POLYMER COLLOIDS GROUP NEWSLETTER

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The N.A.T.O. Advanced Research Workshop on 'New Techniques in Characterisation of Polymer Colloids' held in July at the Johnson Foundation's Wingspread Conference Centre in Racine, Wisconsin was thoroughly successful in all aspects. As can be seen from the Minutes of the Annual Meeting a record number of members (or their alternates) was enabled to attend. The staff work by the Johnson Foundation was excellent despite their being required to work on the 4th of July for the first time ever! Besides the latest developments in the science of polymer colloids we all learned quite a lot about the architecture of Frank Lloyd Wright. All participants were assigned to appropriate groups to draft position papers covering the preparation, rheology, stability, characterisation, and biomedical applications of polymer colloids which have subsequently been edited and which are to be published along with definitive versions of the Introductory Lectures. The Group is greatly indebted to the co-organisers, Bob Fitch and Mohammed El-Aasser who made it all happen. The Group's Poet Laureate - Irv. Krieger - composed an Ode for the occasion which is reprinted on a later page: 'wetback' is American for an illegal immigrant who has entered the United States by swimming the Rio Grande which forms the western part of the border with Mexico!

Alan Rembaum died in June: Bob Fitch has intimated his willingness to act as Treasurer for a Memorial Fund.

The next Group event will be the 1987 Gordon Conference at Tilton School, New Hampshire, July 5-10 chaired by Ron Ottewill. Details should appear in the Spring 'Newsletter' if not before by direct circulation. Outlines of the programmes of all Summer Gordon Conferences appear annually in an issue of 'Science' published in early March.

It may be opportune to remind members that items in the 'Newsletter' are not definitive publications and may only be referred to as 'Private communication' with the consent of the author. The 'Newsletter' is for private circulation only to members and their co-workers. Early intelligence of work in progress should prevent unnecessary duplication of effort. When items are submitted which have been accepted for definitive publication elsewhere it would be helpful to add an 'in press' reference to the appropriate journal.

The deadline for the receipt of copy for the Spring 'Newsletter' will be Tuesday 5th May 1987.

Vivian Stannett has written to say that he will have an item for the Spring issue for which disclosure would be premature at the moment. He expects to be retiring (aged 70) in June 1988 which might be the cue for a Symposium on Emulsion Polymerization Kinetics in the U.S. that year when the Group's meeting is likely to be in France.

G.J.Fleer (Agricultural University, De Dreijen 6, 6703 BC, Wageningen, Holland) is Secretary of the Organising Committee for a Symposium on 'Polymers in Colloidal Systems' to be held in Veldhoven near Eindhoven 7-9 September, 1987. Programme should be available in December but the dealine for offers of Student Posters is 15 June 1987. Irja Piirma will be chairing a session on 'Heterophase Polymerization' for the A.C.S. Division of Industrial and Engineering Chemistry at the Fall 1988 Meeting in Los Angeles: potential contributors shoud contact her as soon as possible.

A.S.D.

MINUTES of the ANNUAL MEETING of the POLYMER COLLOIDS Group held at the Johnson Foundation's Wingspread Conference Centre, Racine, Wisconsin on 3rd July 1986 at 1 p.m.

There were present Francoise Candau, Mel Croucher, Jim Dodge, Wim Donners, Sandy Dunn, Mohamed El-Aasser, Bob Fitch (who presided), Bob Gilbert (vice Don Napper), Jim Goodwin, Jean Guillot (vice Christian Pichot), Finn Hansen, Andy Klein, Irv Krieger, Bengt Kronberg (vice Per Stenius), Mamoru Nomura, Ron Ottewill, Irja Piirma, Gary Poehlein, Derek Rance, Bob Rowell, Bill Russel, Don Sundberg, John Ugelstad, Theo van de Ven, John Vanderhoff, Ritchie Wessling (vice Frank Saunders) in all, 27 members or alternates.

Newsletter. Sandy Dunn said that he had sufficient funds in hand from three company members to defray the cost of reproduction for the Rest of the World distribution of the next 2 or 3 Newsletters. Some members had failed to contribute to several successive issues and appeared to be no longer active but had not resigned. It was agreed that a warning should be included in the reminder notice for the Autumn issue and that the Roll should be revised at the 1987 meetings during the Gordon Conference when there would be time for the necessary consideration.

1987 Gordon Conference. Ron Ottewill reported that plans for the 1987 Gordon Conference were proceeding satisfactorily but that he was awaiting confirmation of the dates which were expected to be 5-10 July at Tilton School. Don Napper would be one of the speakers but he would welcome suggestions for the programme.

Proposed N.A.T.O. A.S.I. at Strasbourg 1988 Francoise Candau had booked a suitable Conference Centre where she had run meetings previously for July 8 - 15, 1988. This would cost about FF 120 per person per day for full board: at this low price those who preferred to go into the town for an evening meal should be able to afford to do so. Gary Poehlein pointed out that it would be advantageous in applying to NATO to have such countries as Greece, Turkey, and Portugal represented on the Organising Committee: Professor Kiparissides would be a possible member particularly if there should be some emphasis on the computer modelling studies of the emulsion polymerisation reaction which were undertaken in several Chemical Engineering Departments. John Vanderhoff mentioned that one of the recommendations which his Copolymerisation Workshop would be making was that NATO Advanced Study Workshops on Emulsion Polymer Reaction Engineering should be organised to apportion tasks to academics who might be able to help in the development of industrial processes. The deadline for the application to NATO would be 15 July 1987 but Ron Ottewill undertook to make informal inquiries earlier.

1989 Gordon Conference. This would be chaired by Irja Piirma.

1990 Mohamed El-Aasser said that it was customary for Lehigh University to host the A.C.S. Colloid and Surface Chemistry Symposium every 10 years and the University's offer to host the 64th Symposium had been accepted. There would be an Emulsion Polymers Symposium honouring John Vanderhoff and he planned to make a preliminary announcement about this at an early date.

The possibility of a meeting in Australia was discussed: it appeared that early January would be the optimum time for this. It seemed unlikely that funding on a scale that would allow more than 6 members from other continents to attend could be obtained but Bob Gilbert would try to discover how Barry Ninham had succeeded in finding massive funding for a recent Australian conference.

Jean Guillot mentioned that the C.N.R.S. intended to hold a second Emulsion Polymerisation Symposium in Lyons, probably in April 1989 following on from the March 1984 Symposium which had been very successful

Membership. The recent death of Alan Rembaum from cancer was noted with regret: John Ugelstad suggested that a Memorial Symposium on Medical Applications of Polymer Colloids should be held not necessarily in Norway although funds could be available for such an event if it was held in Norway.
Hans Kast (BASF A.G. Polymer Forschungs Laboratorium, D 6700 Ludwigshafen, West Germany) and Mitch Winnik (Department of Chemistry, University of Toronto, Toronto, Ontario, Canada, M5S 1A1 were elected to membership

Votes of Thanks. Ron Ottewill thanked Bob Fitch on behalf of the Group for the superb hospitality and excellent facilities provided by the Johnson Foundation for the present meeting. Bob reminded the Group that Mohamed El-Aasser and the Lehigh University Emulsion Polymer Institute had contributed much of the detailed organisation and some of the funds.

The meeting (which was held over lunch) closed at 2 p.m.

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Papers presented at the One-day 'Emulsion Polymers' Symposium at the 60th A.C.S. Colloid and Surface Science Symposium at Atlanta, Georgia 15-18 June 1986.

ON THE PHENOMENON OF ANOMALOUS PARTICLES FORMED DURING THE SURFACTANT-FREE EMULSION POLYMERIZATION OF STYRENE. M.C.Wilkinson, J.Hearn, M.Chainey, & A.R.Goodall.

SURFACTANT EFFECTS IN THE EMULSION POLYMERIZATION OF p-METHYLSTYRENE
I. Piirma, S. Lee & R.Fleckesteiner

HYBRID RUBBER LATEXES POLYMERIZED BY TRANSITION METAL CATALYST IN WATER
K.Kasai, N.Itoh, H.Ono, & H.Hirai (Japan Synthetic Rubber Co., Tokyo)

PREPARATION OF MICRON SIZE POLYMER PARTICLES IN NON-AQUEOUS MEDIA
B.Williamson, R.Lukac, M.Winnik, & M.D.Croucher

THE ROLE OF WATER SOLUBILITY OF THE OIL PHASE IN THE FORMATION OF MINIEMULSIONS
W.M.Brouwer, M.S.El-Aasser, & J.W.Vanderhoff.

ADSORBED SODIUM DODECYL SULFATE BILAYERS AS A TWO-DIMENSIONAL POLYMERIZATION SOLVENT FOR STYRENE. J.Wu, J.H.Harwell, & E.A.O'Reardon (Chem.Eng., Olklahoma Univ.)

MODELLING OF MOLECULAR WEIGHT VARIATION IN CSTR VINYL ACETATE EMULSION POLYMERIZATION. R.G.Mallinson & C.H.Lee (Chem. Eng., Olklahoma University)

SEEDED EMULSION COPOLYMERIZATION OF STYRENE/SODIUM STYRENE SULFONATE COMONOMER SYSTEM. J.H.Kim, M.S.El-Aasser, & J.W.Vanderhoff.

THE ROLE OF SURFACTANT BY-PRODUCTS IN EMULSION POLYMERIZATION. D.E.Lietz (Stepan Co.)

GRAFTING REACTIONS OF METHYL METHACRYLATE ONTO POLYBUTADIENE SEED LATEXES.
M.P.Merkel, V.L.Dimonie, M.S.El)Aasser, & J.W.Vanderhoff.

KINETICS OF THE MINIEMULSION POLYMERIZATION OF VINYL ACETATE AND BUTYL ACRYLATE.
J.Delgado, M.S.El)Aasser, C.A.Silebi, & J.W.Vanderhoff.

AUTOMATION OF AN INTERFACIAL TENSIOMETER. M.L.Alexander & M.J.Matteson
(Georgia Institute of Technology, Atlanta).

WINGSPREAD
THE JOHNSON FOUNDATION
RACINE, WISCONSIN 53401

The Academic Wetback

All over northern Europe
There's always lots of work
For immigrants from southern lands:
Italian, Greek or Turk.
Forgetting all their relatives
Would not be very kind,
So they keep sending money to
The folks they left behind.

In Mexico the working man
Is often unemployed.
A swim across the Rio Grande
Would make him overjoyed.
Once Juan has crossed the border,
He's working in a flash,
And when he visits Mama,
He brings her lots of cash.

In hallowed halls of ivy,
Research support is rare,
Professors leave for industry
To seek their fortunes there.
Here's one who still recalls his roots
Although he's struck it rich,
So lad and lass, let's raise a glass
And drink to ROBERT FITCH!

IMK, (P.L.)
7/2/86

EFFECTS OF NON-IONOGENIC HYDROPHILIC MONOMERS UPON MECHANICAL STABILITY OF NATURAL RUBBER LATEX

3 OCT Recd

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Members may recall that our contribution to a recent number of the Polymer Colloids Group Newsletter took the form of a brief report of some of the results we had obtained in the course of a preliminary investigation into the graft copolymerisation of various non-ionogenic hydrophilic monomers to natural rubber in latex form. Four monomers of varying reactivities and hydrophilicities were used, namely, 2-hydroxyethyl acrylate (HEA), 2-hydroxyethyl methacrylate (HEMA), 2-hydroxypropyl acrylate (HPA) and 2-hydroxyypropyl methacrylate (HPMA). We are now in a position to make a more detailed investigation of this subject, which is technically of some potential importance as well as being interesting. We have commenced this more comprehensive investigation by looking at the important practical matter of the effect of each of the four monomers upon the colloid stability of natural rubber latex. For this purpose, we have taken the mechanical stability, as determined by the conventional test, as a convenient measure of colloid stability. As in the preliminary investigation, we have used so-called "sub-stage" ammonia-preserved natural rubber latex concentrate as the latex, rather than conventional ammonia-preserved centrifuged concentrate. The reason for this is that the "sub-stage" latex has been subjected to a second concentration process, during the course of which further non-rubber constituents are removed. As a consequence, it contains a lower level of non-rubber constituents than does the conventional concentrate, and therefore in principle is more suitable for studies of graft-copolymerisation reactions than is the conventional concentrate.

Results for the effects of 0 - 14 parts by weight per 100 parts by weight of rubber (pphr) of each of the monomers upon the mechanical stability of the latex before maturation are summarised in Table 1. Whereas we expected that each of the monomers would reduce mechanical stability somewhat, perhaps because the degree of hydration of proteinaceous colloid stabilisers would be reduced, in fact it is seen that small additions of all four monomers caused the mechanical stability to *increase*, and further additions cause it to pass through a maximum and then to decrease. The changes were more marked in the case of the methacrylate monomers than in the case of the acrylate monomers. Thus, for example, the addition of 2 pphr of HEMA caused the mechanical stability time to increase by a factor of *ca.* 4. Two features of these results are particularly interesting. The first is that relatively small amounts of these monomers can cause large variations in mechanical stability. The second is that small additions of these monomers cause significant *enhancements* of mechanical stability. We are not at present able to offer even tentative explanations for these observations. They do, however, serve to underline how little we really understand about certain practical aspects of the colloid stability of some of the polymer colloid systems of industrial interest.

In a further series of experiments, we have taken latices which contained amounts of monomers corresponding approximately to the maxima in mechanical stability indicated in Table 1, and then allowed these latices to mature at ambient temperature. Mechanical stabilities were then determined after various periods of maturation. The results are shown in Table 2. The quantities tabulated are the ratios of the mechanical stability time after a particular time of maturation to the initial mechanical stability time. It is evident that in all cases the mechanical stability fell sharply as the latex matured, reaching a steady value after a period between about 25 hours and 50 hours, depending upon the monomer which was present in the latex. In the case of the latex which contained HEA, the mechanical stability fell to a very low level after about 24 hours maturation. Again we are unable at present to offer any explanation for the observed changes. Another rather puzzling effect which we have observed is that it is not in general possible to enhance the mechanical stability of natural rubber latex containing these monomers by adding conventional soaps and surfactants. Rather, we have found that these substances tend to sensitise the latex to gelation. In fact, in order to acheive suficient colloid stability to be able to carry out graft-copolymerisation reactions, it seems to be necessary to rely upon substantial dilution of the reaction system with water to enhance the colloid stability.

