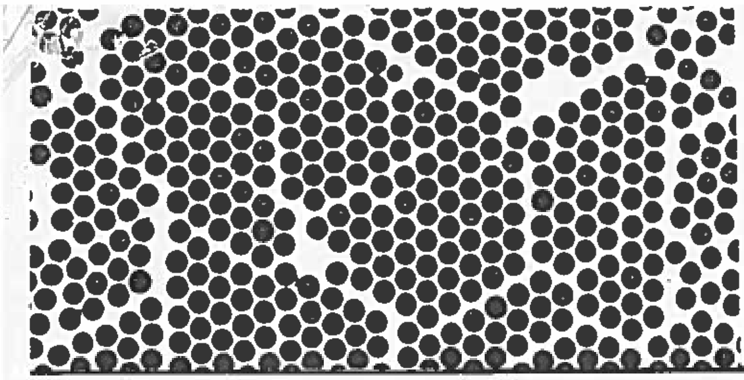

IPCG

INTERNATIONAL POLYMER COLLOIDS GROUP

24 OCT Recd

SEPTEMBER, 1988

VOLUME 19 NUMBER 2

NEWSLETTER

INDEX

CONTRIBUTIONS

FROM THE EDITOR'S DESK

Contributions

I must apologize for the lateness of the reminder notices sent to members regarding their contributions to this Newsletter. The excitement of Strasbourg clearly proved to be too much for my pacemaker (not to mention my CPU). I have delayed collating the contributions in the hope that I would not miss any. Chip Zukoski's contribution arrived too late for the May Newsletter (he had recently become a new father and claimed to 'be suffering from inexperience in that arena') and it was held over to now (belated congratulations, Chip).

Membership

At the recent General Meeting in Strasbourg, the following were invited to become members of the IPCG: Drs. J. M. Asua (Pais Vasco), J. Joosten (DSM), Do Ik Lee (Dow) and G. Riess (Mulhouse). My old cobber, Dr. T. W. Healy, unfortunately ceased to be a member for non-contributory reasons. I would like to welcome all the new members to the Group. Long may your contributions appear in the Newsletter. Membership now totals 46 (see lists).

Past Conferences

The NATO-sponsored Advanced Study Institute on Polymer Colloids in Strasbourg was an outstanding success due in no small measure to hard work of the dedicated organizing team of Francoise Candau/Ron Ottewill/Jean Proctor. We are all in their debt. Strasbourg turned on both delightful weather and an extraordinary fireworks display for the meeting (well, their 2000 year of settlement celebrations may have had something to do with the latter), as well as an exciting leg of the Tour de France. The Institute banquet will long be remembered for its delightful ambience and delicious food, as well as Irv Krieger's wonderfully witty poem (this is attached). The Mayoral reception at the Hotel de Ville would have done justice to Marie Antoinette for the lovely sweetbreads that were served (not to mention the wines). Ron Ottewill's mastery of the French language was most impressive. The tour of Alsace valley, with its picturesque, walled medieval towns, wonderful wineries (marred only by a slightly uncomplimentary reference to Australian wines!) and spectacular castles, will long be remembered (Theo van der Ven's translation of the tour guide's commentary was masterly). The evening boat tour of the canals, with its dramatic silhouettes and fairy lights, was a magic interlude. Incidentally, the lectures proved to be both broad ranging and stimulating and the appearance of the book containing many of them is eagerly awaited.

Future Conferences

The list of forthcoming conferences appears on the next page in a new format. Don't forget the Copolymerization Conference in Lyon, the 7th Gordon Conference in Andover and Polymer Latex III in London. Also please plan to attend the Vanderhoff symposium in 1990.

FAX & BITNET Numbers/Computer Programmes Exchange

Please complete the attached forms and return them to me as soon as possible.

Next Newsletter

Contributions to be forwarded to me by AIRMAIL by 30 April, 1989.

D. H. Napper
Secretary

SCHEDULE OF MEETINGS

1989

Meeting/Course	Location	Date(s)	Contact
Copolymerization Symposium	Lyon	3-7 April	C. Pichot
Heterogeneous Polymerization Microsymposium	Smolenice	10-14 April	J. Barton, Bratislava
20th Annual Short Course	Lehigh Uni	5-9 June	M.El-Aasser
Polymer Latex III	London	27-28 June	A.S. Dunn
7th Gordon Conference	Proctor Academy Andover	9-14 July	I. Piirma
Lehigh European Short Course	Davos	21-25 Aug.	M.El-Aasser
ACS National Meeting	Miami Beach	10-15 Sept.	-
PAC-CHEM	Hawaii	14-16 Dec.	M.Croucher D.H.Napper

1990

Meeting/Course	Location	Date(s)	Contact
ACS National Meeting	Boston	22-27 April	-
Vanderhoff Symposium (part of 64th Colloid & Surface Science Symposium)	Lehigh Uni	18-20 June	M.El-Aasser
IUPAC Polymers	Toronto	8-13 July	T.van de Ven
ACS National Meeting	Washington	26-31 Aug.	-
Faraday Discussion 'Colloid Stability'	Bristol	10-12 Sept.	R.H.Ottewill
European Conference on Colloid and Surface Science	Bristol	12-14 Sept.	R.H.Ottewill

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INTERNATIONAL POLYMER COLLOIDS GROU

Secretary: D. H. Napper
Department of Physical Chemistr
University of Sydney
NSW 2006 Australia

MINUTES OF GENERAL MEETING 1988

Minutes of the General Meeting held in Strasbourg on 12 July 1988.

PRESENT:

D. Bassett, J. Dodge, M. El-Aasser, A. Gast, R. Fitch, I. Kreiger, R. Pelton, I. Piirma, R. Rowell, K. Takamura, J. Vanderhoff, T. van de Ven, D. Sundberg, M. Winnek, F. Candau, J. Goodwin, R. Ottewill (Chair), C. Pichot, A. Vrij and D. H. Napper (Minutes). (20)

MEMBERSHIP:

- Meeting endorsed action of previous secretary in respect to membership of Dr. R. Uschold. Position to be reviewed according to normal procedure.
- Invitations of membership to be sent to: J. Joosten (DSM), Do Ik Lee (Dow) and G. Riess (Mulhouse). Exclusion for non-submission of contributions: T. Healy.
- Mel Sterman (Eastman-Kodak) to be invited to meetings to see if he contributes.
- Secretary to write to Dr. Kast (BASF) to thank BASF for contributions from Ley (6th Gordon Conference) and Hahn (NATO ASI). Also enquire whether he wishes to retain his membership or nominate another BASF colleague.
- Membership to be offered to leader of University of San Sebastian group (Dr. El-Aasser to supply details). Dr. Muroi may have left Ashai (Dr. Takamura to investigate).

MEETINGS: Please see attached list.

- 7th Gordon Conference will be held 9-14 July 1989 at Proctor Academy, Andover (note change of venue). Dr. Piirma has almost finalized program.
- Strong support expressed for the Lehigh 3-day Symposium to honour contribution to polymer colloids by John Vanderhoff (19-21 June 1990). Difficult date for Europeans.
- Session on polymer colloids at IUPAC Polymers meeting in Montreal, 8-13 July 1990 if sufficient support forthcoming.
- Faraday Discussion on "Colloid Stability" at Bristol 10-12 September 1990 to be followed immediately by European Conference on Colloid and Interface Science (12-14 September), also in Bristol.

ANY OTHER BUSINESS:

- Agreed (i) members supply FAX (TELECOPIER) and Bitnet numbers to Secretary , (ii) Bob Pelton to coordinate exchange of computer programs relevant to polymers colloids.
- Bob Fitch pointed out that S.C. Johnson has produced a range of monodisperse latices stabilized by sulfonate groups for sale via commercial channels. Further details to follow.

D. H. Napper
Minutes Secretary

HOMMAGE A STRASBOURG, 1988

Throughout its twenty centuries, Strasbourg has seen it all,
With Viking, Hun and French invaders pouring through the wall,
But never in its history has anything appeared
As motley as the Colloid Group, or nearly half as weird.

They hail from France and Mexico, Australia and Japan,
And lands of NATO, which the backward natives spell OTAN,
They come together every year, the first week in July,
To worship tiny particles unseen by human eye.

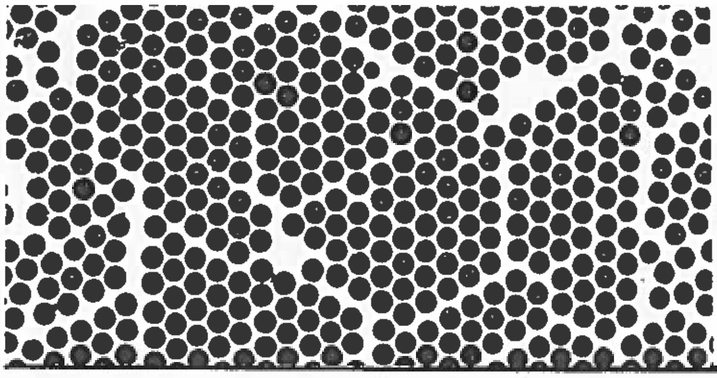
Their Priest is Father Ottewill, their Priestess Mère Candau,
Their Vestal Virgin, is Pascalé; she dashes to and fro,
As shepherdess, she prods the flock to new religious heights,
At Cathédrale, or City Hall, for nightly holy rites.

Their sacred fruit, the cherry, they love with all their heart,
Fresh, stewed, or in a breakfast jam, or baked into a tart,
If you think this peculiar, then you fail to realize
That cherries are both spherical and uniform in size.

They sit all week in darkened halls, each day they start at nine,
On Saturday they roam the country seeking Rhenish wine,
For physical activity, their elders, grey and wise
Search out the nearest bathing spot, to exercise their eyes.

And when at noon on Friday, their frenzy simmers down,
Their rage subdued, their faith renewed, they'll quietly leave town,
They'll board their trains and aeroplanes, and shed a parting tear,
And dream of green New Hampshire, where they meet again next year.

Irvin M. Krieger P.L.
13 July 1988



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INTERNATIONAL POLYMER COLLOIDS GROUP

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(Revised September 1988)

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22.	Dr. V. I. Yeliseyeva	Institute of Physical Chemistry, Academy of Sciences of the U.S.S.R., Leninsky Prospekt 31, V-31 Moscow U.S.S.R.

SULPHUR PREVULCANISATION OF NATURAL RUBBER LATEX

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

For several years now, we have been interested in the so-called "sulphur prevulcanisation" of natural rubber latex. This is a reaction in which the latex is heated with a dispersion of sulphur, one or more organic vulcanisation accelerators (usually but not necessarily insoluble in water) and (possibly) zinc oxide. Although the vulcanising ingredients are initially external to the rubber particles, the end-product of the reaction is a colloidally-stable dispersion of particles of crosslinked rubber. The particle size of the prevulcanised latex is essentially that of the original latex. Prevulcanised natural rubber latex has been known for many years. It is now produced in great quantities industrially, and is widely used in latex dipping processes. Prevulcanisation is probably by far the most important chemical reaction which is carried out industrially on a polymer in polymer-colloid form. It is also possible to prevulcanise natural rubber latex by other processes, such as by reaction with organic peroxides and by irradiation treatment, but present industrial interest is almost exclusively in sulphur prevulcanisation.

Our interest has been firstly in investigating the many factors which influence the rate at which crosslinks become inserted in the rubber molecules, and secondly in attempting to understand the mechanism of prevulcanisation in the light of the mechanisms which are generally accepted for the vulcanisation of solid natural rubber using sulphur and organic accelerators. Whilst considerable progress has been made by others as well as ourselves in achieving the first of these objectives, almost no progress has been made so far towards achieving the second. The question of the structure of films obtained from prevulcanised natural rubber latex has also been a matter of conjecture in the past. The present consensus is that the considerable strength and coherence of such films is primarily a consequence of secondary valence forces which operate between segments of the polymer molecules at the surfaces of the particles in the film, supplemented in industrial practice by crosslinks which have developed during drying and post-vulcanisation at elevated temperatures.

Fig. 1 shows typical results for the variation with the time and temperature of prevulcanisation of the tensile strength of films cast from natural rubber latex. The latex contained 1 pphr of both sulphur and zinc diethyldithiocarbamate. At the same time as the tensile strength (and also the modulus) of cast films increases, the amount of network-combined sulphur in the rubber increases, as also does the concentration of crosslinks as evidenced by swelling in rubber solvents (see below). The tensile strength of films from prevulcanised natural rubber latex is found to increase considerably if the films are leached in water, and still further if the films are leached in acetone; these effects are attributed to the removal of non-rubber substances from between the latex particles which comprise the film.

From the chemical point of view, the first thing which should probably be said about the prevulcanisation reaction is that it should not occur, at least at the temperatures at which it does occur! Quite apart from the initial reactants being in different, though contiguous, phases, the reaction occurs at much lower temperatures than does the vulcanisation of solid rubber using the same vulcanising ingredients. This is illustrated in Figs. 2 and 3, which show the variation with time of prevulcanisation or vulcanisation at 50°C of network-combined sulphur and crosslink concentration for (a) the rubber in a prevulcanising natural rubber latex and (b) solid rubber of the same composition obtained by evaporating to dryness at low temperature the compounded latex which was used for the prevulcanisation experiment. These results confirm what would be inferred from general knowledge concerning the vulcanisation of solid natural rubber, namely, that, notwithstanding that extremely fast vulcanisation accelerators are used for the prevulcanisation reaction, the reaction readily proceeds at far lower temperatures than would be expected. In fact, the reaction proceeds at a measurable rate even at warm ambient temperatures, and use is made of this in certain industrial processes.

It has been supposed that the presence of various non-rubber constituents in natural rubber latex is essential for the occurrence of the prevulcanisation reaction. In particular, the presence of various proteinaceous substances has been regarded as essential. That this is not so is demonstrated by three pieces of evidence. In the first place, it is possible to prevulcanise artificial polyisoprene latices made by dispersing synthetic *cis*-1,4-polyisoprene in an aqueous medium. In fact, using this latex we have obtained results entirely analogous to those shown in Figs. 2 and 3. Secondly, it is possible to prevulcanise synthetic polyisoprene latex obtained by the emulsion polymerisation of isoprene (see below). Thirdly, very recent work has shown that it is possible to prevulcanise highly-purified natural rubber latex from which much of the non-rubber material has been removed, although the rate of prevulcanisation is somewhat reduced. The overall impression gained from these observations is that it is the presence of the water in the latex which is essential for the occurrence of prevulcanisation at unexpectedly low temperatures, although the mechanistic implications of the presence of the water are far from clear.

Using synthetic polyisoprene latices, it has been possible to investigate the effect of latex particle diameter upon the rate at which prevulcanisation occurs. The first point of interest is that, as stated in the preceding paragraph, it is possible to prevulcanise these latices by heating with sulphur and accelerators, thus confirming that the presence of non-rubber substances in natural rubber latex is not essential for the prevulanisation reaction. The second point of interest is that the rate of prevulcanisation increases as the latex particle size decreases. Furthermore, on the basis of the limited data so far available (Fig. 4), the initial rate of insertion of crosslinks varies with latex particle diameter in such a way as to indicate that the rate is directly proportional to latex particle *number* rather than to, say, the aggregate surface area of the latex particles. Again the mechanistic implications are far from clear.

