new research program has been open to study the performance of miniemulsions in continuous polymerization tubular reactors. The high stability and inherent capability of the miniemulsion to be pumped or transferred without breaking them, make the miniemulsion a highly suitable system to use in continuous polymerization processes.

During this period of time five of our graduate students have finished their Ph.D. Dissertations:

P. Abeywardena: "Preparation and Characterization of Poly(Alkyl N-Ethyl Methacrylate Carbamate) Latexes".

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E. S. Daniels: "The Development of Multi-stage Composite Latexes which Simulate the Properties of Thermoplastic Elastomers".

J. Delgado: "Miniemulsion Copolymerization of Vinyl Acetate and n-Bucyl Acrylate".

J. H. Kim: "Sulfonated Polystyrene Model Colloids: Preparation, Characterization and Applications as a Heterogeneous Catalyst".

C. A. Vega: "Cathodic Electrodposition of Latexes".

Copies of these Dissertation abstracts are available upon request.

Our 18th Annual Short Course on "Advances in Emulsion Polymerization and Latex Technology" will be held at Lehigh on June 1-5, 1987 and at Davos, Switzerland, on August 17-21, 1987.

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Contribution from the Pulp and Paper Research Institute of Canada and Department of Chemistry, McGill University, Montreal, Quebec, Canada

by T.G.M. van de Ven

The following are abstracts of papers submitted for publication to various journals:

1. Brownian motion of charged colloidal particles surrounded by electric double layers (G. Schumacher and T.G.M. van de Ven)

Using photon correlation spectroscopy, diffusion coefficients of charged colloidal particles surrounded by electrical double layers have been determined. It was found that the diffusion constant equals the value of a neutral sphere at high and low electrolyte concentrations, but is reduced by several percent when the electrical double layer is comparable to the radius of the particle. The reduction in diffusion constant depends on the zeta-potential of the particle and the sizes of the ions in the double layer. The diffusion of charged particles can be explained by the theory of Ohshima et al (J. Chem. Soc. Faraday Trans. II, 1984, 80, 1299) for the friction coefficient of charged spheres, assuming that the friction coefficient of a charged sphere in Brownian motion equals the equilibrium friction coefficient of a sedimenting sphere.

2. Deposition and detachment of latex particles at glass surfaces exposed to flow (S. Varennes and T.G.M. van de Ven)

Deposition and detachment of 3  $\mu\text{m}$  polystyrene latex particles on clean and surface treated glass slides used as collectors was investigated using the stagnation point flow technique, which was developed to study the deposition of colloidal particles under well controlled hydrodynamic conditions. The deposition can be followed microscopically and recorded on video. This technique allows us to study both particle deposition and particle detachment at the same time.

It was found that the deposition of latex depends on salt concentration but not in the manner predicted by the DLVO-theory, which, combined with transport theory, predicts a sudden change from almost no deposition to fast deposition at a well-defined electrolyte concentration. Instead we find a gradual increase in deposition rates, somewhat below the critical electrolyte concentration. It is very probable that this anomalous deposition behavior is caused by surface protrusions on the latex surface because altering the surface leads to lower deposition rates, despite decreased energy barriers. It is shown that the detachment of particles is governed by a convective-diffusive transport out of an energy minimum, which is enhanced by surface collisions between suspended and deposited particles.

Cont....

3. The existence of coupling forces and torques in hydrodynamic interactions between electrically charged particles (T.G.M. van de Ven)

The trajectory equations usually applied to describe the interaction between two electrically charged particles are shown to be incomplete. Besides hydrodynamic and electrostatic forces, additional forces and torques must be introduced to describe the interaction exactly. It is shown that incorporating these coupling forces and torques leads to correction terms that depend on the surface potentials of the particles and on the mobility and concentration of the ions surrounding them.

4. Why does the size of ions affect coagulation (T.G.M. van de Ven)

It is a well-established fact that the coagulation of colloidal particles suspended in an aqueous medium is affected by the size of the dissolved ions. In general the larger the ions, the more salt that is needed to coagulate a suspension. The explanation most commonly given is that the finite size of ions somehow increases the double layer thickness, resulting in a larger critical coagulation concentration (CCC). Here we show that this explanation is incorrect. The increase in CCC is due to the fact that the diffusion and friction coefficients of charged particles are affected by the presence of electrical double layers around them. The reduction in the diffusion coefficient and the increase in the friction coefficient depends explicitly on the size of the ions in the double layer. It is predicted that the CCC increases linearly with the scaled friction coefficient of the ions, in agreement with literature data.