Table 1
Effect of HEA, HEMA, HPA and HPMA upon mechanical stability of natural rubber latex before maturation

level of addition (pphr)	mechanical stability time (seconds)			
	HEA	HEMA	HPA	HPMA
0	1240	1240	1240	1240
0.06	1333	1425	1455	1630
0.125	1305	1545	1395	1785
0.250	-	2445	-	2370
0.500	1290	2940	1800	3030
1.00	1335	3820	2160	3040
2.00	1440	5138	3005	5088
3.00	-	-	3435	-
4.00	1920	4335	3245	3765
5.00	-	-	3060	-
6.00	2368	3300	-	2095
6.50	-	-	2390	-
7.00	2473	-	1320	-
7.50	-	-	-	855
8.00	-	2843	1750	180
9.00	2865	-	-	-
10.00	2345	1860	1230	-
11.00	-	1411	1080	-
12.00	1673	1275	-	-
14.00	1440	-	-	-

Table 2
Effect of maturation upon mechanical stability of natural rubber latex containing amounts of monomers corresponding approximately to maximum mechanical stability before maturation

maturation time (hours)	ratio of MST after maturation to initial MST*			
	HEA	HEMA	HPA	HPMA
0	1.00	1.00	1.00	1.00
4.5	0.25	0.55	0.40	0.68
24	0.01	0.20	0.13	0.40
48	0.002	0.12	0.14	0.22
120	-	0.10	0.11	0.13

*initial MST values were:
latex + HEA: 2790 seconds
latex + HEMA: 5138 seconds
latex + HPA: 3435 seconds
latex + HPMA: 5088 seconds

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(7)

POLYMER COLLOID GROUP NEWSLETTER

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

by **F. CANDAU**

22 SEP Recd

SALT EFFECTS IN SOLUTIONS OF NONIONIC EMULSIFIERS AND THEIR APPLICATIONS AS STABILIZERS IN MICROEMULSION POLYMERIZATION

(in collaboration with C. Holtzscherer)

We have investigated the effect of various electrolytes on the solubilization properties of nonionic emulsifiers. Turbidimetry experiments were performed on the aqueous surfactant solutions. Cloud points increase or decrease could be expressed in terms of salting in or salting out effects on the emulsifiers respectively. By applying a method proposed by Schott et al.(1) we were able to attribute cloud point shift values to the individual ions which constitute the electrolyte. Our results show that the salting effects observed on the nonionic surfactants is mainly due to the prominent influence of the anions as compared to that of the cations. This anion influence is directly related to its lyotropic number.

These salt effects are shown to affect the stability of inverse latexes prepared by polymerization of acrylamide in microemulsions formed of water swollen droplets stabilized by a nonionic emulsifier blend and dispersed in Isopar M. For example, latexes obtained in presence of salts producing a strong salting out effect exhibit a high stability, contrary to those prepared in the presence of salting in-type electrolytes or in the absence of any salt.

Interfacial tension measurements performed on the systems located in the multiphasic domain of the phase diagram shed some light on the latter phenomena, as summarized below.

- Addition of electrolytes with high salting out efficiency such as sodium acetate induces the so-called Winsor I (oil/water microemulsion in equilibrium with oil) ⟶ Winsor III (microemulsion with a bicontinuous structure in equilibrium with oil and water) phase transition. The bicontinuous microemulsion which consists of oil and aqueous domains loosely interconnected is characterized by a very low interfacial tension (~ 10^{-3} dyn/cm). The role of the salts is to enhance the stability of the systems by decreasing their w/o interfacial tensions allowing thus the polymerization at high monomer contents (~ 25%) in bicontinuous microemulsions.

- Triphasic systems (i.e. Winsor III) cannot be formed in the presence of salting in-type electrolytes such as lithium nitrate or in the absence of salts. As a result, polymerization in these systems lead to unstable latexes with formation of a gel phase.

We are currently investigating the influence of the composition of the microemulsions on the characteristics of the final latexes (size, polydispersity, number of polyacrylamide molecules per particle etc..)

References

1) H. Schott, A.E. Royce and S.K. Han
J.Coll.Int.Sci., 98, n°1 (1984)

Recent publications

a) F. Candau, Z. Zekhnini, F. Heatley and E. Franta
Colloid and Pol.Sci., 264, 676 (1986)

b) F. Candau, Z. Zekhnini and F. Heatley
Macromolecules, 19, 1895 (1986)

Contribution to the Polymer Colloids Group Newsletter

from
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DSM Research
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The Netherlands

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

The effect of variation of the polyethyleneoxide (PEO) concentration (molar mass 20.000 $g.mol^{-1}$) on particle size in the preparation of MAA/MMA (molar ratio 80/20) latices has been studied.
It was found that even for EO/MAA ratios as low as 0.01 the presence of PEO has a considerable effect on particle formation. At EO/MAA ratios above 0,5 monodisperse systems are found the particle size of which decreases gradually with PEO content. At lower EO/MAA ratios bimodal distributions are found consisting of a crop of relatively large monodisperse particles and a second crop of smaller particles with a broader distribution. The results suggest that the first crop of particles are formed under the influence of complexation. This type of particle formation goes on until all free PEO has been consumed in the complexation process.
Oligomers formed after this stage will form particles following the homogeneous nucleation mechanism and are responsible for the second crop of small particles.
More details are given in an article accepted for publication in J. Polym. Sci. Polym. Lett. Ed.

Recent publications:

* The degree of dispersion of poly (vinylalcohol) in water/n-propanol solutions, Eur. Polym. J. 22 (1986) 351-356.

* A ^{13}C NMR study of the microstructure of poly (vinylalcohol) Polymer, 27 (1986) 993-998.

VISCOELASTIC PROBES OF SUSPENSION STRUCTURE

1 OCT Recd

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ABSTRACT

The use of the high frequency elastic modulus, G_∞, to probe particle interactions in weakly agglomerated, concentrated suspensions is discussed. We show that a model based on pair interaction potentials and a statistical description of pair spatial distribution yields accurate prediction of the volume fraction dependence of G_∞. The use of statistical treatments of particle distributions as predicted from particle interaction potentials is found to provide insight on how surface chemistry affects the uniformity of powder compacts.

Introduction

Numerous studies have shown that simply reproducing a set of processing conditions is not enough to insure component reliability (1-3). Instead, these studies indicate that powder processing must reproducibly generate uniform microstructures upon firing and that this uniformity is achieved by starting with monodisperse, unagglomerated powders and packing these powders in a homogeneous manner. Thus, the quest for reliable ceramics has begun to focus attention on the ways in which particle/particle interactions determine the structure (particle and pore distribution) within green powder compacts.

Methods of probing the arrangement of particles in a highly loaded suspension are limited. Here we describe a rheological measurement which can be used to follow the effects of processing conditions on structure development.

Several rheological techniques are available for these purposes. It should be noted, however, that different techniques do not provide equivalent information. For example, viscosities measured as a function of shear rate have been used to follow the breakdown of agglomerates (4). During these measurements a suspension is subjected to an infinite deformation which results in a continuous breakdown and reformation of aggregates. Consequently, from continuous shear measurements, it is difficult to infer properties of the suspension at rest. On the other hand, this technique provides information about the spatial distribution of particles under shear and thus, is valuable in assessing a suspension's moldability.

However, the structure maintained while the suspension is flowing can be quite different from that at rest. After flow ceases, the particle distribution relaxes into its equilibrium or static state. It is this static state which plays a dominant role in the microstructure developed during subsequent firing. A measure of particle interactions (and thus, implicitly, particle distribution) which does not disturb this equilibrium state is provided by the limiting high strain frequency storage modulus of the suspension, G_∞. This parameter is a measure of the energy stored in a suspension due to an infinitesimal strain (5).

In this paper we describe experimental determinations of G_∞ on an idealized system. The goal of this work was to establish that particle distributions derived from molecular statistical mechanics could be used in conjunction with colloidal particle interaction potentials to evaluate the ordering within a suspension and its elastic response to a small deformation.

Experimental

Monodisperse polystyrene spheres were prepared following the methods of Goodwin et al (6). These particles were chosen because their size can be readily controlled and their surface chemistry has been well studied. They thus represent an ideal system with which to test modelling assumptions before proceeding to more complex situations. The latices were stabilized against aggregation by monolayer adsorption of a monodisperse surfactant, hexaethylene oxide dodecyl ether (C_6E_{12}) supplied by Nikko Chemicals Co., Ltd., Tokyo, Japan. Electrophoretic mobilities used to calculate surface potentials, were measured on a Penkem 3000 automated electrophresis apparatus. For our purposes, where the double layer thickness is much smaller than the particle radius ($a\kappa >> 100$, where κ is the Debye-Huckel parameter), the Smoluchowski equation was used to convert mobilities to zeta potentials, ζ (7).

The suspension's wave rigidity modulus was determined as a function of volume fraction with a Rank Pulse Shearometer. For the systems studied here the loss modulus was small at the frequency of the Shearometer (~150 hz) and thus the wave rigidity modulus reduces to the high frequency limit of the storage modulus, G_∞ (5). More detailed descriptions of the experimental procedures are presented elsewhere (7).

Results

Due to space constraints, the results for only one of the particle sizes studied will be described. The interested reader is referred to Goodwin et al (7) for further discussion. The latex studied was composed of polystyrene spheres with an average radius of 487 nm and a standard deviation of 1.05. The surface potential of the latex covered with a monolayer of the surfactant and suspended in 0.5 M NaCl was 9.7 mV. Wave rigidity moduli were measured on suspensions maintained a this ionic strength.

Under these conditions, the particles are weakly flocculated. (The steric layer provided by the surfactant keeps the particles from falling into a primary Van der Waals minimum). Observation of dilute suspensions with an optical microscope showed that the particles clustered together into tight domains which were easily disrupted by tapping the coverglass.

In fig. 1, the volume fraction dependence of the wave rigidity modulus for this latex is presented. For all the latices studied, it was found that G_∞ increased monotonically with volume fraction.

Discussion

Due to the small strain applied by the shearometer, the suspension's equilibrium structure is not disturbed while measuring G_∞ and can be modeled in terms of pair interaction potentials and the equilibrium particle distribution. In this fashion Goodwin et al (7) develop an expression for G_∞ for concentrated suspensions based on a model originally derived by Zwanzig and Mountain (8). The final expression is written:

$$G_\infty = \frac{3C}{4\pi a^3} KT + \frac{3C^2}{8\pi a^6} \int_0^\infty g(r) \frac{d}{dr} \left[r^4 \frac{dU}{dr} \right] dr \qquad (1)$$

This expression relates G_∞ to the suspension volume fraction, C, the particle radius, a, the product of Boltzmann's constant and the absolute temperature KT, the pair interaction potential, U, and the pair distribution function g(r). The first term on the right hand side of eqn. (1) represents an entropic contribution where as the second term, which dominates for the systems at hand, represents the contribution due to particle/particle interactions.

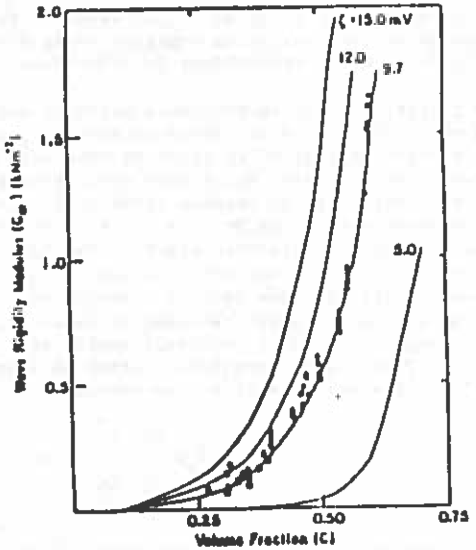

Fig. 1. Wave rigidity modulus, G_∞, as a function of volume fraction, C. Points are experimental values and the solid lines are model predictions discussed in the text.

The interaction potential for the sterically stabilized system studied here can be described by an electrostatic repulsion and a truncated Van der Waals attraction. The surfactant layer extents 3.85 nm away from the particle surface and fixes the minimum approach two spheres can achieve at 7.7 nm. The Van der Waals force originates at the physical surface of the particle and, thus, the surfactant truncates the attractive potential. The electrostatic repulsion, on the other hand, originates at the outer edge of the surfactant layer, and, even though it is extremely short range in 0.5 M salt solutions (the double layer thickness is ~0.4 nm), this repulsive potential plays an important role in determining suspension elasticity (7). The interaction potential is written:

$$U = 2\pi\, \varepsilon\, a\, \zeta^2 \ln\left[1 + \exp\left[-\kappa(h-2d)\right]\right] + U_A + U_{HS}$$

$$\text{where}\quad U_A = -\frac{A}{12}\left[\frac{1}{X^2 + 2X} + \frac{1}{X^2 + 2X + 1} + 2\ln\left[\frac{X^2 + 2X}{X^2 + 2X + 1}\right]\right]$$

$$\text{and}\quad U_{HS} = \infty \text{ at } h < 2d \text{ and } U_{HS} = 0 \text{ for } h > 2d. \qquad (2)$$

for an adsorbed layer of thickness d, a surface to surface separation h, a Hamaker constant A, solvent dielectric constant ε and $x = h/2a$.

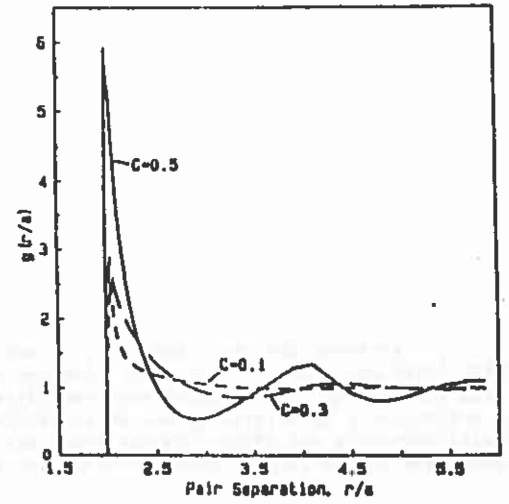

Fig. 2. Pair distribution functions, g(r/a), as a function of pair separation, r/a, at three volume fractions. Note that for all C, g(r/a) = 0 for r/a < 2.0 and g(r/a) → 1.0 as r/a → ∞. As C increases the number of well defined shells of particles (as indicated by maximima in g(r/a)) increases showing increased ordering in the suspension.