I conclude this contribution by referring to one further puzzling observation which so far defies explanation. This concerns the rate at which the free dithiocarbamate accelerator disappears from the reaction system in the absence of added zinc oxide. It has been shown by at least two independent workers that, in any given reaction system, the concentration of free accelerator falls linearly with time of prevulcanisation, indicating that the order of reaction with respect to free accelerator is zero. However, if the initial level of accelerator is varied, although the rate of disappearance is zero order with respect to accelerator concentration in any one reaction system, the zero-order rate is itself first order with respect to the initial level of accelerator. Possible hypotheses to account for this behaviour (*e.g.*, that the rate of disappearance is first order in the number of accelerator particles of given size initially present, or that the reaction is catalysed by impurities in the industrial grades of accelerators used) have been tested and found wanting.

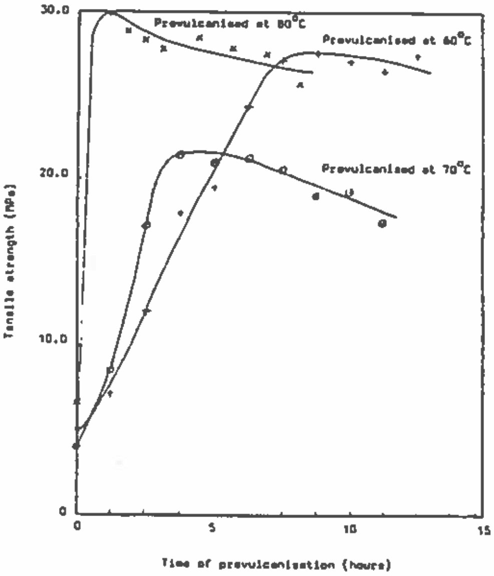


Figure 1

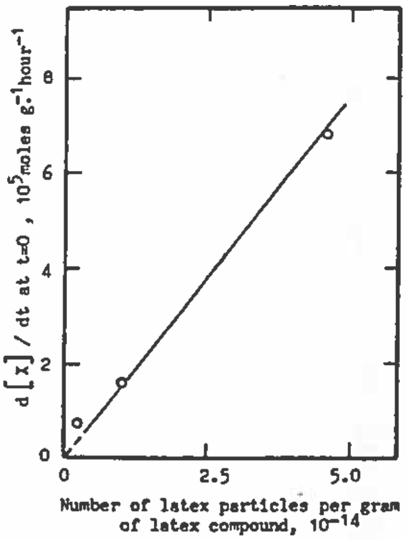


Figure 4

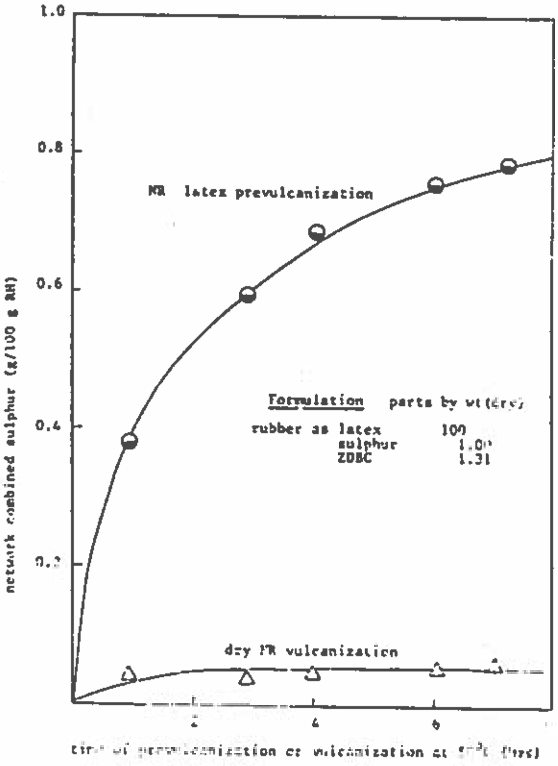


Figure 2

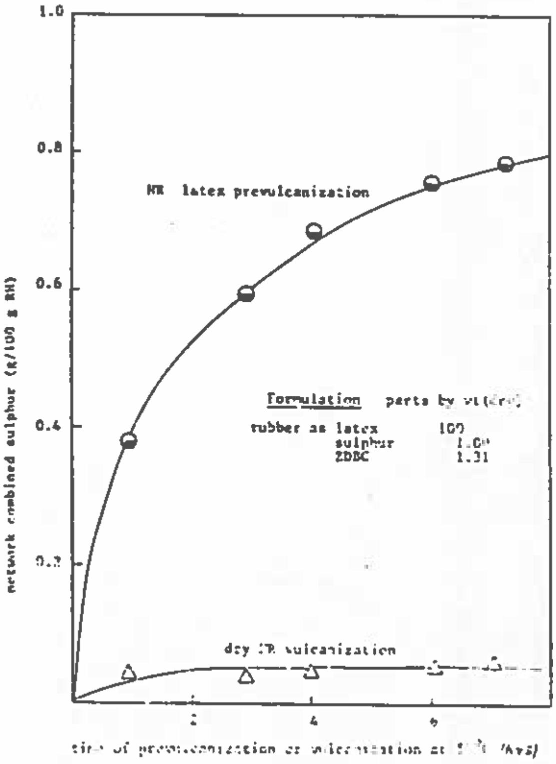


Figure 3

POLYMER COLLOID GROUP NEWSLETTER

Contribution from the Institut Charles Sadron (CRM-EAHP)
6 rue Boussingault, 67083 Strasbourg Cédex

by

Françoise CANDAU

PERCOLATION AND PARTICLE NUCLEATION IN INVERSE MICROEMULSION POLYMERIZATION (M. Carver, E. Hirsch, J.C. Wittmann, R.M. Fitch, F. Candau).

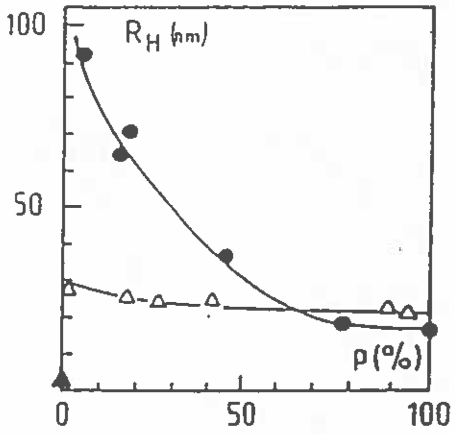
In the last Newsletter, we pointed out that the termination mechanism of the polymerization of acrylamide (AM) in AOT reverse micelles is monoradical, due to a radical transfer from the growing polymer chain to the toluene which forms the continuous medium (1,2). We also showed that both the rate of polymerization and the molecular weight of the polymers are first order in monomer concentration. Nevertheless, much remains to be understood about the processes occuring in these systems, both before and during the polymerization.

In order to better understand the role of AM on the interfacial properties of AOT systems, the electrical conductivity of toluene/AOT/(AM + H_2O) water-in-oil microemulsions was investigated. For microemulsions containing acrylamide, a sharp rise in conductivity (several decades) with increasing [AM] centered around an inflection point was noted and was attributed to a percolation process. For these labile systems, it is commonly assumed that the interfaces must temporarily open to form water-channels between the particles, allowing the current to flow. The effect of AM on the percolative behavior of the micellar systems is directly related to its cosurfactant properties. The presence of monomer molecules in between the AOT molecules increases the flexibility and fluidity of the interface, resulting in a change of its curvature. In systems which are percolating, this structure has an important effect upon the nucleation of particles.

The analysis of the mechanism for particle nucleation involves the determination of the particle size and number as a function of the extent of polymerization p. Previous studies performed by QELS on systems of different compositions have shown that the diameter of the final latex particle is of the order of 40 to 50 nm that is much larger than that of the initial micelles (5 to 10 nm). Moreover, the number of polymer chains per latex particle is very low, often averaging only one molecule per particle. This suggested kinetics characterized by continuous particle nucleation throughout the polymerization.

To assess the validity of the above hypothesis, particle nucleation was investigated by QELS and transmission electron microscopy (TEM). Micrographs show that the diameters of the "dry" polymer particles obtained for samples at various degrees of conversion remain approximately constant and of the order of 40 nm while the particle number grows steadily. These results confirm that the systems undergo new particle nucleation at all stages of the reaction.

Moreover, different behaviors were observed depending on whether the starting systems were percolating or nonpercolating (see Figure).



Hydrodynamic radius as a function of the degree of conversion for (O) an initially percolating system and (Δ) an initially nonpercolating system.

For nonpercolating systems, the hydrodynamic radius R_H exhibits a sharp rise from the micellar size to a value which remains roughly constant up to 100% conversion, in good agreement with the results obtained from TEM.

In percolating systems, the initial rise is much larger, since R_H reaches values as high as 90 nm. When the polymerization proceeds, the size of the polymer particles decreases drastically to reach at high p a value close to that obtained for nonpercolating systems. The different behavior observed in QELS and TEM experiments was attributed to the network structure in the percolating systems. A particle initiated at some point along the percolating chain could grow along the chain, forming a "string of beads" a series of individual micelles held together by the polymer chain. Rather than coalescing to form a single large spherical particle, curvature constrains in these AM-depleted micelles would cause them to maintain their individuality, thus expanding the polymer coil. When the particles are dried for microscopy, they collapse to a much smaller size, as mentioned above. The expanded particles would only be formed while the micellar systems are percolating, during the first 10 to 15% of the polymerization, according to conductivity measurements of the latex solutions. Afterwards, particle nucleation would proceed in the same manner as for nonpercolating systems.

References

1) Carver, M.T.; Dreyer, U.; Knoesel, R.; Candau, F.; Fitch, R. J. Polym. Sci. Polym. Chem. Ed., in press.

2) Carver, M.T.; Candau, F.; Fitch, R. J. Polym. Sci. Polym. Chem. Ed., in press.

TORONTO POLYMER COLLOIDS GROUP

Submitted by: M. D. Croucher and M. A. Winnik

1. Simulation Studies and Geometrical Details of the Internal Morphology of Colloidal Particles.

The direct energy transfer method was used to study the internal morphology of poymer colloid particles produced by non-aqueous dispersion poymerization. These particles with diameters 0.2 to 1.0 µm contain ca. 94 mol% of an amorphous glassy polymer (PVAc) and 6% of a rubbery polymer poly(2-ethylhexyl methacrylate) [PEHMA] which forms both a surface covering and interconnected network within the particle. We employed a fractal analysis technique and the model of restricted geometries to interpret fluorescence intensity decays of excited donors to obtain the apparent dimension of the rubbery phase. Anthracene, selectively doped into the rubbery phase was used as the energy acceptor. Napthalene, covalently bound to the PEHMA serve as the donor. Within the 38Å maximum probing distance between donor and acceptor the apparent dimension d= 2 was measured. When films are prepared by dissolving particles with chloroform and then doping rubbery phase with anthracene, we find d = 1.4. This indicates that even in the film the PEHMA forms a continuous network, and second that the nascent morphology produced when the particle is formed is different from that in the film. In both cases if the PEHMA is swollen with hexadecane, d increases. These results can be interpreted by assuming that the PEHMA is present in the structure as thin cylinders.

Our simulation studies are based on fitting the Kafter-Blumen Equation (fractal analysis) to the donor fluorescence decay expression of DET in non-fractal restricted geometrics. The "apparent dimension" d that is obtained is directly dependent on the geometrical cross-over due to the finiteness and restriction of the media. We have simulated the decay expressions for thin cylinders with donor's on the axis and on the surface of the cylinders. The radius of the cylinders which corresponds to the $d \approx 2$ dimension was found to be 25Å. This model represents a cylindrical network morphology for the colloid particle. Simulation of the decay curve for the spherical surface where both donor and acceptor are located, has also been made this model requires that the radius of the spheres must be larger than 50Å for $d \approx 2$ which correspond to the "bag of marbles" morphology. Swelling results were interpreted either with the cylindrical model by increasing the radius to 50Å or by using the disk shape model with increase in the thickness of the disk to 55Å. At present we believe that further swelling studies are necessary before we are able to judge which model for the morphology of the particle is the more realistic one. (Pekcan)

2. Freeze-Fracture Studies of the Morphology of Colloidal Polymer Particles

We have recently been studying the internal morphology of polymer particles using freeze-fracture electron microscopy. Numerous types of particles have now been studied including PMMA particles prepared from nonaqueous dispersion (NAD) polymerization and PMMA particles prepared by emulsifier free emulsion polymerization. From the freeze-fracture micrographs obtained to date, two types of morphologies of the fractured particles can be identified. The dispersion polymerized PMMA particles show a surface morphology in which peaks and valleys radiate from the centre of the fracture surface of the particles. The emulsion polymers appear to be made up of finely packed grains giving a more homogeneous surface structure. We have tried to interpret the surface morphological features in terms of the growth mechanism experienced by the particle. For instance, it seems plausible that the rather homogeneous morphology exhibited by the emulsion polymerized PMMA particles is due to coagulation of primary particles before the particle achieves colloidal stability while in the NAD particles the radial pattern is due to the particles growing from the centre (or nuclei) of the particles with the radial lines marking the growth pathway of the final particles. The textured "landmarks" can survive until the end of polymerization and suggest that polymerization does not take place uniformly inside particles. Rather, polymerization proceeds primarily in the peripheral zone. Without this type of phenomenon, the radiant texture could not form. At present these interpretations are rather speculative and further work is in hand in order to understand the information that is contained in these freeze-fracture electron micrographs. (Zhao)

3. Dispersion Polymerization of Styrene in Polar Solvents.

The true steric stabilizer in hydroxypropyl cellulose (HPC) stabilized dispersion polymerization of styrene in polar solvents is grafted HPC-polystryerene (formed *in situ*) which ends up in a 10–15 nm layer on the particle surface. Evidence for the grafting mechanism of stabilization includes: (a) direct observation of a surface layer on the particles by electron microscopy; (b) experiments on particles made using pyrene labeled HPC which indicate a molecular weight increase and solubility properties consistent with grafting of PHC to polystyrene; (c) kinetic analysis for grafting via solution polymerization; (d) the observed response of particle size to steric stabilizer concentration ($D\alpha[\mathrm{HPC}]^{-0.5}$); and (e) precipitation experiments which distinguish between nucleation and stabilization. The electron microscopy, kinetic analysis and precipitation experiments are unique tools, heretofore not applied to particle forming polymerizations. In particular, the precipitation experiments isolate stabilization as the key factor controlling particle size -- nucleation is relatively unimportant. Fluorescence quenching results consistent with substantial surface HPC, and the consequences of the grafting mechanism of stabilization are explored in subsequent papers in this series. (Paine, F. Winnik)

Contribution to the Polymer Colloids Group Newsletter

From:

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The effect of emulsifier-polymer complexformation on partide nucleation in emulsion polymerization

In our previous report (Newsletter volume 18 no. 2) the effect of the presence of PEO on the kinetics of 80/20 MAA/MMA emulsion polymerization was discussed in relation to the molar mass of the PEO.
Since then we have paid some more attention to low acid recipes. We have studied the development of particle sixe in the presence and absence of PEO molar mass 20.000 (EO/MMA ratio =1). It appears that the presence of PEO leads to a larger particle size of the latex as compared with the blank. The difference between the two shows clearly from 5 minutes after the start of the polymerization. This leads one to expect that the kinetics of the process are also influenced by the presence of PEO. This, however, has been proven not to be the case within the accuracy with which the kinetic measurements have been performed. It therefore is less probable that PEO interacts with oligomers in a similar way as with anionic emulsifiers, a hypothesis put forward in J. Polym. Sci. Polym. Letter Ed., 25 (1987) 29.
Another possibility that might explain the particle size difference of about 40 nm between PMMA latices prepared in the presence and absence of PEO is that the PEO and some water in some way is incorporated in the particles.
To check this possibility Tg measurements have been performed on various samples after cleaning by serum replacement and drying. The results indicate that low molar mass PEO e.g. 600 can be removed completely by serum replacement irrespective of the fact that it is present during the polymerization or added afterwards PEO molar mass 20.000 can be removed by serum replacement if added after polymerization but not (completely) if present during polymerization. This leaves us with the question whether the PEO is buried inside the particles or bound to the particle surface by grafting. This question was resolved by determining the colloidal stability against flocculation by electrolyte (Na_2SO_4) of PMMA latices prepared in the presence or absence of PEO and before and after cleaning by serum replacement. Latices prepared in the absence of PEO have similar critical coagulation concentrations whether cleaned by serum replacement or not.
The c.c.c. of PMMA latices prepared in the presence of PEO and PMMA latices to which PEO was added after polymerization were much higher when determined before serum replacement. After serum replacement, however, the c.c.c.'s were similar to those of the blank systems.
It has to be concluded, therefore, that PEO 20.000 when present during emulsion polymerization of MMA is (partly) incorporated in the latex, whereas low molar mass PEO is not.
Preliminary result obtained with nonionic emulsifiers with comparable molar masses to the PEO's described above show similar trends.