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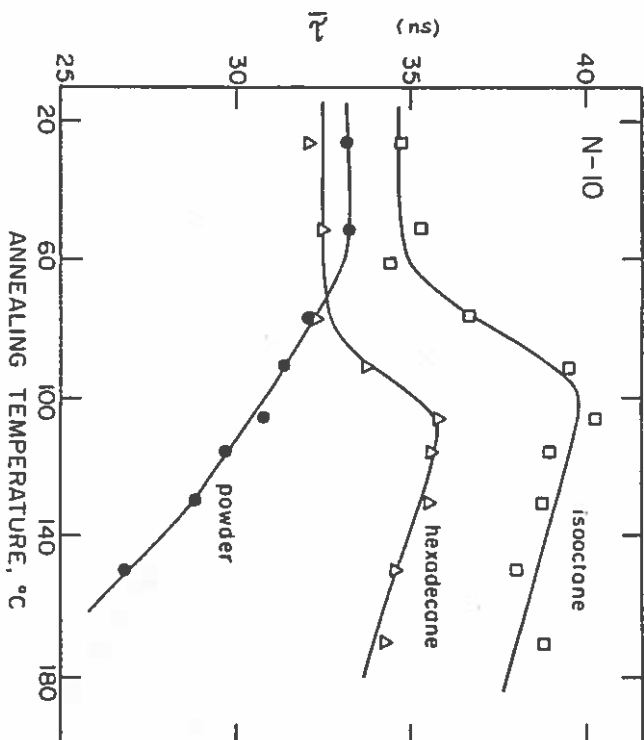
by M.A. Winnik

### Polymer-Polymer Interphases

More than five years ago my co-worker, O. Pekcan, discovered that the fluorescence and phosphorescence lifetimes of naphthalene (N) groups, covalently bound to PMMA chains of polymer colloids, were sensitive to sample history. This sensitivity was most prominent in NAD particles containing significant (10 mol%) N groups. We attributed the decrease in the excited state lifetime at elevated N concentrations to the phenomenon of self-quenching. Self-quenching (or concentration quenching) describes any process of the form  $[N + N \rightarrow 2N]$ , and probably involves formation of non-emissive excimers. For non-diffusing species, the extent of self-quenching reflects the probability that two N groups are nearest neighbors. Swelling or contraction of a phase containing N groups should lead, respectively, to a decrease or increase in the amount of self-quenching one observes.

Annealing PMMA particles (2  $\mu$ m diameter, sterically stabilized with polyisobutylene [PIB]) for three hours at various temperatures, led to irreversible changes in the room temperature fluorescence decay time of N labels. These changes are shown in Figure 1. We initially attributed these changes in decay times to changes in the extent of self-quenching, reflecting local swelling or contraction of the PMMA phases. We now know this explanation is incomplete.

Careful model studies by L.S. Chen in my laboratory show that self-quenching can reduce the mean decay time in PMMA films from 55 ns to 40 ns, but this mechanism alone is not sufficient to account for ca. 30 ns decay times found in the particles. Moreover, model compounds show shorter lifetimes in PIB films (43 ns) and aliphatic hydrocarbon solutions (also 43 ns) than in pure PMMA (55 ns). In order to account for the ca. 30 ns decay times in particle samples, we infer that both environmental factors and self-quenching operate. Since the N groups are chemically bound to the PMMA, this can only occur if a large fraction of the N groups are located in an interphase containing both PIB and PMMA. The lifetime changes shown in Figure 1 upon annealing reflect changes in the composition of the interphase as well as changes in the mean separation of the N groups.



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Contribution to the Polymer Colloid Newsletter  
Submitted by A. Vrij

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POLYDISPERSITY PROBED BY LIGHTSCATTERING OF SECONDARY PARTICLES IN CONTROLLED GROWTH EXPERIMENTS OF SILICA SPHERES.

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From dynamic lightscattering measurements of diluted silica dispersions formed in controlled growth experiments of ~~diluted silica dispersions formed in controlled growth experiments~~ Philippse obtained effective diffusion coefficients,  $D_e(K)$ , which exhibit a pronounced maximum as function of the scattering vector  $K$ . The maximum is due to the presence of particles much smaller than the grown particles and which are formed in a secondary nucleation.

It appears that  $D_e$  is a sensitive probe for the presence of the small particles. Both from theory and experiment we conclude the following. (1) The maximum is a consequence of small particle scattering at a  $K$ -value where the scattering of the large particles is at a minimum. (2) The magnitude of the maximum is a sensitive measure of polydispersity in size of the large particles. Similar conclusions are drawn from measurements of the second cumulant  $Q(K)$ . This function provides a measure of the width of the distribution of diffusion coefficients. Its  $K$ -dependence curve shows a very peculiar shape, due to the presence of the small particles. This shape is also predicted theoretically.

A manuscript has been send to J. Chem. Phys.