The pair distribution function accounts for the ordering of the particles in the suspension. The probability that there is a second particle within the volume r + dr around a central particle is given by;

$$\frac{3r^2}{a^3}\, C g(r) dr.$$

Studies of the pair distribution functions in colloidal systems with light and neutron scattering techniques (9) indicate that like molecular fluids, the pair distribution at high volume fractions is dominated by the particle's rigid, noninterpenetrating properties. Thus it is the short range repulsive portion of U which dominates the spatial distribution of particles in a concentrated suspension. Goodwin et al (7) show how eqn. 1 can be rewritten in terms of a pair distribution function derived for hard spheres (where particles interact only through U_{HS} in eqn. (2)) and a perturbation to this pair distribution function accounting for the electrostatic and Van der Waals forces. Typical pair distribution functions are presented in fig. 2. Numerically carrying out the integral in eqn. (1), Goodwin et al show that the resulting predictions of G_∞ are relatively insensitive to the steric layer thickness, d, or the Hamaker coefficient A. However, G_∞, is very sensitive to variations in ζ. In fig. 1 the predictions of the model calculations for various values of ζ using $A = 9\times10^{-21}$ J and d = 3.85 nm are shown. As seen here, the model predicts the experimental values of G_∞ for a zeta potential very close to that measured electrophorectically. For all the latices studied, the zeta potential required to fit the G_∞ results was within 3-4 mV of the measured value. This agreement suggests that the pair distribution functions predicted from statistical mechanical models provide excellent approximations for weakly flocculated systems and can be used to .

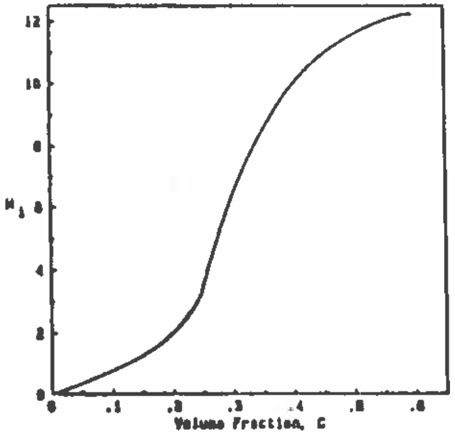

Fig. 3. Average number of nearest neighbors, N_1, as a function of suspension volume fraction, C. As N_1, approaches 12, the short range order in the suspension increases.

predict elastic properties of a suspension.

While G_∞ is important in evaluating the toughness of a powder compact, predictions of the pair distribution function can be used in developing methods of tailoring desired microstructures. As an example of this fig. 3 presents the number of particles in the first shell around a central particle, calculated from the pair distribution function used in the G_∞ predictions according to

$$N_1 = \frac{3C}{a^3} \int_{2a}^{r_1} r^2 g(r)dr$$

where r_1 is the position of the first minimum in $r^2g(r)$ (9). Fig. 3 indicates that the number of nearest neighbors surrounding a central particle rapidly approaches 12 at volume fractions above 0.35. This is the value expected for a close packed array of spheres. That the number of nearest neighbors approaches 12 at volume fractions substantially below the close packed volume fraction of = 0.74 reflects upon the short range order introduced into the suspension by the hard sphere repulsion and Van der Waals attraction. In order to maintain a space filling suspension, however, the order decays rapidly resulting in small domains of order interspersed with regions of disorder. Indeed, such clustering phenomena was observed. When dilute suspensions were studied under an optical microscope, particles formed small highly ordered regions interspersed with areas of much lower volume fraction reflecting the behavior predicted by the statistical model.

The consequences of suspensions which contain regions of short range order but long range disorder on microstructure development upon firing have been explored by Aksay (10). He found that while the close packed domains sintered to completion at low temperatures, the interspersing voids (representing regions of disorder) required much higher temperatures and longer sintering times to result in a ceramic of near theoretical density. Sintering out the disordered regions caused grain growth to occur and the fine microstructure which arose from the close packed regions was lost.

In conclusion, we have shown that weakly agglomerated suspensions acquire substantial elastic moduli and that these moduli can be predicted from a model accounting for pair interactions and the static spatial distribution of pairs. In addition, the perturbed hard sphere model for the pair distribution suggests that the space filling, weakly agglomerated network studied here consists of close packed regions interspersed with regions of lower particle density. While the experimental system was chosen to test the model developed for G', the quality of the model has been verified suggesting that experimental and modelling techniques developed here can now be applied with greater confidence to ceramic precursor particles.

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COLLOID RESEARCH AT MCMASTER UNIVERSITY - RECENT DEVELOPMENTS

by
Archie Hamielec

16 SEP Recd

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

The kinetics of high conversion polymerization of VCM ($X>0.75$) are being investigated to better understand the control of particle porosity resin bulk density and PVC thermal stability.

Extensive experimentation has permitted development of a relationship between temperature, pressure and VCM conversion properly accounting for VCM partitioning in the polymer, water and vapor phases (reactor headspace). Measurements of pressure and temperature should permit the monitoring of VCM conversion beyond the pressure drop. A n-butane tracer technique with the monitoring of VCM and n-butane levels in the headspace by online GC, should also permit the monitoring of VCM conversion.

A comprehensive kinetic model which accounts for diffusion-controlled termination and propagation and for the formation of terminal and internal double bonds, short and long chain branches and t-chlorine atoms, has been developed. The effect of O_2 on rate and thermal stability is also being accounted for.

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

Comonomers dimethyl aminoethylacrylate (quaternary complex with dimethyl sulfate or methyl chloride) (DMAEA), diallyldimethyl ammonium chloride (DADMAC) and dimethyl aminoethylmethacrylate (quaternary complex with dimethyl sulfate or methyl chloride) (DMAEM) with acrylamide, are being studied to elucidate free-radical polymerization kinetics with charged species.

The copolymers are being characterized by NMR, LALLSP and aqueous SEC.

3. EMULSION POLYMERIZATION OF VINYL ACETATE AND VINYL ACETATE/ACRYLIC ACID USING PVOH AS STABILIZER.

A manuscript is being prepared for publication.

4. PRODUCTION OF CROSS-LINKED POLYACRYLATES.

Experiments are being done to control crosslinking architecture. A paper has been submitted to Materials Chemistry and Physics:- W. Klonowski and A.E. Hamielec, "Graph Representation for Crosslinked Polymers and Topological Gelation Criterion".

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15 SEP Recd

POLYMER COLLOIDS AT THE UNIVERSITY OF SYDNEY

Reporters: D. H. Napper
R. G. Gilbert

Coagulative Nucleation and Heterocoagulation

Recent calculations have shown up the importance of heterocoagulation processes in coagulative nucleation. Previously, we have used the simple Deryagin-integration based theory of Hogg, Healy and Fuerstenau (HHF). HHF is adequate in some circumstances but, unfortunately, it sometimes tends to seriously overestimate the magnitude of the electrostatic repulsion between particles of different radii and different surface potentials. Even worse, it can predict repulsion between particles of the same sign where attraction is the dominant interaction. It turns out that interactions of these latter types are crucially important in the coagulative nucleation of latex particles in electrostatically stabilized systems.

A recent theoretical analysis of Barouch and Matijevic (J. Chem. Soc. Faraday Trans. 1, 81, 1797(1985)) appears to have overcome some of the deficiencies inherent in the simpler HHF theory. These authors show that partial attraction is quite common for particles of different particle size and different surface potentials when undergoing close approach. Both differences are important in generating the partial attraction. This partial attraction is responsible for the lowering of the interaction energy over that calculated by HHF.

At first sight, the generation of an attractive interaction between species with the same sign of charge seems counterintuitive. The wisdom of hindsight, however, suggests that its origin is quite straightforward. Consider a flat plate and an approaching sphere, whose surface potentials are very different. The double layer thickness surrounding the sphere and at the flat plate are identical. Initially (i.e., at large distances of separation), the plate "sees" the sphere and its double layer as an uncharged entity, as demanded by electroneutrality. On closer approach, however, as the double layer of the sphere becomes distorted (in the direction normal to the flat plate), the sphere acquires an effective "net" charge. Provided that the surface potentials of the two approaching surfaces are different, part of the flat surface will effectively be of a sign opposite to that carried by the sphere whereas the rest of the surface will have the same sign. This results in a partial attraction

..../2

between the sphere and flat plate. This attraction can even be the dominant interaction.

The effect of the partial attraction on heterocoagulation is profound. Classical concepts applicable to homocoagulation no longer apply. For example, repulsion may *increase* on *increasing* the ionic strength (which may decrease the partial attraction between the sphere and the flat plate more than the partial repulsion).

Coagulative nucleation of latex particles involves both homo- and near homo-coagulation, as well as heterocoagulation, events. Our recent calculations suggest that some of the observed aspects of latex particle formation and growth cannot properly be explained without invoking the Barouch and Matijevic theory. The "switching off" of nucleation, for example, may well be determined *inter alia* by the forces of partial attraction.

Contribution to Polymer Colloids Newsletter from Fukui University

by Mamoru Nomura

The following paper will be presented in "The 2nd International Berlin Workshop on Polymer Reaction Engineering" to be held in October 1-3, 1986 at Institute fur Technische Chemie, Technische Universitat Berlin.

"An Experimental Study on the Optimal Reactor Type and Operation for Continuous Emulsion Polymerization"

ABSTRACT: Studies on the optimal reactor type and its operation method for continuous emulsion polymerization published to date are briefly reviewed first, and then, the performance and the utility of the split feed reactor systems which have been proposed by the present authors1) is experimentally demonstrated. It is shown that the splitting of the monomer feed stream is always effective for increasing the efficiency of the first reactor which play a role as a seeder. but the splitting of the water feed streams is effective only when some kinetic conditions are satisfied. The performance and the utility of the seeding reactor with the splitting of both monomer and water is also discussed.

SUMMARY: As shown in Fig.1, we have found in batch emulsion polymerization of styrene that the number of polymer particles formed begins to increase when the concentration of monomer initially charged is reduced to some level where emulsifier micelles still present even after the monomer droplets disappeared from the water phase due to complete absorption by the existing polymer particles. Based on this finding, we have proposeda new seeding reactor system with the splitting ofthe monomer feed stream between the first seeding reactor and the second large polymerizing reactor, and also with splitting of the water feed stream in addition to the splitting of the monomer feed stream as shown in Fig. 2a and 2b.1) This reactor system was also adopted and discussed by Hamielec et al., as shown in Fig. 3.2) Since, the utility and the validity of the above reactor system were mainly theoretically discussed in the previous paper,3), it is demonstrated experimentally in this paper. First, the utility of the splitting of monomer feed stream in CSTR type seeding reactor is clarified experimentally, as shown in Fig. 4. It was found that the maximum number of polymer particles formed can be increased about two times merely by decreasing the concentration of monomer fed to the first seeding reactor. It is well known that in continuous emulsion polymerization PFR type seeding reactor can produce more particles than CSTR. Fig. 5. shows the effect of the splitting of monomer feed stream in PFR type seeding reactor, where (●) shows the results of perfect PFR reactor(obtained in batch reactor) and (○) indicates the results obtained with a tubular reactor made of a straight glass tube with 1.5 cm I.D. and 110 cm long. Due to backmixing in the reactor, the number of polymer particles produced is somewhat less than those produced in a perfect PFR seeder. However, it is seen that the splitting of monomer feed stream between the first and the second reactors is still effective in increasing the number of polymer particles produced.
As shown in the previous paper3), the effect of the splitting

of water feed stream is effective only when some kinetic conditions are satisfied. The splitting of the monomer feed stream and of the water feed stream can be performed independently. Therefore, the effect of the splitting of both monomer and water feed streams can be superimposed.

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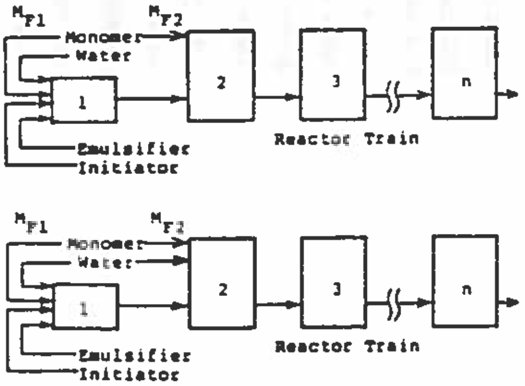

Fig. 2 Schematic diagram of seeding reactor systems: (a) with monomer split feed and (b) with both monomer and water split feeds.

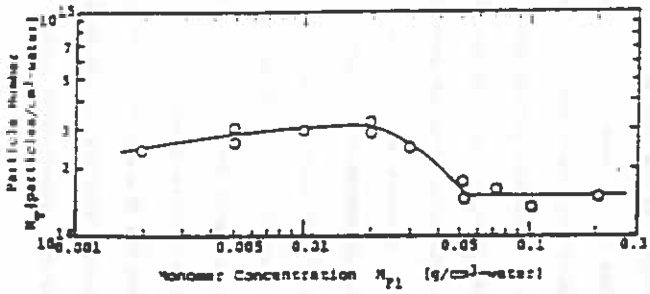

Fig. 4 Effect of monomer concentration fed to the first CSTR type seeder, M_{F1} on the number of polymer particles produced, N_T. (Experimental: S_{F1}=6.25 g/dm^3-H_2O(NaLS); I_{F1}=1.25 g/dm^3-H_2O(KPS); 50°C; Styrene; Mean residence time of the first seeder θ_1=20 minutes)

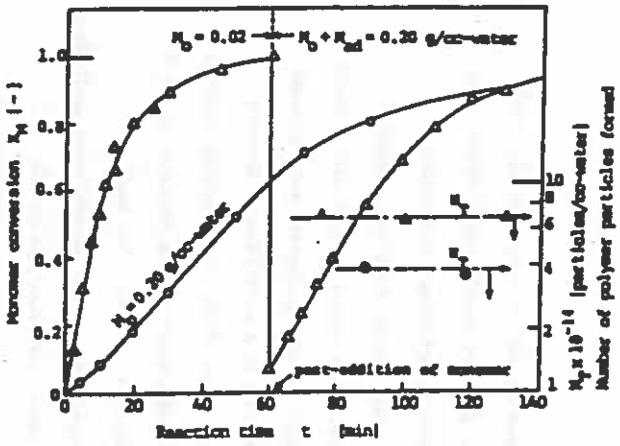

Fig. 1 Effect of initial monomer concentration on the number of polymer particles formed. (Experimental: S_0=6.25 g/dm^3-H_2O(NaLS); I_0=1.25 g/dm^3-H_2O(KPS); Styrene; 50°C; (△)conversion and (▲) particle number at M_0=0.02 g/cm^3-H_2O with post-addition of monomer, M_{ad}=0.18 g/cm^3-H_2O at t_{ad}=60 minutes; (○)conversion and (●)particle number at M_0=0.20 g/cm^3-H_2O)

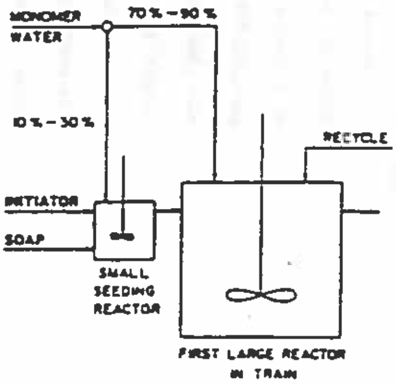

Fig. 3 Reactor configuration with a small seeding reactor preceding the first large CSTR of the train.