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Latex Particle Nucleation in the Emulsion Polymerisation of Styrene

J.P.Congalidis and J.R.Richards of DuPont with Bob Gilbert contributed an important paper to the Session on 'Polymerization Kinetics and Process Modelling' in the Symposium on Computer Applications in Polymer Science at the 3rd Chemical Congress of North America held in Toronto in June 1988, preprinted in Polym.Mat. Sci. Eng.58 (1988) 605 although without the equations because of the limitation on the length of preprints. They get reasonable fits to experimental data in the literature from four different laboratories including the rapid increase of particle number with surfactant concentration which is observed at the surfactant c.m.c. with monomers such as styrene which have a very low solubility in water using an elaborate but convincing procedure based on DLVO theory taking into account the adsorption isotherm for surfactant to calculate the rate of coalescence of primary particles nucleated by oligomeric precipitation without needing to consider nucleation of latex particles from monomer-swollen micelles.

However, even though this work apparently disposes of one of the principal pieces of evidence (the sharp increase of particle number and, consequently, of the Interval II polymerisation rate) favouring micellar nucleation of latex particles in the case of monomers such as styrene with very low solubility in water and although the idea of a single generally applicable mechanism of latex particle nucleation is appealing, several observations which indicate a contrary conclusion remain to be explained.

In general, it is likely (particularly in free-radical chemistry) that if a process is possible it will occur! There is no reason to suppose that latex particles cannot be nucleated from monomer solubilised in micelles when the amount of solubilise monomer is in excess of that in molecular solution. Also:

(1) p-tert-butyl styrene (solubility one-tenth that of styrene) has been found not to form a latex when emulsifier-free emulsion polymerisation is attempted [solub surface-active oligomer might be produced which would be detectable from a reduction in surface tension but this experiment has yet to be tried] but a latex does form immediately when emulsifier is injected.

(2) Although the Interval II polymerisation rate is independent of the amount of monomer solubilised (cf. Dunn & Al-Shahib in Fitch ed. 'Polymer Colloids II' p. 619, Fig. 2), the Interval I polymerisation rate is directly proportional to the amount of monomer solubilised (cf. Kolthoff, Meehan, & Carr, J. Polym. Sci. 6 (1951) 73).

(3) When the concentration of micellar emulsifier differs significantly from the total emulsifier concentration, it is the former concentration which is important (Dunn & Al-Shahib, loc.cit, also J.Polym.Sci. Polym. Chem. Ed. 16 (1978) 677).

(4) Nomura, Satpathy, Kouno, & Fujita(J.Polym.Sci. Letters 26 (1988) 385) find that the composition of styrene-methyl methacrylate copolymers formed at conversions below 2% differs depending on whether emulsifier is present above its c.m.c.: above the c.m.c. the copolymer composition is that expected from the monomer composition in the oil phase.

On the other hand the Sydney group have convincingly demonstrated from the form of the particle size distribution at low conversions, Liesegang rings etc. that latex particles are formed by a coagulative process and we have observed (Polym. Mat.Sci.Eng. 54 (1986) 439) that particle coalescence continues slowly (the rate decreasing with increasing emulsifier concentration) after polymerisation is complete in a polystyrene latex maintained at 70 °C.

Hitherto it has generally been believed the surface of a latex particle nucleated from a micelle would remain saturated with adsorbed emulsifier so long as a supply of unadsorbed emulsifier remained in the system so that it would remain stable and that there would be no need to consider coagulative processes in the presence of sufficient emulsifier (i.e. at emulsifier concentrations above the c.m.c.). Monomer-swollen micelles are thermodynamically stable and are unlikely to be destabilised by polymerisation of the monomer within them.

However growing polymer particles might become unstable if equilibrium adsorption of emulsifier is not maintained on the surface of polymerising particles i.e. if the rate of increase of particle surface area exceeds the rate of adsorption of emulsifier per unit area. This is quite likely because, for a constant rate of polymerisation, the rate of increase of surface area must be larger for small particles than for large ones whereas the rate of emulsifier adsorption is likely to increase with particle size. The difference in Gibbs Energy between an emulsifier molecule in a micelle and one adsorbed on a latex particle presumably increases with particle size otherwise the micelles would not disappear at an early stage in the reaction as is normally observed.

In absence of a separate monomer phase, falling monomer concentration should reduce the particle growth rate, favouring stabilisation of particles at an earlier stage and producing a higher particle number concentration and the high rate of polymerisation observed at high emulsifier/monomer ratios (cf. our contribution to the Spring 1988 Newsletter). Although our particle size measurements suggested that the decrease of particle size was insufficient to account for the increase of rate the measurements were made on latex which had been stored for some time. Nomura has drawn my attention to his paper presented at the Las Vegas 1980 'Emulsion Polymers and Emulsion Polymerization' Symposium which seems to have received much less attention than it deserves. (M.Nomura & M.Harada in A.C.S. Symposium Series <u>165</u> Ed. D.R.Bassett & A.E.Hamielec). From particle sizes measured one hour from the start of the reaction they find particle numbers increase with a constant emulsifier concentration at very low monomer concentration although the particle number is independent of phase ratio with more normal amounts of monomer. On this basis they propose using a small pre-reactor fed with most of the emulsifier and initiator but only part of the monomer to optimise the performance of a CSTR. Pollock, MacGregor, & Hamielec (A.C.S. Symposium Series <u>197</u> (1982) 209 'Computer Applications in Applied Polymer Science' Ed. Th.Provder) confirm this effect independently and show additionally that it has the advantage of eliminating the oscillatory behaviour to which CSTR systems are prone on start-up which can lead to the latex becoming unstable and coagulating.

Has anyone any idea how the postulated disparity between the rate of increase of surface area and the rate of adsorption of emulsifier on small primary latex particles might be demonstrated?

Contribution to the International Polymer Colloids Group Newsletter

M.S. El-Aasser, A. Klein, C.A. Silebi, J.W. Vanderhoff
E.S. Daniels, V.L. Dimonie, O.L. Shaffer and E.D. Sudol

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The titles of our current research projects are given in the enclosed Contents of our Graduate Research Progress Reports, No. 30, July 1988. Copies of any of these reports can be obtained by contacting Ms. Debra Nyby at the above address. Summaries of progress in several research areas are presented here along with abstracts of papers recently presented.

I. <u>Radical Desorption in Emulsion Polymerization</u> (J.M. Asua*)

Smith-Ewart Case 2 kinetics ($\bar{n} = 0.5$) are more the exception than the rule in emulsion polymerization. Deviations to the low side ($\bar{n} < 0.5$) are frequently attributed to radical desorption from the polymer particles. A radical desorption coefficient has been derived for emulsion polymerization which takes into account the possible reactions of the desorbed radical in the aqueous phase, as well as the competition between desorption and termination in polymer particles containing more than one radical. Calculations show that the probability of desorption of a single-unit monomeric radical from a particle containing two radicals is higher than the probability of termination and therefore a significant fraction of the reabsorbed single-unit monomeric radicals will redesorb. These single-unit monomeric radicals, which are considered to arise only from chain transfer to monomer within the particles, can undergo several desorption-reabsorption cycles before terminating or propagating.

The probability, β, that a given monomeric radical reacts in the aqueous phase by either propagation or termination controls its lifetime in the aqueous phase and together with the probability of desorption, the number of subsequent desorption-reabsorption steps. For the case in which $\bar{n}$ is less than 0.5, the desorption rate coefficient (k_d) becomes

$$k_d = k_{fm}\,[M]_p\,(K_o/(\beta\,K_o + k_p[M]_p)) \qquad (1)$$

where k_{fm} is the monomer chain transfer constant, $[M]_p$ the concentration of monomer in the particles, K_o the rate of diffusion of a monomeric radical out of a particle and k_p the propagation constant. An expression for K_o has previously been derived by Nomura. β is given by

$$\beta = (k_{fm}[M]_w + k_{tw}[R]_w)/(k_p[M]_w + k_{tw}[R]_w + k_a\,N_T\,\phi_w^{\,w}/N_A) \qquad (2)$$

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where $[M]_w$ is the concentration of monomer, k_{tw} the termination constant, $[R]_w$ the concentration of radicals and ϕ_w^w the volume fraction of water, all in the aqueous phase. N_T is the number of particles per unit volume of water and N_A Avogadro's number.

The expression for the desorption rate coefficient (Equation (1)) differs from previously reported ones and has been used successfully to describe some experimental results that the previous models failed to fit.

These results are described in detail in a paper submitted to the Journal of Polymer Science.

II. Free Radical Distribution in Emulsion Polymerization Using Oil-Soluble Initiators (J.M. Asua and V.S. Rodriguez)

The kinetics of emulsion polymerization using oil-soluble initiators are known to be similar to those employing the more typical water soluble initiators such as potassium persulfate. Because of the similarity it must be concluded that, although oil-soluble initiators decompose into radical pairs, there must be some mechanism that leads to the formation of single radicals, i.e., those that appear in a particle one at a time. Radical desorption and aqueous phase generation of radicals resulting from the partitioning of the initiator between the phases have both been proposed as mechanisms for this process. Both of these mechanisms have been incorporated in an approach that calculates the whole distribution of particles with i radicals. This distribution is determined by: (i) generation of radicals inside the particles; (ii) desorption of initiator radicals before reacting with a monomer molecule; (iii) termination of radicals by bimolecular reaction in the polymer particles; (iv) desorption of radicals; (v) absorption of radicals from the aqueous phase into the particles; (vi) termination of radicals in the aqueous phase; and (vii) generation of radicals in the aqueous phase by decomposition of the initiator dissolved in that phase. The redesorption/reabsorption of free radicals, as described in I, is also included in this approach.

An algorithm has been developed for solving the particle population balances. This has been applied to calculate the distribution of particles containing i radicals and hence, the average number of radicals per particle during the seeded polymerization of styrene initiated by AIBN under a wide variety of conditions. Figure 1 shows the effect of particle size on $\bar{n}$. Simulations were carried out in which the total solids content as well as the total amount of initiator were kept constant. The present calculations are compared to those obtained using a bulk-like expression for $\bar{n}$ and O'Toole's equation. The figure shows that in the present approach the number of radicals per particle follows an evolution similar to the one expected for a water-soluble initiator, as opposed to the other two which predict a continuous decrease in $\bar{n}$ with decreasing particle size.

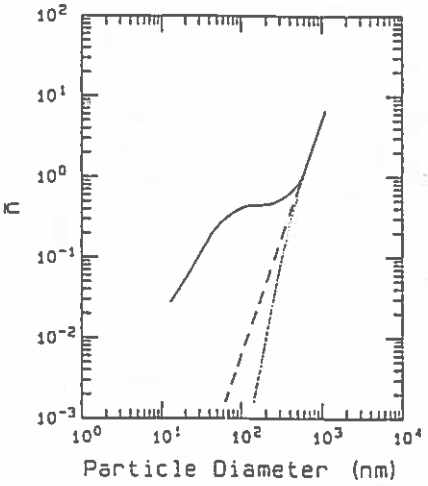

Figure 1: Effect of particle size on the average number of radicals per particle: this model (continuous line); bulk-like equation (dashed line); O'Toole equation (dotted line).

The detailed kinetic expressions, balances and solution algorithm are contained in a paper recently submitted to the Journal of Polymer Science.

Abstracts of Papers to be Presented at the ACS Meeting
Los Angeles, California, September 1988

MASS TRANSFER COEFFICIENTS OF STYRENE AND METHYL METHACRYLATE AT THE INTERFACE BETWEEN MINIEMULSION DROPLETS-AQUEOUS PHASE

V.S. Rodriguez, M.S. El-Aasser, J. Delgado and C. Silebi

The mass transfer coefficients of styrene and methyl methacrylate at the interface between miniemulsion droplets and the aqueous phase were determined. The principle was to obtain the relative concentration of the monomer in the miniemulsion droplets during the mass transfer process by analyzing the composition of the copolymer formed by fast UV initiated polymerization. For these experiments, two miniemulsions were prepared, one of them containing monomer A and a water-insoluble UV photoinitiator (DEAP) and the other containing monomer B and a water-insoluble inhibitor (DTBHQ). The two miniemulsions were mixed for different times and polymerized using high intensity ultraviolet light-initiation. The copolymer formed was recovered and its composition determined using Fourier Transform Infrared Spectroscopy. The composition was then related by the Mayo-Lewis copolymer equation to the relative monomer concentration in the droplets containing the photoinitiator. The equilibrium thermodynamic condition in conjunction with the Ugelstad swelling thermodynamic equation were used to get the equilibrium concentrations of the monomers in the miniemulsion droplets which are used to determine the driving force of the monomer transport at the miniemulsion droplets-aqueous phase interface.