On the factors of stability of concentrated free emulsifier latexes.  
Eliseeva V.I., Aslanmurza T.R.

13 APR 1967

Stable latexes are known to be obtained through emulsion polymerization without emulsifier by using substances disintegrated to micelles as an initiator. It is suggested that stability of these latexes is achieved through the ionized groups of macromolecules /1/ caused by surface-active oligomer substances (SAS) formed in equilibrium by termination reaction of polymeric ion-radicals /2/. Depending on the selection of reactants, their ratio and the reaction conditions latexes differing in stability are formed. The mechanism of particle stabilization of the concentrated latexes remains to be clear out.

In this investigation, free emulsifier polymerization of methyl methacrylate (MMA) at low initiator concentrations of potassium persulfate (PSK) and various organic-aqueous phase ratios was studied to establish the factors which were responsible for stability of concentrated latexes. The critical concentration of latex obtained in the absence of coagulum was determined. Moreover, the values of surface tension  $\sigma$ , pH of latexes,  $\zeta$ -potential and diameter of their particles  $D$  (by using light scattering method) were characterized.

The values  $\sigma$  of latexes given in tabl.1 (less than 72,8  $\mu\text{m}^2/\text{m}^2$ ) testify to the SAS formation in the course of polymerization. The value  $\zeta$  increases as monomer concentration  $[M]$  grows from 10 to 12 vol.% at PSK concentration in aqueous phase ( $I_q$ ) equal 90  $\text{mg/l}$ .

This means that the increased surface of more concentrated latex increases the surplus of SAS formed. By the further increasing of latex concentration up to 16 vol.%  $\zeta$  remains constant. It does not mean  $\zeta$  of water as would be the case of the stabilizing particles with the end groups of macromolecules only. The contribution of the SAS molecules into particles stabilization seems to be different depending on the initiator concentration on the monomeric phase ( $I_m$ ) (at give  $I_q$ ). This contribution can be small enough at small  $I_m$  values: indeed high values of  $\zeta$  of the stable latexes indicate the low SAS concentration both in them and consequently on the particle surface. By further increase of the latex concentration (greater than the critical value 16 vol.%) and corresponding decrease of  $I_m$  value the process is accompanied by decreasing the total surface density of both stabilizing units. The latter results in latex coagulation.

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(run 6, table 1). The obtained data testify for the existence of some critical  $I_m$  value at given  $I_a$  which is necessary for the concentrated latex stability. Indeed the data of the tabl.2 show that at constant  $I_m$  value stable latexes are obtained by increasing latex concentration up to 32 vol.% and herewith keeping  $\delta$ -value unchanged. The  $\xi$ -potential values of these latexes are close to -25 mv. The approximate constancy of  $\xi$ -potential and  $\delta$  values for all stable latexes (tabl.2) indicates that their stability is achieved by some definite value of the total surface saturation by end  $SO_4$  groups and adsorbed SAS molecules; some ratio between both factors exists. The increasing of polymer concentration in latex up to 40% results in coagulum formation at  $\delta$  unchanged (run 5, table 2). This means firstly that "own" SAS are always present in free emulsifier latexes and secondly that a critical  $I_m$  value must exist providing their stability.

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Table 1  
Dependence of stability and surface tension of latexes on polymer concentration at constant  $I_a = 90$  mg/L.  $T = 353$  K. Time 5-6 hours.

No.	Reaction conditions:		pH	Polymer concentration, %	Concentration of coagulum, %	$\delta$
	$[I_a]$ , vol.%	$I_m$ , mg/L				
1	10,0	810	3,75	9,5	no	37,0
2	12,0	675	3,78	12,0	no	30,2
3	14,0	578	3,44	13,3	no	25,1
4	15,0	540	3,52	14,3	no	20,1
5	15,0	506	3,29	15,0	no	70,2
5	12,0	410	-	-	latex coagulates	-

Table 2  
Dependence of stability and surface tension of latexes on polymer concentration at approximately constant  $I_m = 353$ K. Time 5-6 hours.

No.	Reaction conditions:			pH	Polymer concentration, %	Concentration of coagulum, %	$D, 10^{-15} \frac{cm^2}{sec}$	$\sigma, \frac{mN}{m^2}$
	$[I_a]$ , mg/L	$I_a$ , mg/L	$I_m$ , mg/L					
1	18,0	200	910	3,00	17,0	no	226	2,0 70,0
2	20,0	222	888	-	19,0	no	230	3,0 70,0
3	25,0	277	831	2,84	24,3	no	231	3,7 70,1
4	32,0	315	810	2,85	31,0	no	256	3,5 70,2
5	40,0	360	810	2,66	38,0	2,0	266	3,9 70,2