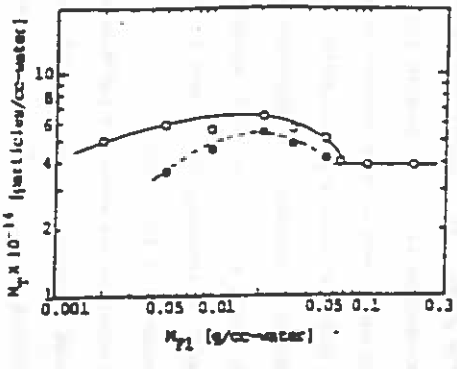

Fig. 5 Effect of monomer concentration fed to the first tubular seeding reactor, M_{F1} on the number of polymer particles formed, N_T. (Experimental: S_{F1}=6.25 g/dm^3-H_2O(NaLS); I_{F1}=1.25 g/dm^3-H_2O(KPS); Styrene; 50°C; θ_1=40 minutes; (o)batch reactor at reaction time t=40 minutes(correspond to an ideal plug flow reactor); (●)tubular reactor with backmixing)

1. INTRODUCTION

Emulsion polymerisation in an aqueous environment provides a well-established method for the preparation of polystyrene latices with narrow particle size distributions (1-4). In general, the use of an ionic surface active agent, and an ionic initiator leads to the formation of particles with charged end-groups on the surface (5,6). Consequently, the particles produced are charge-stabilised and hence, are not colloidally stable at high electrolyte concentrations. Moreover, other treatments such as shearing, freeze-thaw cycling and pH variation can lead to flocculation of the particles.

It follows therefore, to obtain latices which are stable to some or all of these conditions, some advantages can be gained by the preparation of sterically stabilised latices (7). Such latices are well known in non aqueous media where the use of grafting techniques to attach an oleophilic polymer to the core particle ensures latex stability over a wide range of conditions (8,9). The present work describes the preparation of essentially similar latices in an aqueous environment by the use of a nonionic surface active agent and a comonomer which becomes covalently attached to the core particle. As a comonomer methoxy polyethylene glycol methacrylate has been used. Latices prepared in this way are shown to be colloidally stable to high electrolyte concentrations, to wide variations in pH and temperature and to freeze-thaw cycling. Moreover, the latices can be prepared at high volume fractions. In addition they can be freeze-dried and redispersed in other solvents provided the latter are good solvent for the methoxy polyethylene glycol chains.

This paper describes the preparation and properties of polystyrene latices sterically stabilised by methoxy polyethylene glycol chains and compares their properties with the more conventional charge-stabilised polystyrene latices.

2. EXPERIMENTAL

Materials

Double distilled water was used for all the preparations. BDH laboratory reagent styrene was purified by distillation at 40-50°C, in an atmosphere of nitrogen. Potassium persulphate and hydrogen peroxide (20 volumes) were BDH analar grade materials. Ascorbic acid (99%) was obtained from Fluka. The anionic surface active agent Manoxal MA (sodium di-(methyl amyl) sulphosuccinate), was obtained from Mancham Limited as a 60% solution in a water/alcohol mixture. The nonionic surface active agent Levelan P208 (nonyl phenol ethylene glycol condensate with 20 ethylene glycol units) was obtained as a 80% aqueous solution from Lankro Chemicals Limited. The nonionic comonomer/stabiliser, methoxy polyethylene glycol methacrylate containing approximately 45 ethylene glycol units, was supplied by ICI PLC, Paints Division. Sodium bicarbonate and barium chloride were BDH analar grade materials.

Preparation of Latices

Basic Method: The emulsion polymerisation reaction was carried out in a five necked flask (10). The inlets used were used for a glass stirrer with a PTFE paddle, a constant flow of nitrogen gas, a water cooled reflux condenser and a thermometer. The reaction flask was maintained at the required constant temperature, using a thermostatted water bath. The amounts of monomer, distilled water and other ingredients used are listed in Table 1. These were added to the reaction vessel and emulsified for 20 minutes by stirring. The initiator was then added and the polymerisation was taken to completion. The resulting latex was then poured into well-boiled dialysis-tubing, and dialysed against distilled water for a period of two weeks before any testing was performed.

PS* Latex: In the charge-stabilised PS* latex, Manoxal MA was used as the anionic surface active agent and potassium persulphate as the initiator.

PS-10 latex: In the sterically stabilised PS-10 latex, Levelan P208 was employed as the nonionic surface active agent together with methoxy polyethylene glycol methacrylate as the comonomer/stabiliser. The initiator system was ascorbic acid/hydrogen peroxide.

Experimental Techniques

Electron Microscopy: Electron micrographs were taken using a Hitachi HS7 electron microscope. The particle size determinations were carried out with a Carl Zeiss TGZ 3 particle size analyser.

Conductimetric Titration: The surface charge density of the latex particles was determined by means of a conductimetric titration. A Pye dip-type conductance cell was used for conductance measurements in conjunction with a Wayne Kerr B224 bridge.

Electrolyte Stability: The latex stability to added electrolyte (barium chloride) was examined turbidimetrically by examining the changes in optical density of the latices, as a function of electrolyte concentration (11). A Unicam SP-600 spectrophotometer, with an optical cell of path length of 1 cm, was used for this purpose. All measurements were carried out at room temperature using incident light with a wavelength of 546 nm. The dialysed latices were adjusted to give an optical density of about 1.3, by diluting them with double distilled water. A 5 cm^3 aliquot of diluted latex (0.05% w/v) was transferred to a clean tube and then 5 cm^3 of electrolyte of known concentration was added. After initial agitation, the mixture was allowed to stand for 2 hours. It was then lightly centrifuged (2000 rpm for 10 minutes) and the supernatant from the centrifuged mixture was carefully removed for optical density measurement.

Electrophoresis: The electrophoretic mobilities of the latex particles were measured using a Pen-Kem System 3000 electrokinetic analyser. All measurements were done at room temperature using 1 cm^3 of the diluted latex (0.05% w/v) in 20 cm^3 of barium chloride solution of known concentration.

Freeze-Thaw Stability: The freeze-thaw stability of the latices were estimated by a semi-quantitative method using optical density measurements (12). After freezing the diluted latex at -18°C for 3 days, they were allowed to thaw completely at room temperature. The samples were then lightly centrifuged and the optical density of the supernatant was measured. As a control, the same measurement was made for a similarly diluted sample left at room temperature. The ratio of the optical density of the supernatant after freeze-thaw conditions ($OD_{F/T}$), to that of similarly diluted latex which had not been subjected to freeze-thaw conditions (OD_O), was taken as the freeze-thaw stability ratio. Consequently, this ratio should vary from zero for an unstable latex, to unity for a completely stable latex.

$$\text{Freeze-Thaw Stability Ratio} = \frac{OD_{F/T}}{OD_O}$$

Glass Transition Temperature: The glass stansition temperatures (Tg) of the latices were measured using a DSC 1 Perkin Elmer differential scanning calorimeter. The measurements were carried out on vacuum dried latices at a heating rate of 16°C per minute.

3. RESULTS

Electron micrographs of particles from latex preparations PS* and PS-10 are shown in Figures 1a and 1b respectively. The number average diameters of the particles obtained from the electron micrographs are listed in Table 1 together with other information about the latices. The particles from PS* had a diameter of 180 ± 7 nm and those from PS-10 a diameter of 110 ± 15 nm.

The conductimetric titration curve obtained from latex PS* is illustrated in Figure 2. The form of the curve suggests the presence of both weak and strong acid groups on the particle surface, as anticipated from previous work using potassium persulphate as the initiator (5). The surface charge density was estimated to be 3.9 µC cm^{-2}. In the case of latex PS-10 no indication of surface groups was detected and the conductivity increase observed was simply that due to the addition of alkali. It was therefore concluded that the surface charge on this latex was zero or very close to it.

The stability of the latices to added electrolyte was examined turbidimetrically using barium chloride as the electrolyte. The results obtained are represented in Figure 3 in the form of optical density against the logarithm of the added electrolyte concentration. It can be seen from the data for the two latices that PS* coagulated at a barium chloride concentration of 2.1×10^{-2} mol dm^{-3}, whereas PS-10 remained unchanged up to concentrations of 7.5×10^{-1} mol dm^{-3} barium chloride. The small increase in optical density shown in Figure 3 for latex PS* has been observed previously in studies of this type and was attributed to the presence of small aggregates resulting from slow coagulation (11).

Electrophoretic mobility measurements were also made on dilute dispersions of both latices and the results are illustrated in Figure 4 as electrophoretic mobility against the logarithm of barium chloride

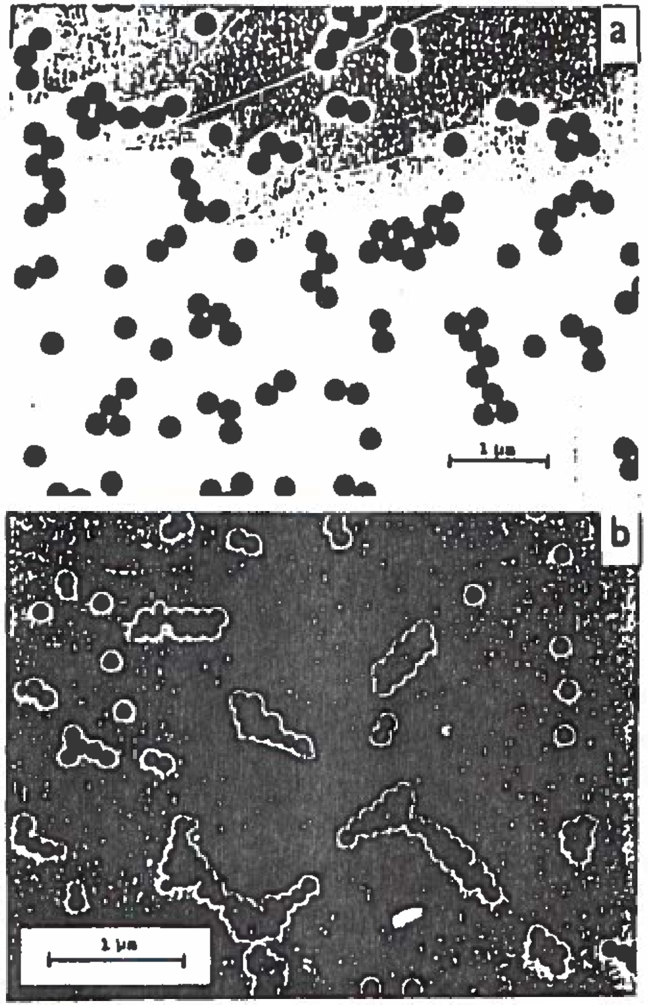

Figure 1: Transmission electron micrographs of ,
a) latex PS*; b) latex PS10.

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Table 1

Polymerisation Recipes and other Details of PS* and PS-10 Latices

Material	Charge Stabilised Latex-PS* (mol dm^{-3} x 10^3)	Sterically Stabilised Latex-PS-10 (mol dm^{-3} x 10^3)
Styrene	1920.0	770.0
Manoxal MA	21.2	-
Lavelan P208	-	6.50
Methoxy polyethylene glycol methacrylate	-	4.10
Sodium bicarbonate	16.7	-
Potassium persulphate	5.34	-
Ascorbic acid	-	1.12
Hydrogen peroxide	-	3.56
Total volume	260 cm^3	250 cm^3
Temperature	80°C	60°C
Polymerisation time	18 h	3 h
% Conversion	98	95
Weight average particle diameter	190 nm	110 nm
Standard deviation of the mean	6.8	15.5

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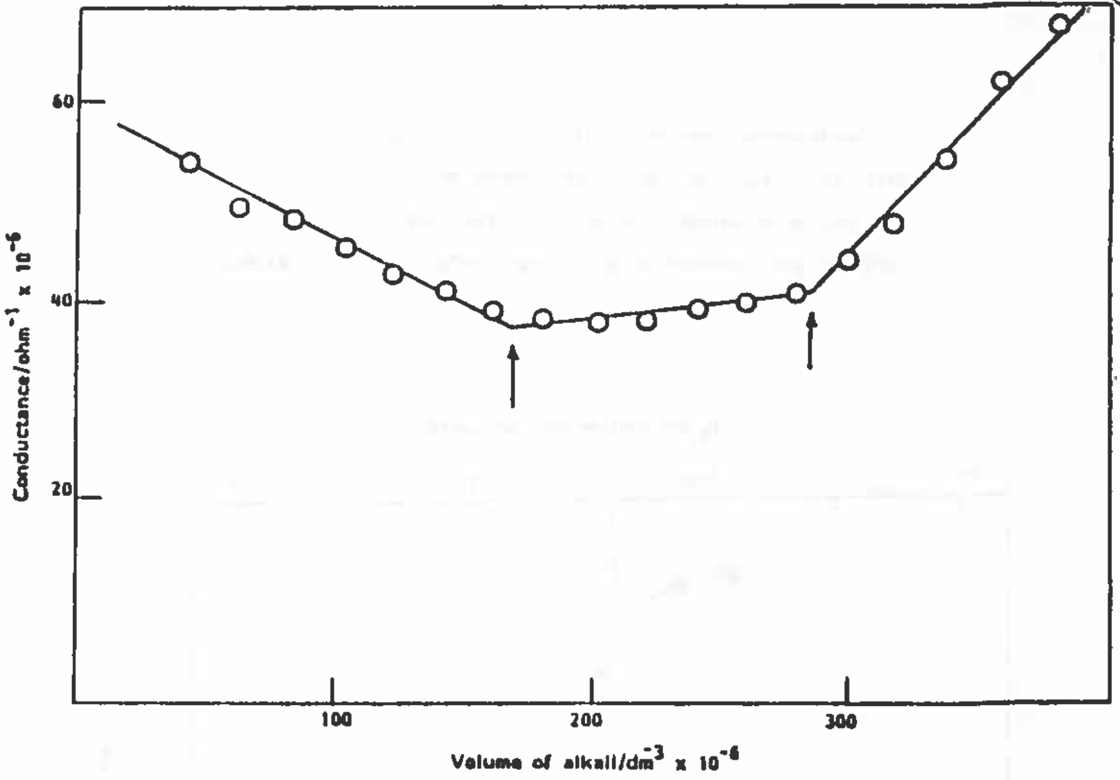

Figure 2: Conductimetric titration curve for latex PS*. ↑, indicate neutralisation points.

concentration. As anticipated in view of the conductimetric titration data and the clear evidence that the latex particles of PS* had charged end-groups on the surface, the particles of this latex exhibited the highest mobilities. At the critical coagulation concentration for barium chloride, 2.1 x 10^{-2} mol dm^{-3}, the mobility was found to be -1.8 μm m V^{-1} s^{-1}. The particles of latex PS-10 also exhibited an electrophoretic mobility, which was lower than observed with particles of PS*, but also varied with barium chloride concentration. This result is not unexpected since for particles of low inherent charge it is often found that negative adsorption of cations occurs leaving an excess of anions near the particle surface (13).