INFRARED STUDIES ON THE GRAFTING REACTIONS OF POLY(VINYL ALCOHOL) DURING THE EMULSION COPOLYMERIZATION OF POLY(VINYL ACETATE-CO-BUTYL ACRYLATE)

N.J. Earhart, V. Dimonie, M.S. El-Aasser and J.W. Vanderhoff

Poly(vinyl acetate-co-butyl acrylate) latexes were prepared by batch polymerization using poly(vinyl alcohol) as the sole emulsifier. The rates of copolymerization of the individual monomers in the initial stages of the reaction were altered by a grafting reaction between the aqueous phase vinyl acetate and the poly(vinyl alcohol).

Fourier-Transform Infrared (FT-IR) Spectroscopy was used to determine the increase in the carbonyl character of the aqueous phase graft copolymer, a result of the poly(vinyl acetate) grafting to the poly(vinyl alcohol) during the course of the polymerization. The aqueous phase of the latex was separated from the copolymer by centrifugation. A potassium thiocyanate (KSCN) solution, the spectral reference standard, was added to the serum and a film cast onto a zinc-selenide (Zn-Se) IR cell. The spectra was obtained and the percent grafting calculated.

INVESTIGATION OF THE PERSULFATE/ITACONIC ACID INTERACTION AND IMPLICATIONS FOR EMULSION POLYMERIZATION

M.R. Lock, M.S. El-Aasser, A. Klein and J.W. Vanderhoff

Itaconic acid, a dicarboxylated monomer, is used in small amounts to prepare carboxylated latexes. Upon copolymerizing itaconic acid with butyl acrylate, less than expected conversions of both monomers were found. Furthermore, increasing reaction temperature in the range of 50-70°C results in even lower conversions. These findings have been related to an induced decomposition of the potassium persulfate initiator caused by the itaconic acid. Detailed examination of this unexpected interaction has shown it to be particularly sensitive to the presence of itaconate anion, which forms as a result of the first ionization of the acid monomer. Kinetic studies have revealed this interaction to be first order with respect to persulfate and three-halves order with respect to itaconate anion. Use of the azo initiator 4,4'-azobis(4-cyanopentanoic acid) avoids these complications and leads to more conventional conversion behavior with regard to reaction temperature.

UNIFORM NONSPHERICAL LATEX PARTICLES AS MODEL INTERPENETRATING POLYMER NETWORKS

H.R. Sheu, M.S. El-Aasser and J.W. Vanderhoff

Polystyrene/polystyrene latex interpenetrating polymer networks were prepared by seeded emulsion polymerization of styrene-divinylbenzene mixtures in crosslinked monodisperse polystyrene particles. The resulting latexes comprised uniform nonspherical particles, e.g., ellipsoidal and egg-like multiplets. The nonspherical particles, which were formed by separation of monomer and soluble polymer from the crosslinked seed network, are excellent models for studying phase separation behavior in interpenetrating polymer networks. The degree of phase separation increased with increasing degree of crosslinking of the seed particles, monomer/polymer swelling ratio, polymerization temperature and seed particle size, and decreased divinylbenzene concentration in the swelling monomer. The results were consistent with a thermodynamic analysis based on the elastic-retractile force of the polymer network, the monomer/polymer mixing force and interfacial tension force.

FLOW PROPERTIES OF CONCENTRATED SOLUTIONS OF ASSOCIATIVE THICKENERS

R.D. Jenkins, C.A. Silebi and M.S. El-Aasser

This work studies the steady shear and dynamic properties of concentrated aqueous solutions of model associative thickeners with a Weissenberg Rheogoniometer and a Bohlin Rheometer. Examination of this data reveals insight into the incompletely understood association mechanism. The model thickeners, provided by Union Carbide, have either a H, C_{12}, or C_{16} group attached to each end of a water soluble linear poly(ethylene glycol) backbone which varies in molecular weight from approximately 54000 to 108000. Trends in the steady shear viscosity data show that the lower molecular weight model thickeners build a strong association network which "physically crosslinks" the solution. The solutions with a strong association network exhibit a dilatant region in the viscosity curve at a shear rate near 10 sec^{-1} and exhibit shear thinning at higher shear rates. A viscoelastic characterization shows that elasticity accompanies the dilatancy, which suggests that a stretching of the network causes the dilatancy.

Abstracts of Papers to be Presented at the 7th International Symposium on Surfactants in Solution

Ottawa, Canada, October 1988

THE VARIATION OF SURFACE PROPERTIES OF DOWFAX^{TM} EMULSIFIERS WITH ALKYL SUBSTITUTION

V.L. Dimonie, M.S. El-Aasser, J.W. Vanderhoff and
L.A. Settlemeyer*

Dowfax^{TM} 2A1 is a branched C_{12}-alkylated diphenyl ether disulfonate surfactant widely used as an emulsifier in industrial emulsion polymerization because of its electrolyte tolerance, stability in concentrated acids and alkalis, oxidation resistance, temperature stability, efficiency in solubilization and moderate foaming. The surface properties of this emulsifier and other emulsifiers similar to the Dowfax^{TM} 2A1 surfactant used as emulsifier were determined. Variation of the alkyl substituents included Dowfax^{TM} 3B2 (linear C_{10}), 8390 (linear C_{16}), 8292 (linear C_6), 8174 (linear C_{12}) and various laboratory monoalkylated and dialkylated variations. Sodium lauryl sulfate and Aerosol MA (dihexyl sulfosuccinate sodium salt; American Cyanamid) were used as standards. The adsorption isotherms of the Dowfax™ emulsifiers at the styrene-water interface were measured. Typical emulsifier surface properties such as the critical micelle concentration, adsorption at interface saturation and the standard free energy of adsorption and micellization were determined in the presence and absence of electrolyte, and the efficiencies and effectiveness of the emulsifiers in reducing the interfacial tension were estimated. To determine the effect of the emulsifier type and concentration in emulsion polymerization, and to correlate their surface activity with the latex particle size, 50%-solids 60:40 styrene-butadiene copolymer latexes were prepared and characterized. The results showed that the hydrophobic part of the emulsifier molecule, particularly the number of carbon atoms in the alkyl substituent, determined the particle size of the latex.

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*Applied Organics & Functional Polymers Research, The Dow Chemical Company.

THE ROLE OF AVANEL™ S SURFACTANTS IN EMULSION POLYMERIZATION

E.S. Daniels, M.S. El-Aasser and J.W. Vanderhoff

A new family of sulfonated anionic surfactants called the Avanel™ S surfactants (PPG Industries, Inc.) have been developed with the following general structure:

$$C_mH_{2m+1}O(C_2H_4O)_nCH_2CH_2SO_3Na$$

where m = 12 to 15 and n = 3 to 15.

Four different Avanel™ S surfactants (Avanel™ S-30, S-70, S-90 and S-150) which differ in their degree of ethoxylation (with S-30, the lowest, and S-150, the highest) were evaluated in a series of emulsion polymerizations of vinyl acetate at 60°C. In addition, sodium lauryl sulfate (SLS) and sodium dodecyl benzene sulfonate (SDBS) were investigated in the same master latex recipes in equimolar concentrations for comparison with the Avanel™ surfactants. Polymerization kinetics, final latex particle size, latex electrolyte tolerance level and latex film water sensitivity were compared in these studies. The interfacial tension behavior between the Avanel™ S surfactants and SLS with both vinyl acetate and styrene at room temperature was also studied.

No appreciable kinetic differences were observed for latexes prepared with equimolar concentrations of the four Avanel™ surfactants or SLS. Latexes synthesized with SDBS exhibited slightly slower polymerization rates. The final latex particle diameters fell within a 160-180nm size range, with recipes employing Avanel™ S-30 or SDBS resulting in the larger particle sizes. Comparison of latexes produced with equimolar concentrations of the four Avanel™ surfactants showed a marked effect of the ethylene oxide (EO) unit length on the stability of these latexes to added divalent ($CaCl_2$) electrolyte. Latex stability dramatically increased with increasing EO length. The stability of the latexes prepared with SLS or SDBS was similar to those produced with Avanel™ S-30. Water sensitivity of films prepared with these latexes generally increased with increasing EO length.

The interfacial tension behavior between the Avanel™ S surfactants or SLS and vinyl acetate or styrene showed a decrease in the critical micelle concentration (cmc) of the surfactant with increasing EO unit length. Sodium lauryl sulfate exhibited a much higher cmc than did the Avanel™ surfactants in either monomer system.

Recent Publications

"Sulfonated Latex Particle as Acid Catalysts for the Continuous Inversion of Sucrose", J.H. Kim, M.S. El-Aasser, A. Klein and J.W. Vanderhoff, J. Polym. Sci.; 35, 2117 (1988).

"Miniemulsion Copolymerization of Vinyl Acetate and Butyl Acrylate. II. Mathematical Model for the Monomer Transport", J. Delgado, M.S. El-Aasser, C.A. Silebi, J.W. Vanderhoff and J. Guillot, J. Polym. Sci.: Part B: Polym. Phys. 26, 1495 (1988).

"Dispersion Polymerization of Styrene in Ethanol: Monomer Partitioning Behavior and Locus of Polymerization", Y.Y. Lu, M.S. El-Aasser and J.W. Vanderhoff, J. Polym. Sci.: Part B: Polym. Phys., 26, 1187 (1988).

"Preparation of Large-Particle-Size Monodisperse Latexes in a Rotating-Cylinder Reactor", J.H. Kim, E.D. Sudol, M.S. El-Aasser, and J.W. Vanderhoff, Chem. Eng. Sci., 43(8), 2025 (1988).

Recent Ph.D. Dissertations

"Preparation, Swelling and Phase Separation of Large-Particle-Size Monodisperse Latexes", Hrong-Roang Sheu.

"Dispersion Polymerization of Styrene in Ethanol", Ying-Yu Lu.

Copies of the abstracts are available upon request

The Emulsion Polymers Institute's 20th Annual Short Course, "Advances in Emulsion Polymerization and Latex Technology", will be held at Lehigh on June 5-9, 1989. The European Short Course will be given August 21-25, 1989 in Davos, Switzerland.

The 64th National Colloid and Surface Science Symposium will be held at Lehigh University on June 18, 19 and 20, 1990. A Special Symposium on "Polymer Colloids" will be a part of this meeting. For further information contact Mohamed El-Aasser.

EMULSION POLYMERS INSTITUTE
Lehigh University

Graduate Research Progress Reports
No. 30 July 1988

CONTENTS

PREPARATION OF POLYMER COLLOIDS

CHARACTERIZATION OF POLYMER COLLOIDS

POLYMERIZATION KINETICS, REACTOR DESIGN AND CONTROL

APPLICATIONS OF POLYMER COLLOIDS

Contribution to Polymer Colloids Newsletter
Current Research Projects - Alice P. Gast
August 1988

Mobility of Proteins Adsorbed at the Solid-Liquid Interface

with Robert Tilton

Goal: To understand the mobility of adsorbed proteins as a function of surface characteristics, residence time, surface concentration, and shear rate.

Summary: This work represents a shift in the emphasis of protein adsorption studies toward the investigation of the complex behavior of adsorbed proteins on the molecular level. The mobility of adsorbed proteins may play a fundamental role in the formation of ordered arrangements of proteins on solid surfaces. Mobility is quantified by a combination of total internal reflection fluorescence and fluorescence recovery after pattern photobleaching. A key feature of the technique is the use of intersecting coherent laser beams to create an interference fringe pattern for pattern photobleaching and for monitoring the fluorescence of adsorbed fluorescently labelled proteins. By changing the angle of intersection, we change the characteristic length for transport in order to distinguish between diffusion and linear flow. We are currently experimenting with different surface-protein pairings in order to determine those surface and protein properties that afford the greatest mobility.

The Effect of Water in Micellar Solutions of Polystyrene-Poly(ethylene oxide) Diblock Copolymers

with Kathleen Cogan

Goal: To investigate the influence of water content on the size and aggregation number of saturated and unsaturated micelles formed from diblocks of varying composition and molecular weight.

Summary: Trace amounts of water are inevitably found in most organic solvents. Due to its compatibility with poly(ethylene oxide), we find water plays an important role in the structures formed by polystyrene-poly(ethylene oxide) diblock copolymers in solvents selective for polystyrene. Present work utilizes coulometric Karl Fischer titration to measure water content and dynamic light scattering with Provencher's data analysis technique "CONTIN"[1] to obtain size *distribution* information. We find unusually large aggregates that are stable for periods longer than a month in solutions with low water content. Addition of water promotes the formation of monodisperse spherical micelles from both single chains and large aggregates. Further addition of water results in a solution of swollen micelles, i.e., a polymeric microemulsion. A second aspect of this study focuses on the properties of saturated micelles. Preliminary results reveal the micelles solubilize water on the order of one water molecule per poly(ethylene oxide) repeat unit.

[1] S. W. Provencher, Makromol. Chem. **180**, 201-209 (1979)

Fluorescence Studies of Polymer Adsorption: A Simplified Theoretical Model Describing Rearrangement of Adsorbed Polymer

with Kookheon Char (jointly advised with C. W. Frank)

Goal: To understand the conformational behavior of polymer chains confined to colloidal surface as a function of surface chemistry, surface curvature, and polymer solution thermodynamics.

Summary: A simple theoretical model considering the rearrangement of tracer chains due to the presence of displacing polymer is developed and predictions from the model are compared with the fluorescence experimental data obtained previously[1]. A Gaussian random flight chain for a tracer polymer adsorbing on a planar surface is assumed. The rearrangement of tracer chains on the surface is assumed to be affected only by a displacer field using a modified diffusion equation similar to a self-consistent equation. The displacer field used here is separately calculated from the self-consistent equation. The approximate analytic expression derived here shows a qualitative agreement with what we observed from the fluorescence experiment[1]. To make a direct comparison with the fluorescence experiment, the hydrophobic attraction between hydrophobic pyrene ends attached to a hydrophilic poly(ethylene glycol) chain in water has been considered by using a capture process[2] and corrections for the displaced tagged chains have also been taken into account. Comparison of the theoretical predictions with the fluorescence experimental data, as illustrated in Figure 1, shows a qualitatively good agreement for tracer polymers of two different molecular weights (4250, 8650) except in plateau region. We speculate that the discrepancy in the plateau region is due to the entrapment of tracer chains by the adsorption of higher molecular weight displacers before their rearrangement on the surface. This hypothesis is not included in the theory, yielding a notable difference between the predictions and the experimental data.

Publication: submitted to Langmuir

1. Char, K; Gast, A. P.; Frank, C. W. *Langmuir* **1988**, *4*, 989.
2. Char, K; Frank, C. W.; Gast, A. P. *submitted to Macromolecules.*

Kinetic Studies of Poly(ethylene oxide)-polystyrene Diblock Copolymer Adsorption

with Mark R. Munch

Goal: To understand the mechanisms involved in diblock copolymer adsorption as a function of copolymer concentration above and below the critical micelle concentration, molecular weight, and chain composition.

Summary: A non-invasive, optical techique for studying the kinetics of block copolymer adsorption at the dielectric solid-liquid interface has been developed. This technique utilizes total internal reflection of visible light to probe the interface. Laser light is directed through a glass reflection prism designed to give many internal reflections, enhancing the signal. The light experiencing reflection undergoes a phase change monitored by a Mach-Zehnder type interferometer that is thermally and vibrationally isolated. This phase change is sensitive to copolymers adsorbing at the interface. The phase change of the light as copolymers adsorb is measured by monitoring fringe positions of the interference pattern produced by the interferometer. A linear photodiode array is used as the detector. Phase changes for two orthogonal polarizations are monitored simultaneously to study the adsorbed amount as a function of time. Computerized data acquisition allows tenth second sampling. The experiments are performed under gentle flow conditions in order to limit diffusion as the rate-controlling process for the adsorption. The surface concentration of poly(ethylene oxide)-polystyrene copolymer of molecular weight 184,000 in cyclopentane at 20°C increased exponentially at early times reaching saturation at approximately three hours. Also, the block copolymers appear to be irreversibly adsorbed with respect to the addition of pure solvent.

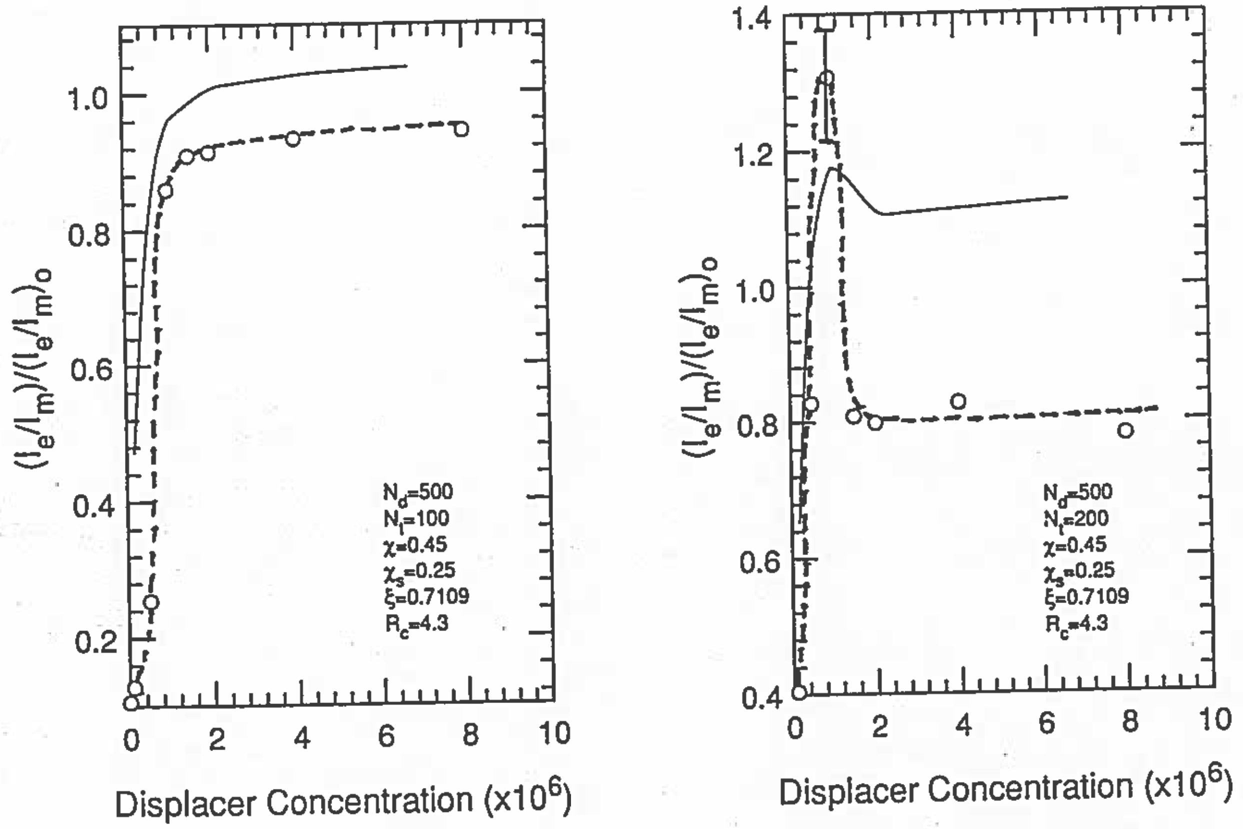

Figure 1. Comparison between theoretical predictions and fluorescence experimental data: ----- theory, - - - experiment.

CASE WESTERN RESERVE UNIVERSITY

Polymer Colloids Newsletter Contribution
August 31, 1988

For the past two years, the focus here has been on forming polymer colloids where the polymer is the continuous phase. The best developed example is a polymer foam. A water-in-oil emulsion is prepared in which the continuous oil phase is styrene. After polymerization of the styrene, the water is driven off by low-pressure evaporation. This work was initially supported by the U.S. Department of Energy, who wanted a foam of very low polymer volume fraction (< 10%) and with very low pore size (< 3 microns).

The method selected uses as stabilizers short-chain diblock AB and ABA triblock polymers, in which the A block is hydrophobic and the B block hydrophilic. Similar methods were developed by Riess, Rogez et al. (1), who prepared their stabilizers by anionic polymerization, with polystyrene A blocks and poly(oxyethylene) B blocks. We used instead the cationic ring-opening polymerizations of substituted oxazolines, as developed by Litt et al. (2). Our work went somewhat beyond that of Riess' group, in that we studied the effect of various parameters on pore size.

The hydrophilic A block in our work was a polymer of commercially available 2-ethyl-2-oxazoline. We wanted hydrophilic groups which would form films of low surface energy. Reference (3) describes the synthesis of two new monomers: 2-[4-(t-butyl)phenyl]-2-oxazoline and 2-[(3,5-di-t-butyl)phenoxy)propyl]-2-oxazoline, as well as the properties of homo- and block polymers prepared from these monomers. Reference (4) shows how the relative proportions of styrene, stabilizer and water influence the stability of water-in-oil emulsions and the pore size of the resulting foams. More recent work has shown that triblock polymers of a given overall composition are more effective as stabilizers than are diblock polymers. Average pore sizes as small as 5 microns were obtainable with 90% void space and 10% polymer by volume.

Characterization of average pore size and pore size distribution formed a key part of this study. A method was developed (4) which allows pore size distribution to be calculated from the distribution of chord lengths intercepted by the pores when random lines drawn through the foam. This is equivalent to drawing random lines through a micrograph of a fracture surface of the foam. The method was tested by computer simulation of the line-drawing experiment with uniform, monomodal and bimodal sphere distributions.

Polymer colloid work at CWRU is being conducted collaboratively by Irvin Krieger and Morton Litt, and independently by Syed Qutubuddin. This report brings things more or less up to date after a long lapse; future reports will concentrate on work in progress.

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1. D. Rogez, S. Marti, J. Nervo and G. Riess, Makromol. Chem. 176, 1393 (1975) (and references therein).

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4. M. Litt, B. R. Hsieh, I. M. Krieger, T. T. Chen and H. L. Lu, J. Colloid & Interface Sci. 115, 312 (1987).

5. J. Z. Ruan, M. H. Litt and I. M. Krieger, J. Colloid & Interface Sci. (accepted).

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Polymer Colloids at the University of Sydney

Reporter: D. H. Napper

The Entry of Free Radicals into Latex Particles

Although emulsion polymerizations have now been studied for over 50 years, a detailed understanding of the mechanism whereby free radical activity generated in the aqueous phase is transferred to the latex particles is still lacking. It has long been postulated that the primary free radicals (e.g., $SO^{\overline{\cdot}}$, $\cdot OH$), which are too polar per se to enter the organic interiors of the swollen latex particles, add on monomer molecules to generate oligomeric free radical species that possess surface activity. These oligomers then adsorb onto the surfaces of the latex particle, allowing the free radica activity access (by some unspecified mechanism) to the monomer located in the interior of the latex particles. There is little, if any, direct experimental evidence to confirm or refute such a mechanism, although there is some indirect evidence that supports it. Nevertheless, it provides a useful working hypothesis in the absence of alternative entry mechanisms. But other mechanisms, not necessarily mutually exclusive with the oligomeric entry mechanism, can be envisaged. For example, if the oligomeric species were to add on more monomer to the point where the species become insoluble, free radical entry would occur via an insoluble, colloidal species rather a soluble oligomer. Entry would thus proceed by heterocoagulation rather than by adsorption and/or absorption mechanism which might be expected to display different phenomenology.

In an attempt to differentiate between those two competing theories for free radical entry, experiments have been undertaken to measure the activation energy for entry. This can be most readily accomplished by using γ-irradiation as initiator. The activation energy for the first order rate coefficient ρ was found to be 25 $\pm$ 3 kJ mol. The problem with the first order rate coefficient is that it depends upon the free radical concentration $[R\cdot]_\omega$ in the aqueous phase. The second order rate constant k_e (related to ρ by $\rho \simeq k_e [R\cdot]_\omega$) is more informative and its activation energy can be shown to be less than or equal to that of ρ. The measured value of the activation energy suggests that the rate determining step is physical rather than chemical in character, although propagation events cannot be rigorously excluded. The precise nature of the rate determining entry step remains elusive: electrostatic interactions are not apparently important because ρ is not influenced by changing the ionic strength or the surface charge density of the particles, when peroxydisulfate was the initiator. Whether it has anything to do with the coalescence of the free radical species with the particle or the dehydration of the entering species remains to be determined.

Recent Publications

1. G. A. Leslie, I. A. Maxwell, M. J. Ballard, R. G. Gilbert and D. H. Napper, Aust. J. Chem. 41, 279)1988).

   'A New Method for Determining Propagation Rate Coefficients at High Fraction of Polymer'

2. G. T. Russell, D. H. Napper and R. G. Gilbert, Macromolecules, 21, 2133 (1988). 'Termination in Free Radical Polymerizing Systems at High Conversions'

3. G. T. Russell, D. H. Napper and R. G. Gilbert, Macromolecules, 21, 2141 (1988) 'Initiator Efficiencies in High-Conversion Bulk Polymerizations'

4. M. Buback et al., J. Polym. Sci. C. Polym. Lett., 26, 297 (1988) 'Consistent Values of Rate Parameters in Free Radical Polymerization Systems'

Contribution to Polymer Colloid Newsletter R. Pelton

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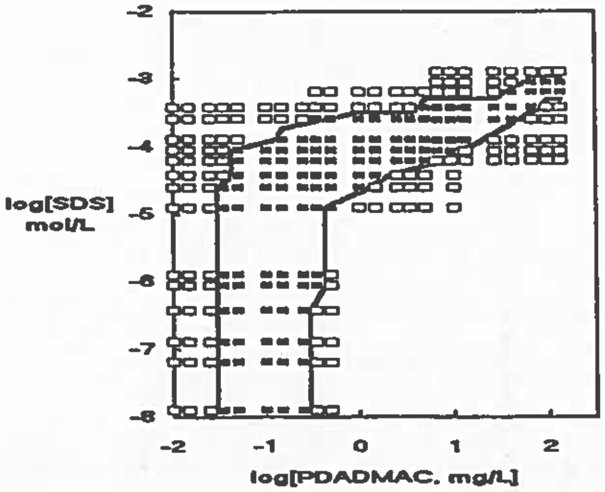
LATEX FLOCCULATION BY POLY(DIMETHYLDIALLYL AMMONIUM CHLORIDE) IN THE PRESENCE OF ANIONIC SURFACTANT. R. Pelton and D. Lawrence

Persulfate initiated, surfactant-free, polystyrene latex was flocculated by mixtures of poly(dimethyldiallyl ammonium chloride), PDADMAC, and anionic surfactants. The Figure 1 shows the flocculation domain diagrams for PDADMAC plus sodium dodecyl sulfate, SDS. The flocculation behavior is believed to be dominated by the properties of the surfactant-polymer complex which forms between the anionic surfactant and the cationic polyelectrolyte. At surfactant addition levels greater than $10^{-3.6}$ M the flocculation boundary corresponds to the first appearance of insoluble complex which was characterized by PCS and microelectrophoresis. Therefore latex flocculation was believed to a heteroflocculation process between polymer-surfactant complex particles, with diameters between 30 and 2000nm, and the latex particles. The restabilization boundary corresponded to the complex, and presumably the latex, having a high positive mobility.

At surfactant concentrations below $10^{-3.8}$ M insoluble complex was not observed and the mechanisms determining the shape of the flocculation boundary have not been determined. Limited experimentation with Aerosol OT and poly(vinylacetate) latex showed the same trends.

Figure 1 - flocculation domain for polystyrene latex. The solid points denote SDS, PDADMAC combinations, in 0.001 M NaCl, giving flocculation whereas the latex was colloidally stable in combinations corresponding to the open points.



NON-AQUEOUS DISPERSION POLYMERIZATION OF SILICONE STABILIZED PMMA.

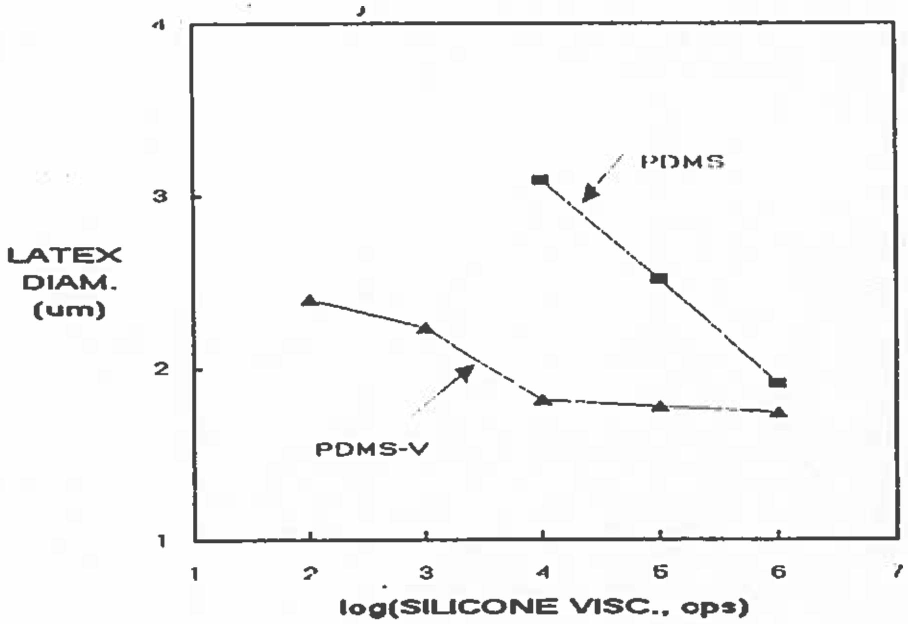
R.H. Pelton, M.A. Brook, and A. Osterroth

The polymerization of methyl methacrylate in heptane in the presence of polydimethylsiloxane (PDMS) was systematically investigated. The siloxane is thought to be grafted onto the surface of the PMMA particles thus giving steric stabilization. The variables considered included the type of initiator, silicone concentration, silicone molecular weight and silicone end groups (trimethyl silyl versus vinyl).