The freeze-thaw stability results obtained are given in Table 2. For the charge-stabilised latex PS* a ratio close to zero was obtained indicating that it became colloidally unstable following a freeze-thaw cycle. This is a consequence of the fact that as ice crystallises out, the concentration of electrolyte increases and exceeds the critical coagulation concentration of the latex. As further ice separates out the particles are forced together in the primary minimum. For the methoxy polyethylene glycol stabilised latex PS-10, however, the experimental ratio obtained lay in the mid-range implying a reasonable stability to freeze-thaw conditions. This is consistent with the colloidal stability experienced at high electrolyte concentrations and confirms the operation of steric stabilisation under frozen conditions. It also confirms that the stabilising chains of methoxy polyethylene glycol are firmly anchored to the surface of the particle, since it would be anticipated under these conditions, nonionic surface active agent would be desorbed from the surface.

Table 2

Freeze-Thaw Stability Ratios and Glass Transition Temperatures of PS* and PS-10 latices

Latex	Freeze-Thaw Stability Ratio	Glass Transition Temperature (°C)
PS*	0.03	103
PS-10	0.60	77

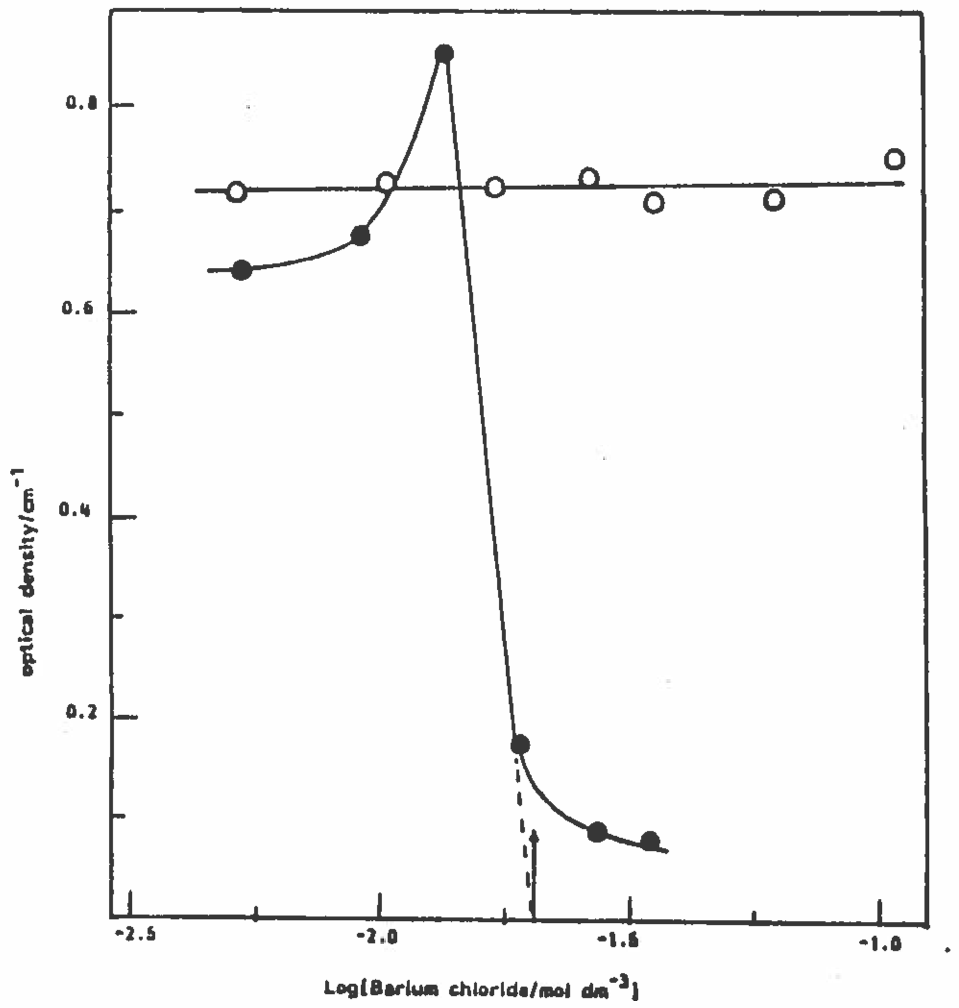

Figure 3: Optical density of latex supernatant 2h after adding electrolyte against logarithm of barium chloride concentration. —●—, latex PS*; —○—, latex PS 10; ↑, critical coagulation concentration.

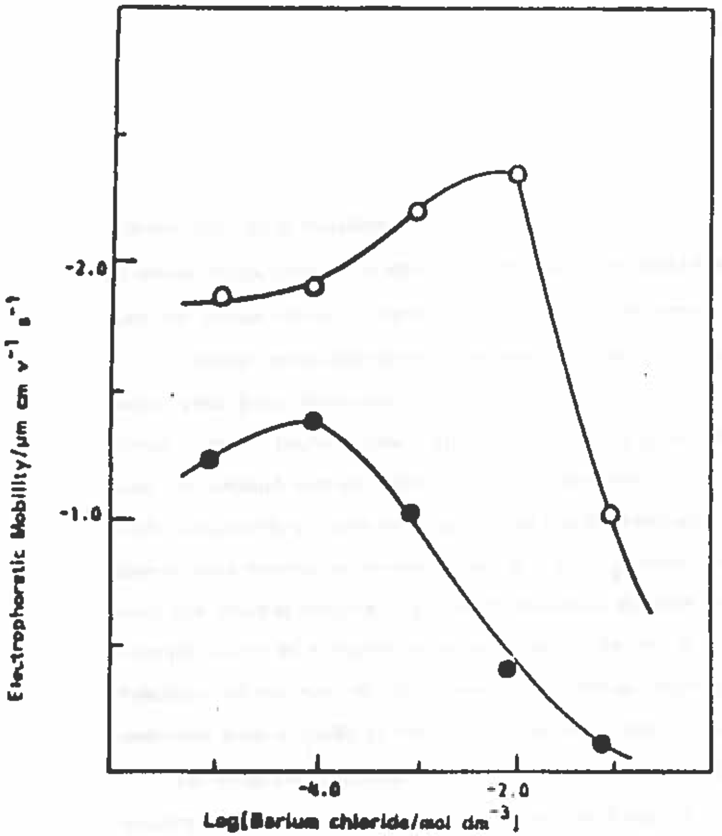

Figure 4: Eletrophoretic mobility against logarithm of barium chloride concentration. —○—, latex PS*; —●—, latex PS 10.

Some additional evidence for differences in the prepared latices was obtained from measuring the glass transition temperature by differential scanning calorimetry. The results are shown in Figure 5 and Table 2. For latex PS* the Tg occurred at the temperature normally expected for polystyrene. In the case of PS-10 a substantial decrease in the Tg was observed with PS*. These results appear to indicate that either the comonomer/stabiliser or the nonionic surface active agent are able to plasticise the polymer chains in the particles, a result which will be discussed in a later publication (14).

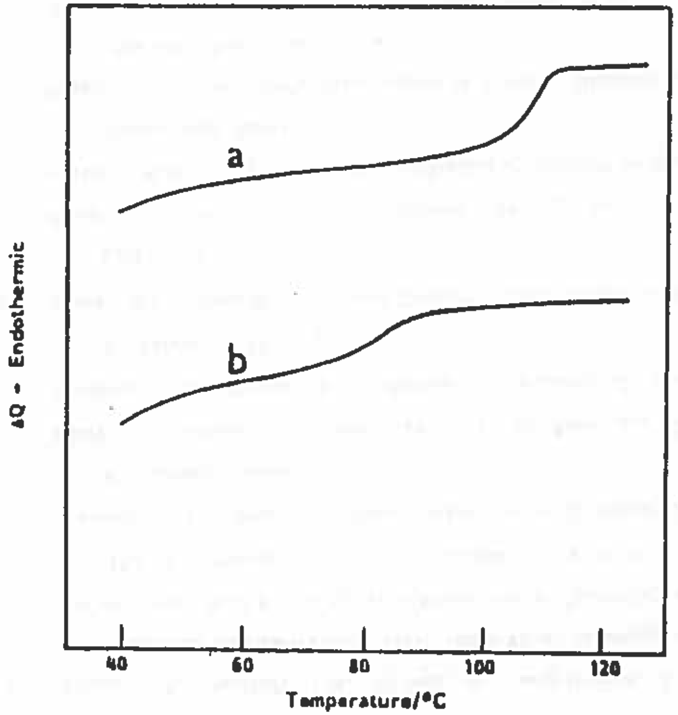

Figure 5: Thermograms obtained by differential scanning calorimetry for. a) PS* b) PS 10.

DISCUSSION

A method has been developed, using methoxy polyethylene glycol methacrylate as a comonomer/stabiliser in the presence of a nonionic surface active agent, for the preparation of non-surface charged polystyrene latices. The particles as prepared exhibited no titrateable charge and were stable at barium chloride concentrations of 7.5×10^{-1} mol dm^{-3}. In addition they were colloidally stable at temperatures up to 90°C and to freeze-thaw cycling. The evidence obtained suggests that the methoxy polyethylene glycol chains are grafted to the particle surface and effectively sterically stabilise the particles.

Although the particles of latex PS-10 exhibited electrophoretic mobilities over a range of electrolyte concentrations it seems most probable, in the view of the absence of titrateable charge, that the mobility arises as a consequence of a surface excess of anions occurring near the particle surface. The electrophoretic mobility in fact approaches zero at barium chloride concentration of 1×10^{-2} mol dm^{-3}, whereas the latex maintained colloidal stability to very high electrolyte concentrations. Had the mobility results simply been a consequence of movement of the plane of shear further from a charged surface, a titrateable charge would have been observed.

It seems reasonable to conclude therefore that the latex PS-10 had the properties of a nonionic latex. This latex showed excellent stability under conditions where the conventional charge-stabilised latex became colloidally unstable.

(34)

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CONTRIBUTION TO POLYMER COLLOID GROUP NEWSLETTER
FROM
LABORATOIRE DES MATERIAUX ORGANIQUES (CNRS)

2 OCT Rec'd

SUBMITTED BY C.PICHOT

1-STRUCTURE-PROPERTIES-SIMULATION IN EMULSION COPOLYMERS (B.Schlund-A.Cruz)

The research project is curently directed on the relationships between the morphology of latex particles and the mechanical properties of films.

A previous study was carried out with butyl acrylate (BuA) and vinyl acetate (VAcv) (x.z kong et al.). In this project, BuA and styrene (S) were copolymerized in various proportions (0/100,25/75,50/50,75/25,100,0) and different polymerization processes were used: controlled batch, 1/2 continue addition, step-wise. Three types of morphology were synthesized homogeneous, core-shell (core: PS; shell: homogeneous copolymer PS/ABu),multi-layered (core: PS, shell 1: copolymer, shell 2: PABu).

Morphologies of such particles were observed by electron microscopy using various staining agents : OsO_4, RuO_4, phosphotungstic acid. Films were formed by casting latex onto pretested glass with silane. Resulting from coalescence and according to the particle morphology various organic composite films were obtained: composites with homogeneous inclusion , with composite inclusions and with composition gradient inclusions.Dynamic mechanical properties were carried out with viscoelasticimeter from METRAVIB C^{ie}. The complex YOUNG modulus were obtained as a function of temperature (-100 to 150 °c), (frequence = 7.8 Hz).

Simulation of the mechanical properties were performed using simple KERNER's and DICKIE's equations. The simulation should allow the prediction of the dynamic mechanical properties of latex films from the properties of homopolymers (PABu or PS) and processes of polymerization.

2-The following are abstracts of recent papers (submitted or in press)

I)Acrylonitrile-styrene copolymerisation:contribution to the azeotropy in emulsion (S.Djekhaba,C.Graillat,J.Guillot):Batch emulsion copolymerisation of styrene(S) and acrylonitrile (AN)have been carried out at various monomer feeds and solid s contents in order to check previous predictions derived from simulation computations.for monomer feed compositions with lower AN content than the azeotropic feed (33 mol %) studied by Dimonie et al ,homogeneous copolymers were obtained with the same composition as the feeds,but at lower solid contents ,in very good agreement with the theoritical optimum monomer(M)/water(W) ratios.In addition , as also predicted, above this optimum M/W ratio, the monomer feed composition drift is in the opposite direction than at lower M/W ratio , as the polymerization proceeds.Similar behavior is observed up to 40-43 mol %, at increasing solids contents.Above 43 mol% AN ,i.e the bulk or solution azotropic composition , azeotropes are not observed and the composition drift is always in the same direction ,viz in favor of copolymers richer and richer in styrene , whatever the M/W ratio.

II)Emulsifier-free emulsion copolymerisation of styrene and butyl acrylate (J.L. Guillaume,C.Pichot,J.Guillot)

I:KINETIC STUDIES IN THE ABSENCE OF SURFACTANT: Soapless emulsion copolymerisation of styrene(S) and butyl acrylate(BuA) has been investigated using two types of initiator and different comonomer feed mixtures.When using $K_2S_2O_8$ as initiator , the particle size and size distribution of the final latexes (respectively 500 nm and 1.003) is not significantly affected by the comonomer feed composition , whereas the molecular weight and surface characteristics were found to sharply change at high BuA content.Base on the most probable particle nucleation mechanism and type of chain termination in the monomer swollen particles , a tentative explanation of these results has been proposed.Replacing persulfate by a carboxylic initiator(sodium 4-4'- azobis cyanopentanoate) results in the formation of stable latexes with the same size then observed with persulfate, provided the aqeous phase ph is fixed in between 6 and 7.Results on the inititior residue location as a function of the conversion point out that the particle flocculation mechanism is strongly significant in the preparation of such latexes.

II:KINETIC STUDIES IN THE PRESENCE OF IONOGENIC COMONOMER: Batch emulsifier -free copolymerisation of S and BuA have been performed for a S/BuA weight ratio=50/50 in the presence of two types of functional monomers ,methacrylic acid(MAA) at two dofferent ph's or potassium sulfo propyl methacrylate(SPM) and two initiators(potassium and sodium4-4' azobiscyano pentanoate(AZO).The use of AZO/MAA system results in the formation of particles with only surface carboxylic end -groups .The particle size of the final latexes can be adjusted with the MAA concentration provided the polymerisation is carried out at ph>6.5.However the higher the MAA concentration , the sooner the polymerisation levels off in the conversion .With the $K_2S_2O_8$/SPM system , particles bearing only sulfate and sulfonate groups are produced and the polymerisation is completed . In that case, the particle size of the final latexes is smaller than in the previous system and 30% of the SPM is fixed on the surface instead of 10% with MAA. Using a too high SPM concentration results in the latex destabilization caused by the formation of a large amount of polyelectrolytes .Kinetic studies indicate that most of the functional monomer is incorporated onto the particle surface during the last 30% conversion of the polymerisation. A tentative explanation of such behavior is discussed based on the existance of two polymerisation loci in these systems.

III:KINETIC STUDIES IN THE PRESENCE OF A SURFACE ACTIVE COMONOMER, THE SODIUM ACRYLAMIDO UNDECANOATE: Emulsion terpolymerisation of S,BuA and sodium acrylamido undecanoate(AUA) have been carried out using a batch process in the presence of sodium 4-4' azobis cyanopentanoate as initiator.Varying the AUA concentration, stable particles bearing only carboxylic charges have been produced with diameters ranging from 200 nm to 500 nm at solids content as high as 30%. However a low AUA yield at the particle surface has been found(30 to 35%), which could be explained by very unfavorable reactivity ratios of AUA with S and BuA.Most of the AUA seems to be wasted in the water phase (unpolymerized and forming hydrosoluble chains).Furthermore ,a concentration of AUA higher than 10^{-2} mol results in the latex destabilization presumably caused by the formation of a large amount of polyelectrolytes.Kinetic studies of the AUA consumption show that AUA is mostly fixed at the particle surface between 90 and 100% conversion which indicates that the AUA is mainly polymerized in the water phase and not at the particle surface.An attempt has been made to increase the surface charge density by polymerizing a shell of AUA/S/BuA on a seed latex.It turned out to be unsuccessfull (low surface yield,formation of new particles).

Contribution to Polymer Colloids Newsletter

Case Western Reserve University

September 5, 1986

23 SEP Recd

The polymer colloids group at CWRU has as its faculty members I. M. Krieger, M. H. Litt and S. Qutubuddin. This group has not reported recently to the Newsletter, so that a survey is timely.

Rheology: Gerald Choi's doctoral thesis on Rheology of Sterically Stabilized Dispersions has just appeared in two papers (J. Colloid & Interface Sci. 113, 94-100, 101-120 (1986)). A new student (H.-L. Lu) has started a continuation of this research, to include dispersions and solutions which contain dissolved polymers. He has just received samples of the poly(dimethylsiloxane)/polystyrene/poly(dimethylsiloxane) triblock copolymers which were prepared for us by Dr. E. M. Firer at the University of Akron.

Emulsion Polymerization Studies: Short-chain diblock copolymers were prepared by ring-opening polymerization of substituted oxazolines in Professor Litt's laboratory. When these were used as stabilizers in the emulsion polymerization of styrene, the result was a solid which consisted of water droplets in polymerized styrene. Similar results have been reported by G. Riess at Mulhouse. Solid dispersions were obtained containing as high as 95 volume % water. Under vacuum, the water evaporates, leaving a microporous foam. Papers describing this process have been prepared for the Journal of Colloid and Interface Science, for which abstracts are appended to this report. This research, initially funded by the Center for Adhesives, Sealants and Coatings (CASC) at CWRU, is now funded by the Lawrence Livermore Laboratories of the U.S. Department of Energy.

Syed Qutubuddin: There is some research related to polymer colloids in our Department of Chemical Engineering under Professor Syed Qutubuddin. Syed is investigating interactions between dispersed pigments and soluble binders, and also is initiating a program of research on microemulsions.

Finally, it should be added that I. M. Krieger will be on sabbatical leave from January through July of 1987, in Mulhouse, France. He will be working officially with Professor Riess at the Ecole Nationale Superieure de Chimie de Mulhouse, but will be working also with Professor Claude Wolff on Rheology of Dispersions, and hopes to interact also with the CNRS on the Physical Chemistry of Solid Surfaces. He will also be visiting many academic and industrial laboratories in Europe on behalf of CASC.

LOW SURFACE ENERGY POLYMERS AND SURFACE ACTIVE BLOCK POLYMERS
I. t-Butylphenyl Containing Polymers

Morton Litt, Tien-Teh Chen, *Bing R. Hsieh
Department of Macromolecular Science and Center for Adhesives, Sealants and Coatings, Case Western Reserve University, Cleveland, Ohio

Two new monomers in the 2-oxazoline series were synthesized and polymerized. These were 2-[4-(t-butyl)phenyl]-2-oxazoline (I) and 2-[(3,5-di-t-butyl)phenoxy)propyl]-2-oxazoline (II). The polymer from I crystallized readily during bulk polymerization and showed T_m at 592°K (319°C). After annealing, the polymer showed a critical surface tension of 23.2 dynes/cm. Polymer from II was amorphous; hence, annealing showed little effect on contact angles. Block polymers were made with I (X_n=10) and ethyl oxazoline (X_n=6,20,60). Very sharp molecular weight distributions were obtained. All samples crystallized when annealed. Surface tension measurements in glycol-water mixtures showed maximum activity at 60% water. The block polymer was an effective emulsifier for emulsion polymerization of butyl acrylate at 0.1%.

LOW SURFACE ENERGY POLYMERS AND SURFACE-ACTIVE BLOCK POLYMERS
II. Rigid Microporous Foams by Emulsion Polymerication

Bing R. Hsieh and Morton H. Litt, Irvin M. Krieger,
H. L. Lu and T. T. Chen
Departments of Macromolecular Science and Chemistry
and Center for Adhesives, Sealants and Coatings
Case Western Reserve University, Cleveland, Ohio

Block polymerization of different weight ratios of 2-(p-t-butylphenyl)-2-oxazoline (B) and 2-ethyl-2-oxazoline (E) with methyl p-nitrobenzenesulfonate as the initiator gave diblock co-oligomers with narrow molecular weight distributions in 100% yields. Co-oligomers with 40-50 wt% of B were excellent inverse emulsifiers for styrene/water (St/W) polymerizations. Water-in-oil solid emulsions with internal phase ratio as high as 90% have been obtained using small amounts of the oligomers (> 1 wt% of the total system). The total surface area of the water droplets is approximately proportional to the number of surfactant molecules, and thus the average pore diameter is proportional to the water volume divided by the surfactant concentration. For any given St/W volume ratio, there is a maximum amount of emulsifier which can produce stable solid foams; higher amounts cause the emulsions to break.

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Department of Chemistry

01 OCT

NMR STUDIES OF XENON AND COBALT AS A PROBE OF ASSOCIATED POLYETHYLENE OXIDE POLYMER-SURFACTANT MIXTURES. S.M. Hosseini and R.L. Rowell, 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_{12} or C_{16}). 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 arises mostly from Van der Waals interactions. Natural Xenon gas contains two isotopes suitable for NMR studies: $^{129}X_e$ with $I = \frac{1}{2}$ and $^{131}X_e$ with $I = \frac{3}{2}$. ^{59}Co NMR shift of solubilizate Co(acac)$_3$ in the aqueous polymer solution has also been studied. $^{129}X_e$ and ^{59}Co shifts and $^{131}X_e$ relaxation time T_1 vs. concentration of aqueous solutions of polymer are presented, along with preliminary results of surface tension and visible adsorption studies.

*Presented at the American Chemical Society Meeting, Anaheim, CA, September, 1986.

THE PARTIAL VOLUME AS A PROBE OF THE INTRINSIC PROPERTIES OF BINARY MIXTURES INCLUDING BOTH COLLOIDAL AND TRUE SOLUTIONS. R.L. Rowell, Department of Chemistry, University of Massachusetts, Amherst, MA 01003.*

It is shown that the mass fraction is the most general independent variable to choose for the determination of the partial properties of mixtures. The methods of differential calculus are used to obtain exact relationships that are true at constant composition at any instant of time. The theory may be used to explore time-dependent changes that occur in a variety of systems, such as wetting, pore penetration, gas evolution from micropores and in general any interaction that leads to changes in the partial volume properties.

*Presented at the Colloid and Surface Science Symposium, Atlanta, June, 1986. To be published in the special issue of COLLOIDS AND SURFACES dedicated to the memory of Geoffrey Parfitt, 1986.

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Princeton University

15 SEP Recd

Recent Publications:

"Nonequilibrium statistical mechanics of concentrated colloidal dispersions: Hard spheres in weak flows", J. Chem. Phys. 84, 1815 (1986) [with A. P. Gast].

"An experimental and theoretical study of phase transitions in the polystyrene latex and hydroxyethylcellulose system", J. Colloid Interface Sci. 109, 161 (1986) [with A. P. Gast and C. K. Hall].

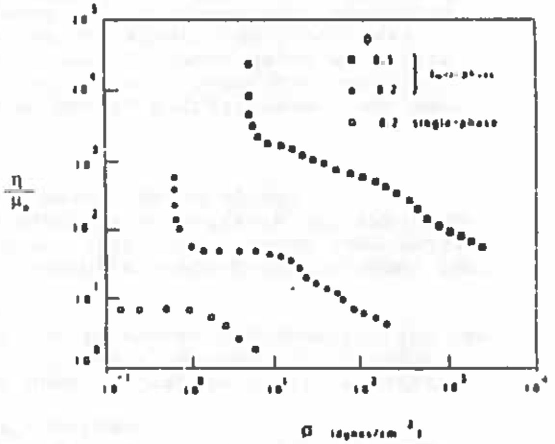
"On the theory of dilute polyelectrolyte solutions: Extensions, refinements, and experimental tests", J. Poly. Sci. B 24, 511 (1986), [with R. H. Davis].

Papers Presented at Meetings:

1. Society of Rheology Meeting, Tulsa Oklahoma, 1986.
"Rheology of Phase Separated Colloidal Suspensions: Theory and Experiments". P. D. Patel and W. B. Russel.

Addition of polymer to an otherwise homogeneous colloidal suspension causes a phase separation which depends on the size of the polymer and the particle, the charge on the particle, and the solution ionic strength.

Present work examines the rheological behavior of these systems both near the phase boundary where an equilibrium state exists and well into the two-phase region where the strong attractions produce a non-equilibrium structure. A self consistent field theory incorporating both hydrodynamic and thermodynamic interactions predicts the structure both at rest and under flow, determining rheological parameters such as low shear viscosity, modulus, and plastic flow behavior. The theory is complemented by experiments on a system of polystyrene lattices containing fractionated dextran.

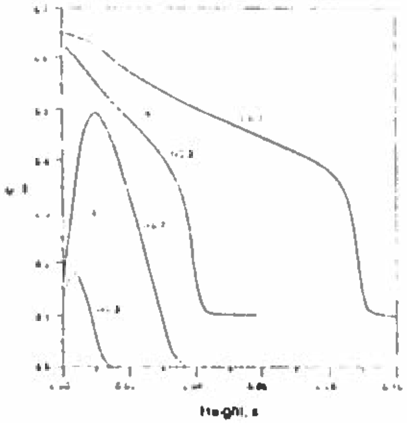


Steady shear viscosity as a function of applied stress for polystyrene latices in dextran/water solution.

2. Conference on Ceramic Powder Technology and Science, Boston, Massachusetts, August 1986. "A Model of Crystal Growth in the Sedimentation and Ultrafiltration of Colloidal Hard Spheres." K. E. Davis and W. B. Russel.

Processes typically used to concentrate colloidal suspensions include ultrafiltration, slip casting, and sedimentation. Understanding of morphological evolution in these systems is pertinent due to the strong influence of microstructure on final product performance characteristics.

These processes share a common mathematical description. Previous theories have dealt primarily with the dilute phases, treating the filter cake or sediment as an incompressible solid. Here we present a conservation equation valid throughout the dilute and dense phases. An appropriate theoretical equation of state for the osmotic compressibility and a simple correlation for the sedimentation coefficient for hard spheres apply over the entire range of concentration.



Volume fraction ϕ and degree of crystallinity f as functions of position and time during sedimentation.

Numerical solutions of the governing equation for moderate Peclet numbers, characterizing the ratio of sedimentation to diffusion, complement matched asymptotic expansions valid at large Peclet numbers. These solutions indicate a nearly uniform concentration in the dense phase, becoming more compressible and less uniform with decreasing Peclet number. The dilute phase increases in concentration as the Peclet number decreases, while the transition layer between these phases becomes broader. An exact equilibrium solution provides the long time limit.

This macroscopic description has been coupled with a microscopic model for the growth of crystallites within the filter cake or sediment. Solutions indicate that rapid sedimentation results in a disordered sediment, whereas slower rates result eventually in full crystallinity, in qualitative agreement with observations.

T-2

Newsletter Contribution
from The University of Akron

The Use of Poly(p-methylstyrene-g-oxyethylene) as a Polymeric Surfactant

17 SEP Recd

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Introduction

Steric stabilization of colloidal particles is achieved by macromolecules that are attached to the particle. The most effective stabilizers are amphipathic block or graft copolymers[1]. For stabilization in aqueous media, poly(ethylene oxide) is often used as the soluble moiety of the copolymer.

Various methods have been used to prepare graft copolymers containing ethylene oxide[2,3,4]. At present the ability of these graft copolymers to stabilize latices in emulsion polymerization has not been thoroughly investigated.

Graft copolymers of poly(p-methylstyrene-g-oxyethylene) have been prepared using a "grafting onto" technique. These amphiphilic copolymers have been shown to be suitable surfactants for the emulsion polymerization of styrene and methyl methacrylate.

Experimental

First, anionically produced poly(p-methylstyrene) was partially brominated in the methyl position with N-bromosuccinimide (NBS) in carbon tetrachloride using benzoyl peroxide as an initiator. Next, poly(ethylene glycol methyl ether) (MW 2,000) was coupled onto the brominated backbone in the presence of potassium tertiary butoxide and 18-crown-6-ether in dry THF. The copolymer was then fractionated using an acetone/hexane solvent mixture. By varying the amount of sites brominated, the amount of polyethylene oxide grafted on could be controlled. The molecular weights of the starting material and the percent polyethylene oxide grafted on as determined by T-60 NMR are given in Table I.