Figure 2 shows average latex particle diameter as a function of silicone viscosity as determined by using a dynamic light scattering. Usually, the standard deviation in diameter measurements was less than 22%. The minimum molecular weight for stable particles was much less with the vinyl end blocked silicones. Presumably, the relatively high reactivity of the vinyl end groups gives, on average, longer tails than random grafting along the PDMS chain.

Experiments are underway to verify the absence of PDMS in the particle core and to modify the silicone steric barrier in situ.

Figure 2: PMMA latex diameter as a function of the viscosity (i.e. molecular weight) of the silicone polymer used to form the steric barrier.



Newsletter Contribution from the University of Akron
(Professor Irja Piirma)

From: Gary Jialanella
Subject: Progress Report

A polymeric surfactant, poly(methyl methacrylate)-graft-poly-(oxyethylene) was prepared utilizing a "grafting onto" technique in which poly(methyl methacrylate), PMMA, was transesterified with poly (oxyethylene), PEO, under alkaline conditions. This reaction can be carried out in a three step process as described in the previous report. Recently, the effect on the yield of the graft copolymer was studied as a function of reaction conditions, i.e. temperature, solvent and time. The optimum temperature and time were found to be approximately 100^{oC} and 20 hours respectively. It was discoved that the solvent can dramatically effect the copolymer yield depending on the solubility of the by-product, potassium methoxide. In polor solvents such as THF, the by-product is soluble. Thus, it is difficult to drive the reaction towards completion even after quenting the reaction with isobutyric acid and distilling off the methanol. It has been found that by running the reaction in nonpolar solvents, such as toluene or pyridine, the by-product is not soluble. Precipitation of the by-product drives the reaction toward completion, and thus, higher graft copolymer yields are obtained.

The effect of the molecular weight of the hydrophobe (PMMA backbone) on the emulsion polymerization of MMA has been studied. The rate of polymerization and the particle size of the latex was found to be independent of the molecular weight of the PMMA backbone within the range of 2,500 g /mol - 12,000 g /mol. In these cases, highly stable latices with similar rates ($R_p \sim 2.5 \times 10^{-2}$ mol /l-sec) and similar particle sizes ($D_z \sim 100$nm) were observed. However, the amount of PEO contained in the graft copolymer was found to greatly influence the rate of polymerization and particle size. Quantitative results are presently being investigated.

Research Progress by Wen-Lin Wu
Title: Synthesis of Methyl Methacrylate-b-Ethylene Oxide
Coplymers and Their Application as Stabilizers in
Emulsion Polymerization of Methyl Methacrylate

Diblock PMMA-PEO and triblock PMMA-PEO-PMMA coplymers have been synthesized for use as polymeric stabilizers in the emulsion polymerization of methyl methacrylate. The synthesis involves the following two methods: (1) Reflux hydroxyl terminated PEO in benzene in the presence of benzoyl peroxide, which is capable of hydrogen abtraction upon decomposition, to generate alkoxide radicals and hence propagate upon adding methyl methacrylate subsequently. (2) Synthesize carboxylic acid terminated PMMA with methyl methacrylate/benzoyl peroxide/3-mercaptopropionic acid in toluene and then couple with hydroxyl terminated PEO by esterification.

All possible di- or triblock methyl methacrylate-ethylene oxide copolymers with different molecular weights or hydrophobic-hydroplilic ratios will be synthesized and thereafter used as steric stabilizers in methyl methacrylate emulsion polymerization. Variations in kinetics and stabilities of the resulting latices will be investigated by changing the structure and composition of these methyl methacrylate-ethylene oxide copolymers.

Research Progress Report
By: Tammy McCartney
Title: Synthesis of Water-Soluble Polyester Surfactants

Water-soluble polyesters with surfactant properties have been synthesized for use as stabilizers in the emulsion polymerization of styrene. The surfactants were prepared by first reacting 2 moles poly(ethylene oxide) (PEO) with 1 mole dimethyl 5-sulfoisophthalate, sodium salt under nitrogen at 200°C using titanium isopropoxide as catalyst. The second step involved addition of phthalic anhydride to the system with a small quantity of N-methyl-2-pyrrolidinone (NMP) and reheating to 240°C under nitrogen for 3 hours. The solvent (NMP) and water by-product were then removed with a nitrogen purge. Products were washed three times with boiling hexane and dried in a vacuum oven. Two surfactants have been synthesized using PEO of molecular weights 200 and 1000. Very viscous, brown products were obtained in each case.

An emulsion polymerization using the product prepared with PEO-200 yielded a stable latex which remained stable for several days.

Contribution to Polymer Colloids Newsletter

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Recent Publications

"The resolution of shocks and the effects of compressible sediments in transient settling", Journal of Fluid Mechanics 195 437 (1988).

"A mean field theory for the rheology of phase separated or flocculated dispersions", Colloids and Surfaces 31, 355 (1988) [with P. D. Patel].

"Self-consistent field model of polymer adsorption: Generalized formulation and ground state solution", Macromolecules 21, 1075 (1988) [with H. J. Ploehn and C. K. Hall].

"An experimental study of aqueous suspensions containing dissolved polymer: Part B: Rheology"' Journal of Colloid and Interface Science (submitted) [with P. D. Patel].

A Two Component Model for the Phase Behavior or Colloidal Dispersion Containing Associative Thickener

Maria M. Santore
William B. Russel
Robert K. Prud'homme

Associative polymer, a water-soluble backbone containing 1-2 wt. % hydrocarbon arms (C_{10}-C_{20}) is added to stable colloidal dispersions to control their rheological properties, for example, their resistance to shear thinning. In addition, the associations of the hydrophobic arms with each other and with hydrophobic surfaces such as those of latex particles, induce complex equilibrium phase behavior, the subject of our research. We model these systems as binary mixtures of hard sphere particles and Gaussian coils with adhesive end groups or "stickers." The polymer-polymer and polymer-particle pair potentials derive from Gaussian statistics and the strength of the stickers. Figure 1 shows the dependence of the polymer-particle potential on the adhesion energy between the sticker and the wall. The potential consists of a repulsive core, and when the sticker-wall adhesion is stronger than 2.5 kT, an attractive well. This well diminishes if the stickers are moved from the ends of the chain or if the backbone is made more flexible by increasing the number of Gaussian segments. Such interaction potentials are incorporated into Barker-Henderson perturbation theory to determine macroscopic thermodynamic variables such as pressure and chemical potentials, which must be equal in all phases at equilibrium. This criteria is used to generate fluid-fluid phase diagrams, summarized in figure 2 which shows the minimum polymer required to flocculate a dispersion of 20% solids. In the limit of weak stickers, 0.40 volume fraction polymer based on radius of gyration will flocculate the system via volume restriction flocculation. When two particles approach such that their exclusion layers overlap, the polymer concentration outside the pair is greater than that between the particles, generating an osmotic force to drive the particles together. As the sticker-particle and sticker-sticker adhesion increases (right branch of the curve) the system is stabilized against volume restriction flocculation because the stickers attract the polymer to the particle surface. Increasing only the sticker-sticker adhesion (left branch) destabilizes the system at strong sticker strengths, since the system has its lowest energy when polymer chains group together. The model predicts that moving the stickers away from the chain ends or increasing the backbone flexibility minimizes the effects of the stickers, favoring volume restriction flocculation.

These trends generally agree with experimental data with polymethyl methacrylate /polybutyl acrylate copolymer latices and hydrophobically modified polyethylene oxide and hydroxyethyl cellulose. The model's major shortcoming is that it does not predict the bridging flocculation observed for strong sticker strengths and low polymer concentrations. The modeling of bridging flocculation is an area of ongoing research.

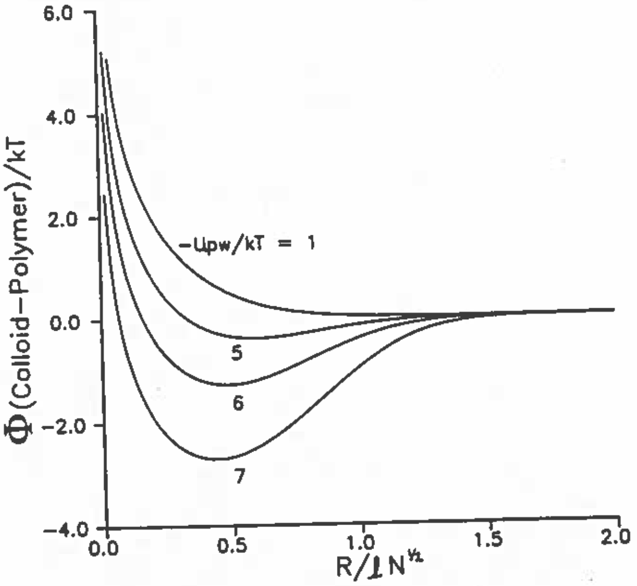

Figure 1. The effect of sticker-particle adhesion, u_{pw}, on the polymer-particle interaction potential. N=1000 Gaussian segments. u_{pp} = -kT.

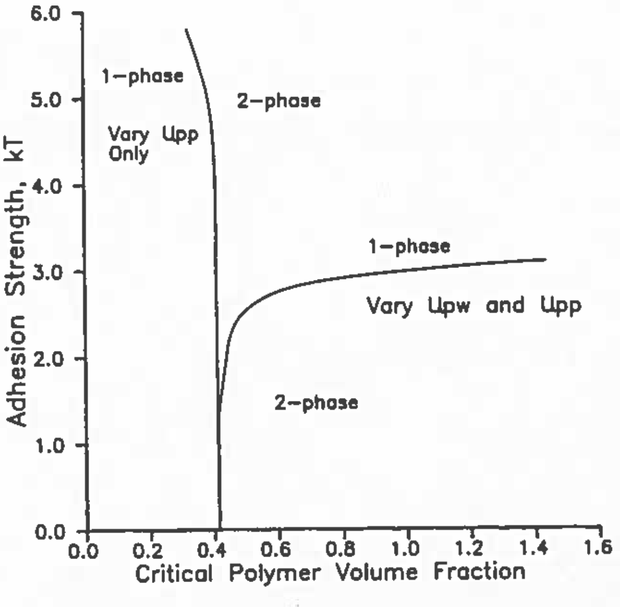

Figure 2. The minimum volume fraction polymer (based on radius of gyration) neeeded to flocculate a dispersion containing 20% solids. N = 1000 Gaussian segments. Particle/polymer diamter ratio = 2. On right curve, $u_{pp} = u_{pw}$. On left curve, $u_{pw} = 0$.

Elasticity of Sterically Stabilized Dispersions in Poor Solvents

Mae Chen
William B. Russel

Colloidal spheres bearing grafted octadecanol chains dispersed in hexadecane flocculate with decreasing temperature. Consequently the rheology changes from that of a fluid to a solid with a finite low frequency modulus and a yield stress. Our experiments capitalize on the thermal reversibility of the process to characterize the mechanical response as a function of the volume fraction of particles and the strength of the attraction for samples with no mechanical prehistory. The structure then reflects only the flocculation process induced by lowering the temperature of the sample within the rheometer.

Small amplitude oscillatory tests characterize the non-equilibrium structure of the gel. A low frequency plateau in the shear modulus appears at a temperature which depends on volume fraction, defining the onset of gelation (Figure 1), and thereafter increases with volume fraction and temperature (Figure 2). Under an applied constant stress the gels respond elastically until the yield stress, which varies much as the plateau modulus, is exceeded. The structure of the gel, reflected by the volume fraction dependence of the modulus, depends on both the temperature and the volume fraction.

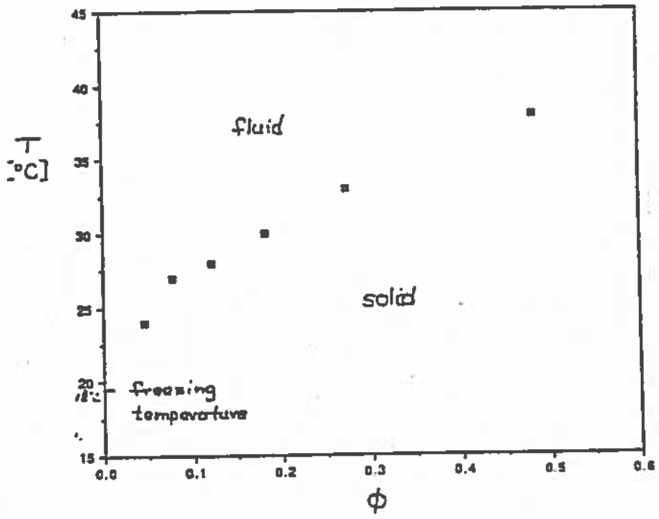

Figure 1: Gelation temperature as function of volume fraction for 25 nm radius spheres in hexadecane.

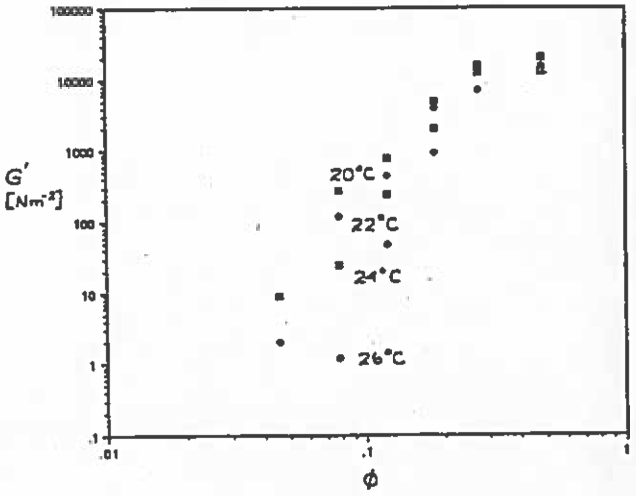

Figure 2: Low frequency plateau modulus as function of volume fraction for temperatures below gelation.

YKI YTKEMISKA INSTITUTET
Institute for Surface Chemistry

CONTRIBUTION TO THE POLYMER COLLOID GROUP NEWSLETTER

submitted by Per Stenius
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Abstract of paper to be presented at the 7th Int. Symp. on Surfactants in Solution, Ottawa, Canada (oct. 1988)

COMPETITIVE ADSORPTION OF SURFACTANTS AND POLYMERS IN LATEX AND TITANIUM DIOXIDE SUSPENSIONS

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The competitive adsorption of nonylphenol deca(oxyethylene glycol) monoether (NPE_{10}) and sodium dodecyl sulphate (SDS) on poly(butylmethacrylate) latex confirms the analogy between mixed adsorption and mixed micellization. The competitive adsorption can therefore be calculated from the critical micelle concentrations (cmc) of the two surfactants. Further, the influence of small amounts of organic solvent can be rationalized based on their effect on the cmc's of the surfactants.

Coating of TiO_2-pigment with different mineral oxides has a great influence on the adsorption. This can be understood in view of the different acid/base characteristics of the coatings, e.g. TiO_2 coated with Al_2O_3 and Al_2O_3+SiO_2 result in a basic and an acidic pigment surface, respectively. The sodium salt of polyacrylic acid (PAA), ethyl hydroxyethyl cellulose (EHEC) and SDS do adsorb on this basic pigment but not on the acidic one. NPE_{10} adsorbs on neither pigment.