Emulsion Polymerization

The polymerization recipe is shown in Table II. In the present study styrene and methyl methacrylate monomers were both investigated.

Results and Discussion

Using surfactant D (see Table I), the effect of the polymeric surfactant concentration on the emulsion polymerization of styrene was investigated. The monomer conversion versus time curves are shown in Figure 1 for surfactant concentrations of 7-30 phm. The latex prepared at 7 phm coagulated at a conversion of less than 40%. From the constant rate regions in the curves for 13 to 30 phm, the rate of polymerization was found to increase with increasing emulsifier concentration, whereas the particle size found from electron microscopy was found to decrease (see Figure 2).

The effect of varying the backbone length with constant PEO content was studied using surfactants A, B and D. For the emulsion polymerization of styrene at an emulsifier concentration of 18 phr, all three surfactants gave similar results: Rp ~3.2 x 10^{-4} mol/ℓ sec and particle size ($\bar{D}_n$) ~53 nm.

Using surfactants B and C, the effect of varying the PEO content for the same backbone was investigated. Surfactant B (81% PEO content) gave a rate of 3.2 x 10^{-4} mol/ℓ sec and particle size ($\bar{D}_n$) 53 nm, whereas for surfactant C (70% PEO) a rate of 2.6 x 10^{-4} mol/ℓ sec and size of 88 nm was obtained.

The emulsion polymerization of methyl methacrylate was investigated using 18 phr of surfactant B. The rate of polymerization was found to be 8.7 x 10^{-4} mol/ℓ sec and the particle size ($\bar{D}_n$) 42 nm.

Conclusions

(1) Poly(p-methylstyrene-g-oxyethylene) was synthesized by grafting poly(ethylene glycol methyl ether) onto partially brominated poly-(p-methylstyrene).
(2) This copolymer was successfully used to prepare stable latices in the emulsion polymerization of styrene.
(3) The rate of polymerization increased and particle site decreased with increasing emulsifier content.
(4) For the range studied, varying the backbone length of the polymeric surfactant at constant PEO content had no influence on the rate or particle size.
(5) Decreasing the PEO content at a constant backbone length resulted in a decrease in polymerization rate and particle size.
(6) The polymeric surfactant also stabilized poly(methyl methacrylate). The rate of polymerization for MMA was found to be faster and particle size smaller than that found for styrene.

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TABLE I

Characterization of the Polymeric Surfactants

M_n	PMeSty backbone (by GPC)	wt. % PEO in surfactant (by NMR)
A	1100	82
B	4300	81
C	4300	70
D	24000	81

Note: $CH_3(OCH_2CH_2)OH$ MW = 2000

TABLE II

General Recipe for Emulsion Polymerization

Material	Weight (grams)
Polymeric surfactant	7-30
Monomer	100
Water	666
Initiator ($K_2S_2O_8$)	1.3

Polymerization Temperature 50°C

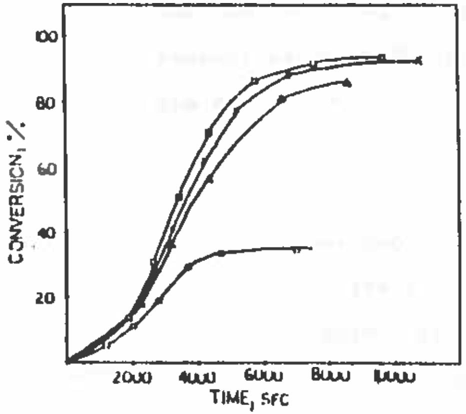

Figure 1. Polymerization of styrene at different surfactant concentrations (phm). ○-7, △-13, ●-18, □-30

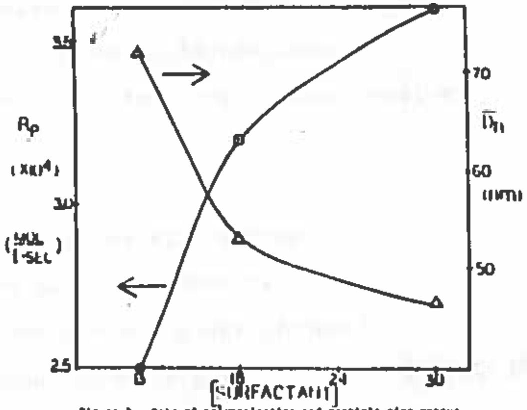

Figure 2. Rate of polymerization and particle size versus surfactant concentration

THE APPLICATION OF THE HIGH SPEED INTEGRATED COMPUTERIZED HYDRODYNAMIC CHROMATOGRAPHY FOR MONITORING PARTICLE GROWTH DURING LATEX POLYMERIZATION*

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29 SEP Recd

In the earlier publications (1,2), it was shown how hydrodynamic chromatography (HDC) could be applied in the study of polymer latexes to determine particle-size. An improved technique for the HDC was developed which utilized higher efficiency and resolving power columns to significantly reduce the analysis time (3). A high speed integrated computer was included in this improvement so that both particle-size and particle-size distribution of latexes could be quantified in the relatively short period of time. This high speed computerized version of the HDC has been used extensively for measurements on the final latex.

There is considerable interest in monitoring an emulsion polymerization by following the growth rate of latex particles. It is well known that in addition to a well-controlled particle growth pattern significant deviations can result from particle association or nucleation during the growth stage. A method which would define when such deviations occur during the latex polymerization would be of obvious value and would lead possibly to more efficient optimizations of different latex polymerizations.

The computerized hydrodynamic chromatograph (HDC) technique has been used successfully to detect agglomeration and new-particle generation as significant deviations from the controlled particle growth during latex polymerizations. It was possible to use this high speed integrated computerized HDC technique to determine when these deviations started and how the growth pattern developed during the polymerization. Transmission electron micrograph data supported the results by the computerized HDC analysis.

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*Presented at the Fall 1985 ACS Meeting, Chicago, IL. Polymeric Materials Science and Engineering Div. Proceedings 53, 440 (1985). "To be published in ACS Symposium Series."

701

YKI YTKEMISKA INSTITUTET
Institute for Surface Chemistry

POLYMERIZABLE SURFACTANTS

6 OCT Recd

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The aim of this work is to investigate the surface chemical properties of surfactants that can be polymerized to macromolecules after the adsorption at an interface. The expected advantages of this type of chemicals are a lower tendency for desorption and foaming. They also offer possibilities to obtain interfacial membranes with controlled permeability, i.e. encapsulating membranes.

One class of polymerizable surfactants we have been investigating is quaternary ammonium compounds containing a vinyl group as the polymerizable unit, e.g. cetylvinylbenzyldimethyl ammonium chloride (CVDAC). CVDAC is obtained by refluxing cetyldimethylamin and vinylbenzylchloride in acetonic solution. CVDAC is very powerful in reducing the surface tension of water at low concentrations. The critical micelle concentration, cmc, is considerably lower compared to that of similar substances containing only one hydrocarbon chain, figure 1. The pronounced surface activity is further reflected in a strong adsorption on polystyrene latex.

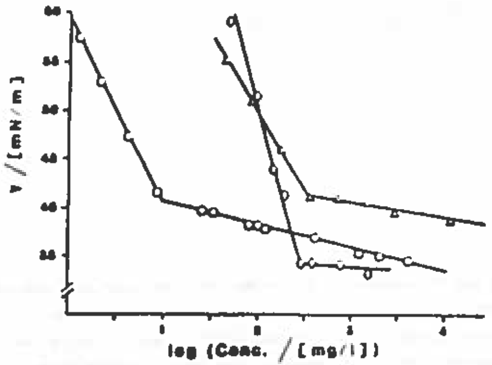

Figure 1. Surface tension at 25°C as function of concentration cetylvinylbenzyl ammonium chloride (CVDAC) (O), cetylallyldimethyl ammonium chloride (Δ) and cetyltrimethyl ammonium bromide (◊) in water.

Figure 2 shows the effect of added CVDAC on the stability of a PVC-latex. As the surfactant concentration exceeds 1.5 mg/m^2 the mechanical stability rapidly increases to 100%, i.e. complete stability. On the other hand, CVDAC does not stabilize the latex when frozen, figure 2. This is to be expected since CVDAC stabilizes the latex electrostatically, while a sterical stabilization mechanism is a necessity in order to achieve freeze-thaw stability.

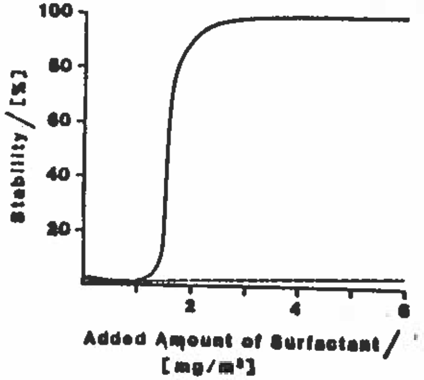

Figure 2. Mechanical stability (——) and freeze-thaw stability (------) of monodisperse PVC-latex as fraction of added amount of cetylvinylbenzyldimethyl ammonium chloride (CVDAC) per unit latex surface area.

CVDAC is easily polymerizable both in aqueous solution and in suitable microemulsion systems. The evaluation of quaternary ammonium compounds of the vinylbenzyl type in emulsion polymerization of latex is in progress. This work is performed in collaboration with Åbo Akademi and the University of Lund (Professors Stenlund and Törnell, respectively).

Forces Between Surfaces Immersed in Aqueous Solutions

Thesis, Per M. Claesson, 1986

ABSTRACT

This thesis concerns interactions between surfaces immersed in aqueous solutions. It is based upon direct force measurements between molecularly smooth modified mica surfaces. The forces acting between the surfaces depend on both surface modifications and solution compositions.

Between mica surfaces immersed in aqueous solutions of symmetric quarternary ammonium bromides repulsive double-layer forces dominate the long-range interaction (Paper I). The resulting forces are similar to the ones measured between mica surfaces in solutions of simple monovalent electrolytes. However, with quarternary ammonium ions as counterions the double-layer forces are somewhat weaker, and an effect of the ion size on the forces is observed at small separations.

When coating a mica surface with a hydrophobic thightly packed layer of dimethyldioctadecyl ammonium ions ($DDOA^+$), and measuring the interactions between such a surface and a bare mica surface in aqueous KBr solutions one observes purely attractive forces (Paper III). These forces are, at least to the largest extent, attractive double-layer forces.

Between two mica surfaces hydrophobised with $DDOA^+$ ions the attractive short-range forces ($D < 25$ nm) observed in aqueous solutions are far too strong to be explained by conventional DLVO theory (Paper II). (With conventional DLVO theory is meant van der Waals forces in the Lifshitz-approximation and double-layer forces in the Poisson-Boltzmann approximation.) The origin of this force is not clear, but such a force has been observed between all hydrophobic surfaces investigated. This indicates that its origin might be overlapping regions with an enhanced but dynamic water structure.

When pentaoxyethylene dodecyl ether surfactants, $C_{12}E_5$, adsorb on to $DDOA^+$-coated mica surfaces the long-range hydrophobic attraction observed between such surfaces disappears (Paper IV). Instead, the force measured between ethylene oxide surfactant covered surfaces has a marked temperature dependence at separations less than about 4 nm. With increasing temperature the force becomes more attractive or less repulsive depending on temperature and surface separation.

Forces were also measured in Polyethyleneoxide-lysine solutions in order to investigate the effect of oligomeric ethylene oxide chains on the interaction between surfaces (Paper V). The positively charged lysine group served to anchored the about 43 unit ethylene oxide chain to the mica surface. Purely repulsive forces, which changed dramatically with the addition of salt and with temperature, were observed.

ESCA has been used for characterizing modified mica surfaces. Inorganic ion adsorption has been investigated (Paper VI). Results supporting the hypothesis that adsorption of hydrated cations on the mica surface causes the appearance of repulsive hydration forces were obtained.

In order to quantitatively determine surfactant adsorption on mica by means of ESCA the known number of exchangeable ions on the basal plane can be used as an internal standard (Paper VII). The adsorption of primary alkylammonium surfactants from solutions was investigated as well as Langmuir-Blodgett monolayers of $DDOA^+$ ions.

1. PAPERS INCLUDED IN THE THESIS

I Claesson, P.M., Horn, R.G. and Pashley, R.M.,
"Measurements of Surface Forces between Mica Sheets Immersed in Aqueous Quaternary Ammonium Ion Solutions",
J. Colloid Interface Sci. 100, 250 (1984).

II Claesson, P.M., Blom, C.E., Herder, P.C. and Ninham, B.W.,
"Interactions between Waterstable Hydrophobic Langmuir-Blodgett Monolayers on Mica",
J. Colloid Interface Sci., in press.

III Claesson, P.M., Herder, P.C., Blom, C.E. and Ninham, B.W.,
"Interactions between Dissimilar Surfaces: One Positively Charged Hydrophobic Surface and One Negatively Charged Hydrophilic Surface",
J. Colloid Interface Sci., submitted.

IV Claesson, P.M., Kjellander, R., Stenius, P. and Christenson, H.K.,
"Direct Measurements of Temperature-Dependent Interactions between Nonionic Surfactant Layers",
J. Chem. Soc. Faraday Trans. 1, in press.

V Claesson, P.M. and Gölander, C.G.,
"Direct Measurements of Steric Interactions between Mica Surfaces Covered with Electrostatically Bound Low Molecular Weight Poly(ethylene oxide)",
J. Colloid Interface Sci., submitted.

VI Claesson, P.M., Herder, P.C., Stenius, P., Eriksson, J.C. and Pashley, R.M.,
"An ESCA and AES Study of Ion-Exchange on the Basal Plane of Mica",
J. Colloid Interface Sci., 109, 31 (1986)

VII Herder, P.C., Claesson, P.M. and Blom, C.E.,
"Adsorption of Cationic Surfactants on Muscovite Mica as Quantified by Means of ESCA",
Preliminary manuscript.

Preparation and Properties of Functionalized Polymer Surfaces

Thesis, Carl-Gustaf Gölander, 1986

ABSTRACT

The experimental work described in this thesis deals with different techniques of introducing and characterizing functional groups on polymer surfaces and studies of the adsorption of some well-defined proteins on these surfaces.

By treating polyethylene (PE) in a mixture of $KMnO_4/H_2SO_4$, polar and ionic groups, especially hydroxy, hydroperoxy, carboxyl and sulphate groups were introduced in the surface, Paper I. The various functional groups were quantified by using ESCA analysis in combination with chemical derivatization reactions and a radiotracer technique.

Adsorption of colloidal particles composed of an ionic complex between heparin and hexadecylammoniumchloride, HDAHCl, was explored by ellipsometry, Paper II. The change of the thickness and the optical properties of the layer upon reacting the amine constituent with glutaraldehyde were also examined.

The heparin layer was chemically characterized by means of ESCA, Paper III. In particular the glutaraldehyde "stabilizing" reaction resulted in an extra peak in the deconvoluted N1s signal originating from the Schiffs base product formed. Albumin adsorbates on heparin and some additional surfaces were furthermore investigated.

Upon glutaraldehyde reacting polyethyleneimine, PEI, the adsorption to hydrophobic PE increased (ESCA) due to the stronger hydrophobic interaction, Paper IV. On a charged surface like mica this reaction was found to have a minor influence on the adsorbate thickness presumably since electrostatics dominates the interaction in that case.

Acrylic hydrogels containing amino-, carboxyl- and ethyleneoxide (EO) groups were prepared by photopolymerization, Paper V. While albumin adsorbed extensively on amino- as well as carboxyl functional hydrogels, exceptional low albumin adsorption was found for EO containing hydrogels. The EO content of the surface as measured by ESCA was correlated inversely to the contact angle of the layer. The albumin adsorption was likewise inversely related to the surface content of EO.

Interaction forces were measured between mica surfaces immersed in polyethyleneoxide-lysine solutions, Paper VI. The positively charged lysine group adsorbs electrostatically to the anionic sites on the mica surface. Only repulsive interaction forces were observed between the surfaces. The repulsion was drastically reduced upon adding salt or raising the temperature.

Adsorption of albumin, globulin, fibrinogen and polylysine on PVC, a polymethacrylic acid/methacrylate copolymer and surfaces covered with covalently bonded PEO was studied by ellipsometry, Paper VII. The isotherm shapes could partially be accounted for by considering i) the different shapes and possible orientations of the proteins at the interface and ii) the different expected sizes of the hydrophobic and electrostatic contributions to the interaction. In particular on hydrophilic PEO surfaces very low extent of protein adsorption was generally recorded.

2. PUBLICATIONS INCLUDED IN THE THESIS

The thesis is based on the following publications which will be referred to by Roman numerals.

I Characterisation of $KMnO_4/H_2SO_4$ Oxidized Polyethylene Surfaces by Means of ESCA and ^{45}Ca Adsorption.
Eriksson, J C, Gölander, C G, Baszkin, A and Ter-Minassian-Saraga
J. Colloid Interface Sci. 100, 2 (1984).

II Heparin Surface Film Formation Through Adsorption of Colloidal Particles Studied by Ellipsometry and Scanning Electron Microscopy.
Gölander, C G, Arwin, H, Eriksson, J C, Lundström, I and Larsson, R
Colloids and Surfaces, 5 (1982) 1-16.

III ESCA Studies of Heparinized and Related Surfaces.
Lindberg, B, Maripuu, R, Siegbahn, K, Larsson, R, Gölander, C G and Eriksson, J C
J. Colloid Interface Sci. 95:2, 308-321 (1983).

IV ESCA-Studies of the Adsorption of Polyethyleneimine and Glutaraldehyde - Reacted Polyethylene imine on Polyethylene and Mica Surfaces.
Gölander, C G and Eriksson, J C
Submitted for publication in J. Colloid Interface Sci.

V Preparation and Protein Adsorption Properties of Photo Polymerized Hydrophilic Films Containing N-vinylpyrrolidone (NVP), Acrylic Acid (AA) or Ethyleneoxide (EO) Units.
Gölander, C G, Jönsson, S, Vladkova, T, Stenius, P and Eriksson, J C
Colloids and Surfaces. G D Parfitt Memorial Issue. Accepted.

VI Direct Measurements of Steric Interactions Between Mica Surfaces Covered with Electrostatically Bound Low Molecular Weight Poly(ethylene oxide).
Claesson, P M and Gölander, C G
J. Colloid Interface Sci. Accepted.

VII Protein adsorption to Functionalized and ESCA Characterised Polymer Films Studied by Ellipsometry.
Gölander, C G and Kiss, E
Submitted for publication in J. Colloid Interface Sci.

25 SEP Recd

Contribution to the Polymer Colloid Group Newsletter

Submitted by A. Vrij,
van t Hoff-Laboratory of Physical and Colloid Chemistry,
University of Utrecht, Padualaan 8, 3584 ch Utrecht.

We are synthesizing already for several years silica spheres which are made lyophilic ("oil-soluble") by etherification of the surface hydroxyls with octadecyl alcohol(1). The spheres which are in the colloidal size range of 20 to 300 nm, can be dispersed in organic solvents like cyclohexane and toluene.
To study interparticle interactions at high concentration we perform small-angle X-ray and neutron scattering experiments. The thesis of Moonen on this subject will be reported in the next issue of this letter. We report now on the theoretical study of the structure factor in such dispersions. This structure factor is analogeous to the structure factors found in simple liquids like argon.

$$S(K) = 1+4\pi\rho\int_0^\infty r^2[g(r)-1](\sin(Kr)/(Kr))\,dr$$

where g(r) is the radial distibution function.
One model to describe such systems is the hard sphere model. This model gives a good description of particles interacting with steep repulsive forces.
In colloids however, the particles are ,because of their nature, polydisperse in size (and therefore in scattering power) but also polydisperse in the hard-sphere size(=interaction range).
In the past we were able to solve this problem for polydisperse hard-sphere interactions in the (fairly good) Percus-Yevick approximation.
Recently we were able to check these calculations with computer simulations which were performed by Frenkel in collaboration with us (2). The results show that our theoretical equations fit very well with the Monte-Carlo simulations.
An example is shown in figure 1.

(1) A.K van Helden, J.W. Jansen and A. Vrij, J. Colloid Interface Sci., 81(1981)354.

(2) D. Frenkel, R.J. Vos, C.G. de Kruif, and A. Vrij, J. Chem. Phys. 84(1986)4625.

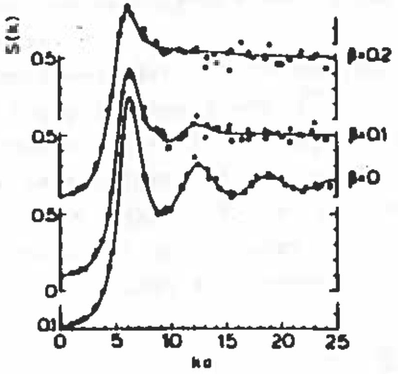

FIG. 2. Average structure factors for 108 homogeneous scattering spheres with diameters equal to those of the hard spheres. The scaling distance σ is defined as $(\overline{\sigma^3})^{1/3}$. The upper curve is a second sample taken from a log-normal distribution of β = 0.2. The volume fraction φ = 0.2.

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18 AUG Recd

ON THE MECHANISM OF FREE EMULSIFIER LATEX POLYMERIZATION

Eliseeva B.I., Aslamazova T.R.

The latex polymerization of methylmethacrylate (MMA) was studied in the absence of emulsifier to establish the role of initiation in the mechanism of the process. The initiation rate (V_{in}) in MMA polymerization kinetics (at the organic-aqueous phase ratio 1:9) was studied by changing temperature (T) and the concentration of the initiator-potassium persulfate (PSK) (C_{in}). It is known that the rate of initiator decomposition depends on C_{in} and T. The quantitative dependence for PSK was established in /1/. That dependence was used here to equalise the initiation rate at various concentrations of the initiator by changing temperature. The transition from the initiator decomposition rate to the initiation rate is valid as the formation of primary radicals occurred in the aqueous MMA solution of equal concentrations that corresponded to its maximum solubility 1.5%

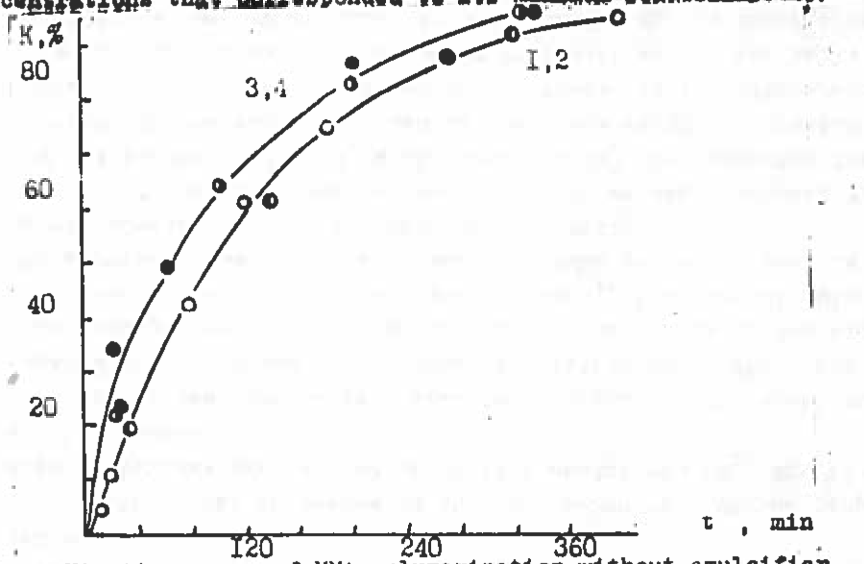

Fig.1. Kinetic curves of MMA polymerization without emulsifier. C_{in}, mg/l: ○-90, ◐-130, ◑-180, ●-260, T,K: 1.3-353; 2.4-348.

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* The polymerization kinetics was studied by sampling latex during the process and by chromatographically determining the residual monomer.

/2/. Thus, the initiation efficiency at different PSK concentrations in the experiments (table 1) may be assumed to be the same.

Fig.1 gives the kinetic curves of MMA polymerization for the two cases when the initiation rates were equalized by the change in T and C_{in}. It may be seen that the kinetic curves 1-2 and also 3-4 coincide at the same initiation rate but different T and C_{in}. It also follows that the overall rate increases with the increasing V_{in} similar to the homophase polymerization.

It must be noted that the increase in temperature should result in the increasing rates of the individual stages of the process. It has been pointed out /3/ for MMA homophase polymerization that at 5°C temperature rise the termination rate constant remains unchanged while the growth rate constant (K_p) increases by 1.1 times.

Table 1

The properties of latices synthesized under various temperatures and initiator concentrations

No[1]	Conditions of synthesis: T,K	C_{in},mg/I	Decomposition rate PSK.10^{10} mol/l.s	MM[2]	d, nm [3]	N.10^{-13}/cm^3 [3]	pH[**]
I	353	90	3.88	1380380	300	3.5	3.7
2	348	180	3.88	1412540	323	3.7.	3.0
3	353	130	5.62	1253140	285	6.8	3.2
4	348	260	5.62	1288250	281	6.0	3.0

1) No. of an experiment corresponds to the number of a kinetic curve in Fig.1.

2) The molecular mass of PMMA was determined viscosometrically in benzene solutions by Ubellode equation.

3) The number and size of particles was determined using the data of electron microscopy (EVM-100LK).

4) The universal ionometer EV-74 was used to determine pH of latices.

**) The latex pH values are in good agreement with the notion on PSK decomposition in aqueous solution and on the acidity of the ions formed in the process /5/. At C_{in} increasing from 90 to 260 mg/l the high concentrations of HSO_4^- ions are formed.

It may then be concluded (fig.1) that the change in K_p affects the process kinetics less than the initiation rate.

The different concentrations of electrolytes in the experiments (curves 1-2 and 3-4) do not noticeably affect the polymerization kinetics. Apparently this is due to their extremely low values.

Further, the influence on the initiation rate on the properties of latices synthesized in various conditions (C_{in} and T) was studied (table 1).

It follows from table 1 that the polymers of the equal molecular mass are formed at the equal initiation rate. Therefore, the identical polymerization kinetics in the conditions of the experiment was once more confirmed. When T and C_{in} increase stimulates the growth of the initiation rate, the PMMA molecular mass is reduced, similar to the homophase polymerization.

The table data draw attention to the relation between V_{in} and the number of formed latex particles (N). By comparing the experiments 1-2 and 3-4 it can be seen that at the initiation rate increased by 1.5 times N grows by 1.7 times. As the polymerization rate is proportional to the number of particles /4/ the table data corroborate once more that it is determined by the initiation rate at equal V_{in} the latices with near sizes of particles are formed. At higher initiation rate the particles are smaller. It means that

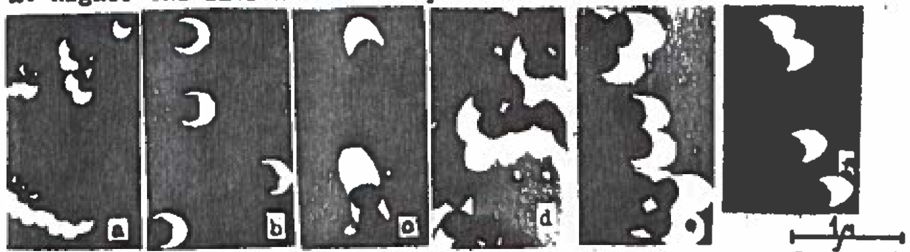

Fig.2. Electron microphotographs of MMA latex particles.Conversion during the process,%: a-5, b-12, c-42, d-75, e-95, f-100*

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*) The absence of regularity in the increase in particle size with conversion (fig.2) is due to the deformation of polymer-monomer particles swelled in monomer. Starting with appr. 28% conversion MMA polymerization proceeds in the swelled discrete particles due to th already absorbed monomer (fig.c,d,e,f).Therefore the particles in fig.c,d,e,f are near in size, while the dia of the final latex with 100% conversion (fig.f) is even slightly smaller due to the complete transformation of the absorbed monomer into polymer.

the concentration of nucleation centres is higher in the beginning of the process.

The electron microphotographs of particles formed in polymerization without emulsifier are given in fig.2 (in conditions of experiment 1 table 1). It is clear that the particles are mainly monodisperse starting with 5% conversion. Therefore, it may be concluded (fig.1 and 2) that polymerization mainly proceeds within the bulk of discrete particles, similar to the mechanism of micell polymerization /5/.

The kinetic data on MMA latex polymerization without emulsifi at low initiator concentrations show that the overall polymerization rate and the polymer molecular mass are determined by the ini ation rate. The process proceeds in the discrete substantially monodisperse particles. The number of particles grows with the incre in the initiation rate and determines the rate of polymerization.

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