The competitive adsorption of PAA and EHEC on Al_2O_3-coated TiO_2 depends on the order of addition of the polymers. Preadsorbed EHEC does not influence the adsorption of PAA compared to the adsorption on the naked pigment. About 20% of the preadsorbed EHEC desorbes wher PAA is adsorbed. If the order of addition is reversed, EHEC adsorbs to the PAAcovered pigment surface in a much lower degree than on naked pigment and very small amounts of the PAA desorbs. The results are of relevance for understanding the behavior of paint dispersions.

Institute for Surface Chemistry

SURFACE MODIFICATION OF POLYSTYRENE LATEX BY POLYMERIZABLE SURFACTAN

E. Sjöblom and J. Kovacs, Institute for Surface Chemistry,
Box 5607, S-114 86 Stockholm, Sweden

Monodisperse, emulsifier-free polystyrene latex (ϕ =320 nm) has been surface modified by adsorbing and polymerizing lauryl vinylbenzyl dimethyl ammonium chloride (LVDAC). The result was evaluated by measuring the electroforetic mobility of the latex as function of volume distilled water passing through a serum replacement cell containing the modified latex, figure 1.

Provided Γ/Γ_{max} is > 95%, a high positive and constant mobility is observed. This is interpreted in terms of a successful polymerization resulting in a permanent surface modification. As the degree of coverage of adsorbed surfactant is reduced, not only the initial mobility but also the mobility after replacing the serum is significantly reduced, i.e. the surface layer is partly desorbed. However, if the polymerizable surfactant is adsorbed either after preswelling the latex by styrene or styrene is added together with the surfactant, the polymerization is successful and the surfactant is anchored at the particle surface also at lower degrees of coverag This indicates a possibility of making polymer particles with controlled surface properties.

The technique has also been used for surface modification of minera and cellulose containing materials.

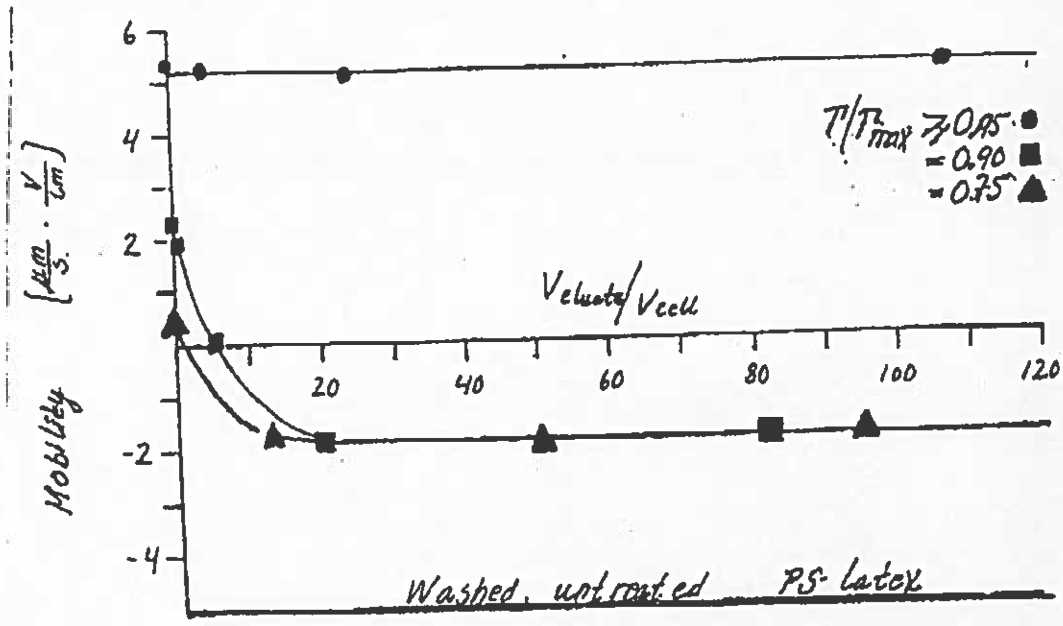


Figure 1. Electroforetic mobility as function of volume distilled water passing through a serum replacement cell containi polystyrene latex modified with lauryl vinylbenzyl dimethyl ammonium chloride (LVDAC). The cell volume V_{cell} 17 ml. The amount of surfactant is expressed as Γ/Γ_{max}

Contribution to the Polymer Colloids Group Newsletter
Fall 1988

Polymer Research Laboratory
University of New Hampshire

Donald C. Sundberg

Morphology Control in Polymeric Microparticles

A more complete thermodynamic analysis for the equilibrium morphology of two phase polymer particles dispersed in water has been accomplished. The thermodynamic relationships are derived from a surface free energy analysis of the formation of particular types of morphologies from an initial state comprising of a pure bulk phase polymer completely separated from an aqueous dispersion of the other polymer. The free energy equations are normalized by the initial particle surface area of the dispersed polymer and as such have units of mN/m, or dynes/cm. Designating the first state polymer as "O" for original polymer, and the other polymer as "P" for post-formed or second stage polymer, the following equations express the reduced surface energies of each morphology as a function of volume fraction of second stage polymer, ϕ_p.

Core-shell: $(\Delta\gamma)_{CSPO} = \gamma_{op} + \gamma_{pw}(1-\phi_p)^{-2/3}-\gamma_{ow}$

Inverted core-shell:

$$(\Delta\gamma)_{CSPO} = \gamma_{wo}\{[1-\phi_p]^{-2/3}-1]\} + \gamma_{op}\{\phi_p/(1-\phi_p)\}$$

Hemisphere:

$$(\Delta\gamma)_{HS} = (1-\phi_p)^{-2/3}\{\gamma_{pw}(h/2R) + \gamma_{wo}[1-(h/2R)-(1-\phi_p)^{2/3}] + \gamma_{op}(h/2R)[1-(h/2R)]\}$$

where

$$4\phi_p = 6(h/2R) - 1 + [1-2(h/2R)]^3$$

Computation of $(\Delta\gamma)_{HS}$ must be done by using the latter equation to obtain the value of (2h/R) from the chosen ϕ_p. A more accurate analysis of the free energy change for the hemispherical morphology can be obtained, but it involves a trial and error solution for the interfacial energy at any given volume fraction of polymer 2.

It is of significant interest to look at the limiting behavior of the $(\Delta\gamma)$ equations as the volume fraction of polymer 2 approaches zero. Such a situation is approximated in practice when it is desired to produce a core-shell morphology (CSOP) with an extremely thin shell of the second polymer. Taking the limit of above equations as ϕ_p goes to zero,

$$\lim_{\phi_p \to o} (\Delta\gamma)_{CSOP} = \gamma_{op} + \gamma_{pw} - \gamma_{ow}$$

$$\lim_{\phi_p \to o} (\Delta\gamma)_{CSPO} = \lim_{\phi_p \to o} (\Delta\gamma)_{HS} = 0$$

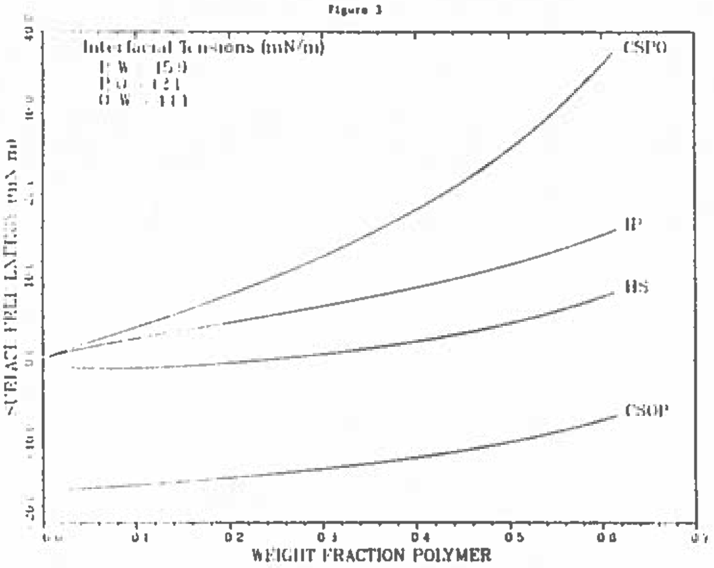
These thermodynamic relationships have been applied to the experimental systems discussed in our contribution to the Spring 1988 IPCG Newsletter. Figures 3, 4 and 5 shown on the next page give an idea of the type predictions one can make using only interfacial tension data. Comparing figures 3 and 4 shows that by only changing surfactants in the PMMA/Decane system, the preferred morphology can be changed from core-shell to hemisphere (the IP designation is an "individual particle" reference state and can be ignored in the present discussion). On the other hand, changing the decane to 1-decanol while maintaining the presence of PMMA and the same surfactant, one expects the morphology to shift from core-shell to inverted core-shell. These predictions are in concert with the experimental results presented in our last newsletter contribution.

Effect of Fillers on the Kinetics of Free-Radical Polymerization

We have concluded the first stage of a study on the influence of particulate fillers such as glass, carbon blacks and pigments on the course of the free radical polymerization of MMA in the bulk state. Results at this stage indicate that when filler particles are less than about one half a micron, they can restrict the diffusion of PMMA macroradicals and enhance the normal gel effect. This has been shown for silica and titanium dioxide fillers. The use of carbon black fillers severely retards polymerization rates due to surface chemistry effects upon the normal free radical initiators (B_2O_2 , AIBN, etc). However, when the inhibitory effects of the carbon black surface can be normalized out of the kinetic results (as in the case of AIBN initiator), an enhancement in reaction rate can be seen as compared to an unfilled sample. This work will be presented at the ACS meeting in Los Angeles in September, 1988.

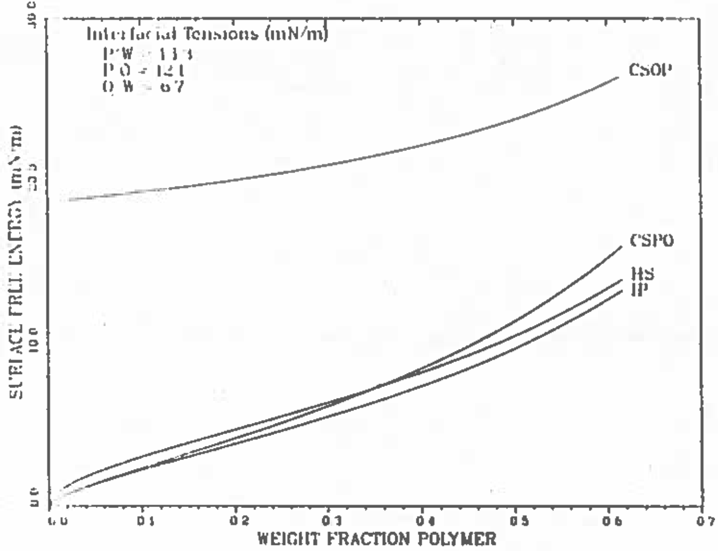
PMMA/DECANE/MXP XSS100 SYSTEM

Figure 3



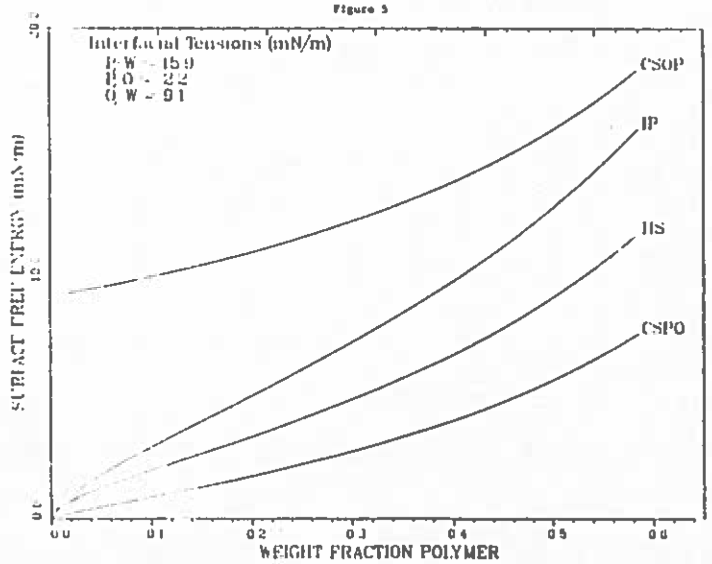
PMMA/DECANE/SLS SYSTEM

Figure 4



PMMA/DECANOL/MXP XSS100 SYSTEM

Figure 5



Contribution to the Polymer Colloid Newsletter submitted bij A. Vrij

a) ADHESIVE HARD-SPHERE COLLOIDAL DISPERSIONS: FRACTAL STRUCTURES AND FRACTAL GROWTH.

P.W. Rouw and C.G. de Kruif,
Van't Hoff Laboratorium, Rijksuniversiteit Utrecht, 3584 CH Utrecht, The Netherlands.

Silica particles coated with octa-decyl chains and dispersed in linear alkanes (dodecane and higher alkanes) show gelation upon cooling. The structure of these gels can be characterized in terms of a fractal dimension $d_f = 2.1$.

Aggregation and gelation at temperatures just below the cloudpoint is studied by light-scattering and described by using a finite cluster size of the growing fractal. Aggregate size is found to increase linearly with time. The influence on d_f of quench temperature, volume fraction, particle size and solvent type is discussed.

b) ADHESIVE HARD SPHERE COLLOIDAL DISPERSIONS. DIFFUSION COEFFICIENT AS A FUNCTION OF WELL DEPTH.

P.W. Rouw and C.G. de Kruif,
Van't Hoff Laboratorium, Rijksuniversiteit Utrecht, 3584 CH Utrecht, The Netherlands.

When dispersed in a marginal solvent like benzene, sterically stabilized silica particles exhibit an effective attraction. This attraction is due to the interaction of solvent molecules with the stabilizing chains and is modelled by a square-well potential; the well has a depth of $\varepsilon/kT = L(\theta/T - 1)$, $\sigma \leq r \leq \sigma + \Delta$. L is an interaction parameter, θ the theta temperature of the chain-solvent pair, σ the particle diameter and Δ the width of the square well.

An expression for the diffusivity of adhesive hard spheres is derived with the help of the general Stokes-Einstein equation. The model allows scaling to one master plot of experimentally determined diffusion coefficients for samples of 6 volume fractions, at 20 different temperatures and for each sample at 3 scattering angles. Additional results obtained with the model are discussed as well. Phase separation in the above-mentioned silica dispersions occurs at a well-depth of about 5 kT.

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c) STRUCTURE FACTOR DISTORTION FOR HARD-SPHERE DISPERSIONS SUBJECTED TO WEAK SHEAR FLOW: SMALL ANGLE NEUTRON SCATTERING IN THE FLOW-VORTICITY PLANE.

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[2] Institut Laue-Langevin, 156 x Centre de Tri, 38042 Grenoble Cedex, France.

Small angle neutron scattering (SANS) was used as a probe of the structure factor distortion for concentrated hard-sphere dispersions subjected to steady shear flow. The dispersions consisted of stearically stabilized silica spheres of 40 nm radius suspended in cyclohexane, with volume fractions $0.36 < \phi < 0.52$. We subjected the dispersions to weak shear flow (Peclet number Pe<1) in a Couette flow cell, and we collected intensity measurements in the flow-vorticity plane. We conducted the experiments using the D11 spectrometer at the Institut Laue-Langevin in Grenoble, France.

The data permit a thorough evaluation of the existing theories for the shear-induced distortion of the structure factor. We find that the theories as they stand severely under-predict the distortion at low wavevectors ($|k| < 0.1\ \text{nm}^{-1}$), but the theories can be made to qualitatively agree with the data by adjusting Pe to a higher value in each calculation. The theories are based on a perturbation expansion that is linear in small Pe, but such a perturbation expansion is inadequate for describing our data. We show that the non-equilibrium contribution to the structure factor is proportional to fractional powers of Pe, with the exponent depending on volume fraction ϕ. The failure of the theories is probably due to their neglect of hydrodynamic interactions, which are important in concentrated dispersions.

The distortion of the structure factor is greatest around its first maximum, with significant distortion being exhibited in both the flow and vorticity directions. The peak in the structure factor broadens, indicating that weak shear flow produces a more disordered structure relative to the equilibrium structure. The data reveal that the shear flow results in a decreased concentration of particles in the flow direction. The concentration of particles in the vorticity direction increases when shear flow is applied, and the formation of temporal clusters is probable.

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REPORT FROM
THE COLLOIDS LAB AT THE UNIVERSITY OF ILLINOIS, URBANA

C. F. Zukoski

The Steady Shear Behavior of Electrorheological Suspensions With L. Marshall, D. J. Klingenberg and J. W. Goodwin

The continuous shear response of electrorheological (ER) suspensions is characterized by a shear rate and field strength dependant apparent viscosity. Based on the data gathered by L. Marshall for her Ph. D. dissertation under the guidance of J.W. Goodwin at the University of Bristol, we have developed a model which is capable of predicting observed behavior.

Primarily, the suspension studied (hydrated poly(methacrylate) particles with an average effective radius of 4.5 ± 45% microns suspended in a chlorinated hydrocarbon) were found to be shear thinning in the absence of an applied field and to approach a limiting Newtonian viscosity at shear rates between .01 and .1 s^{-1}. Based on electrophoretically determined surface potentials (46 mV with aκ of 46) and typical Hamaker constants, this behavior is attributed to the weak agglomeration of the particles in the absence of viscous stresses.

As shown in Fig.(1), in the presence of an applied field, the apparent viscosity increases dramatically showing three orders of magnitude change from the non-electrofied suspension at 400 V/mm at low shear rates. The electrofied suspensions were also found to be shear thinning and to approach the same limiting Newtonian viscosity as the non-electrofied suspensions at large shear rates. Analyzing these results in terms of the forces acting on the particles four dimensionless force ratios can be defined on which the macroscopic properties of the suspension should depend. These are:

i) the ratio of thermal to polarization forces which is always small ,

ii) the ratio of van der Waals attractive forces to polarization forces which takes on values of $10^{-3}-10^{-2}$,

iii) the ratio of double layer forces to polarization forces which has values of $10^{-4}-10^{-2}$ and,

iv) the ratio of viscous forces to polarization forces.

Polarization forces are those generated due to the action of the electric field on particles with dielectric constant ϵ_p suspended in a solvent of dielectric constant ϵ_c and they scale as $12\pi\epsilon_0\epsilon_c(a\beta E)^2$.

From this analysis, it becomes clear that for the suspensions studied, Brownian forces are not important, and polarization forces are capable of completely rearranging the weakly flocculated network which exists in the absence of the applied field. This gives rise to the fibrinated networks observed in ER suspensions and shown in Fig.(2).

The fifth group, which we call the Mason number (Mn) after the pioneering work of Stan Mason and co-workers on the effects of combined shear and electric fields on the behavior of suspensions (1) is written.

$$Mn = \eta_c \dot{\gamma} / 2 \epsilon_c \epsilon_0 (\beta E)^2$$

where $\beta = (\epsilon_p-\epsilon_c)/(\epsilon_p+2\epsilon_c)$ (0.42 for the system studied) and takes on values of 10^{-6} - 10. We conclude that at low shear rates (Mn<<1), the suspension structure will be dominated by polarization forces, while at elevated shear rates (Mn>1) the viscous stresses dominate the suspension's response. At a fixed volume fraction and temperature, we thus expect the relative viscosity of the ER suspensions to depend only on Mn. As shown in Figs.(3-4) all of the shear rate and field strength data collapse onto one curve suggesting that the dominant forces are polarization and viscous in origin. The scaling of relative viscosity on $E^2/\dot{\gamma}$ has been observed by other authors (i.e., the region of slope -1 in Figs.(3-4)) (2), however the smooth transition to a constant viscosity has not been previously reported.

Based on these observations and our studies of the fibrinated structures under continuous shear, we have developed a shear zone model (3) to account for the nonuniform degradation of the structure at finite shear rates (see Fig.(2)) and the smooth transition to Newtonian behavior at high shear rates. In this model we postulate two regions in the flowing suspension. In one, polarization forces dominate and the fibrinated structure responds like an elastic solid. In the second region, the suspension behaves as a Newtonian liquid with a viscosity of the suspension in the absence of an electric field. If these regions are to coexist, then at the interface, there must be a balance of viscous and electrical forces. If the fluid region has a thickness Δ , the local rate of deformation is $\dot{\gamma}.L/\Delta$, where $\dot{\gamma}$ is the macroscopic (or apparent shear rate) and L is the separation between the electrodes. If $\dot{\gamma}$ is increased, then to maintain a balance between the viscous and electrical forces at the boundary between the solid and fluid regions, Δ must increase in magnitude (i.e., the shear forces act to degrade the solid structures). By postulating a spatial dependance in volume fraction and allowing for a yield stress at the boundary that depends on volume fraction and field strength, we are able to predict shear rate, shear stress curves as shown in Fig. (4).

Also shown in Fig.(4) is the prediction of a Bingham model. Note that the shear zone model is capable of reproducing the Bingham behavior and thus provides a rational for origin of the good qualitative fit of this model to the experimental data. From the small differences between the shear zone and Bingham models, we conclude that the parameter of greatest importance in predicting the response of ER suspensions is the yield stress. Based on exact calculations of the force between two dielectric spheres in a dielectric fluid in the presence of an external field of magnitude E, a single strand model for the yield stress yields,

$$\tau_y = 18\phi\epsilon_0\epsilon_c f_m(\beta E)^2$$

where ϵ_0 is the permitivity of free space, ϕ is the volume fraction and f_m is the maximum force required to separate two spheres due to a strain perpendicular to the applied field. Each of the terms in this equation can be calculated from a knowledge of ϵ_p and ϵ_c . For the data gathered by Marshall and Goodwin, we are able to make predictions of the yield stress with no adjustable parameters. As shown in Fig.(5), these predictions overestimate the yield stress at low volume fractions but become increasingly accurate at elevated volume fractions. We attribute this to rearrangements in the structure which can occur at low volume fractions and are currently investigating this behavior.

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3. D.J. Klingenberg, Masters Thesis, University of Illinois, 1988.

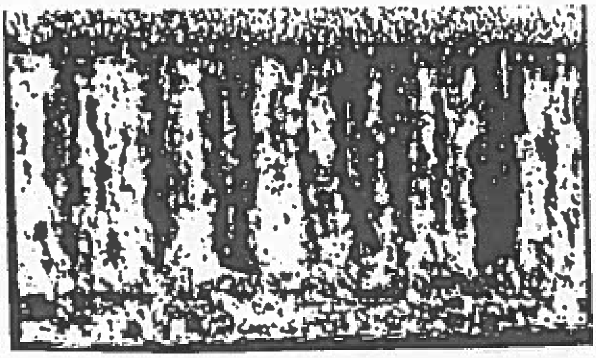


Fig.(2 a) E = 750 V/mm, $\dot{\gamma}$ = 0

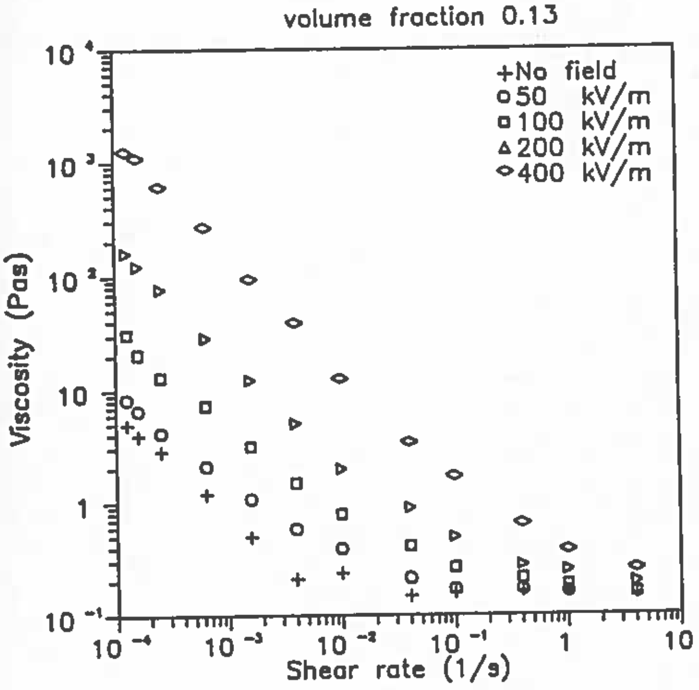


Fig.(1)

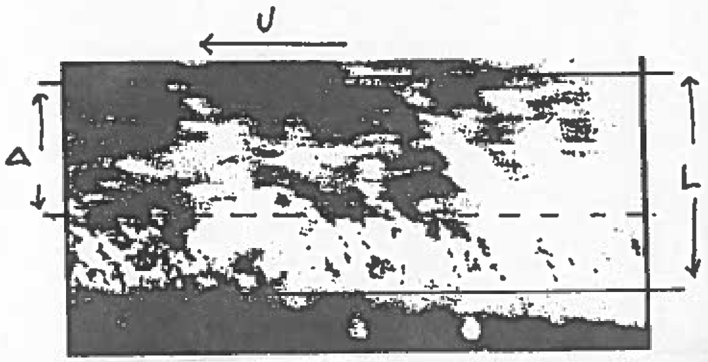


Fig.(2 b) E = 750V/mm, = 10 s-1

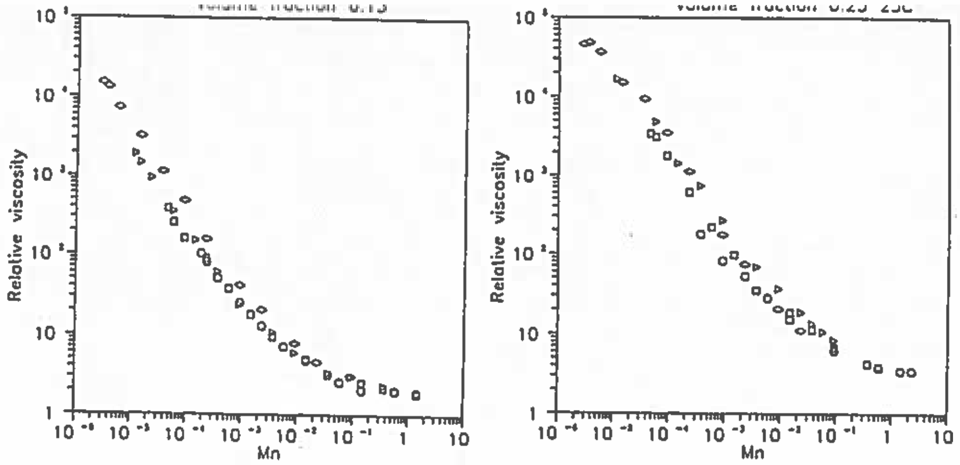


Fig.(3)

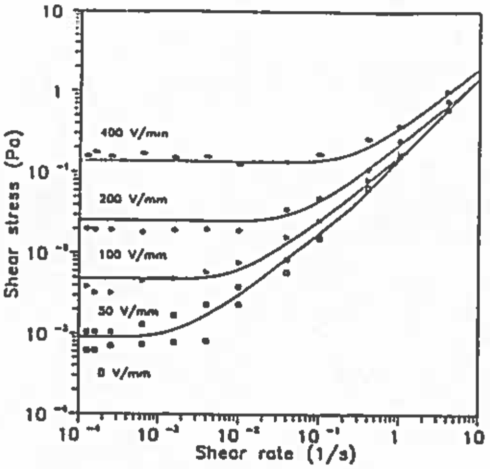
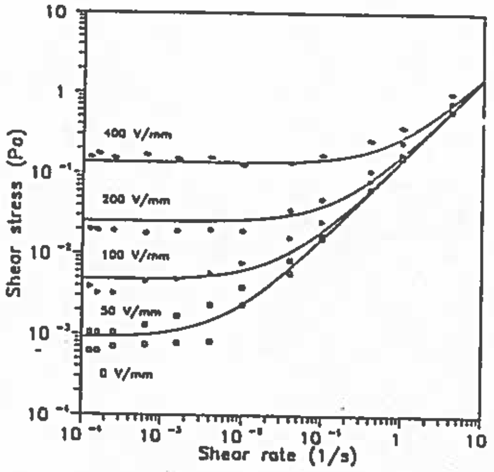


Fig.(4a) Shear Zone Model



(4b) Bingham Model

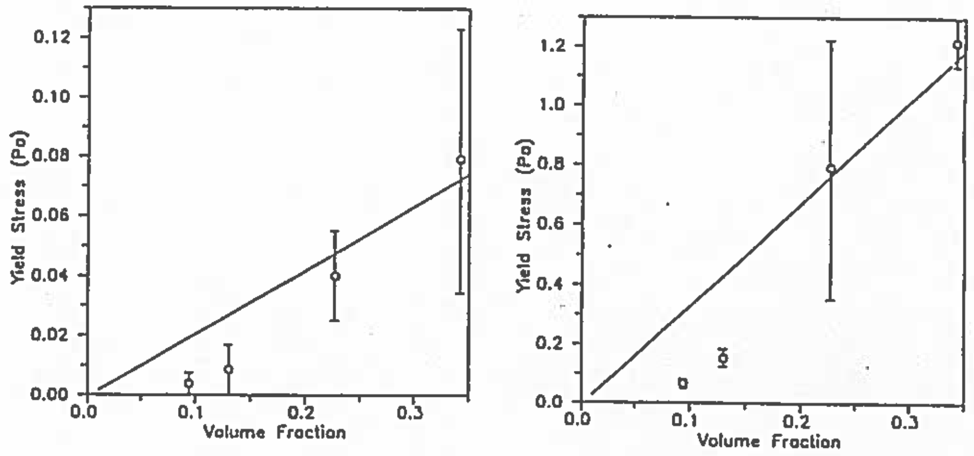


Fig.(5) Yield Stress at 50,100,200 and 400 V/mm as a function of volume fraction. Solid line is prediction