

POLYMER COLLOIDS GROUP NEWSLETTER

Vol. 15 No. 2

25 October 1985

The A.C.S. Division of Polymeric Materials Science and Engineering got its act together shortly after the despatch of the Spring Newsletter and prevailed on Mohamed El-Aasser and Irja Piirma to organise the 'Emulsion Polymerization' Symposium at the Spring 1986 Meeting in New York City, April 13-18. This issue of the Newsletter is appearing a few weeks later than usual and the deadline for the despatch of preprint copy will have passed before Group members receive their copy so it will be necessary for anyone who wants to contribute and had not received earlier notification to contact Mohamed or Irja by phone to see if there is any leeway!

But if there is not you will see from the report of the Annual Business Meeting that a further Emulsion Polymerization Symposium is to be held during the 60th Colloid and Surface Science Symposium at Atlanta, Georgia, 15-18 June. Presumably Gary Poehlein of the School of Chemical Engineering, Georgia Institute of Technology, Atlanta, Georgia 30332-0100 (Telephone: (404) 894-2867) will be organising this and prospective contributors should contact him.

These two meetings should provide ample scope for papers on emulsion polymerization kinetics so it has been decided that the Wingspread Conference, June 30 - July 4, should be an Advanced Research Workshop on the Characterization of Polymer Colloids dealing with the morphology of latex particles, latex rheology, steric stabilization and determination of surface charge. Members can obtain any further information required from Mohamed El-Aasser.

For the last few years Dow Central Research has undertaken the reproduction and mailing of copies of the Newsletter for members in North America. Increasing financial stringency has now made it necessary to seek the help of the industrial members for the circulation to the rest of the world for whom DSM, Geleen, Holland has undertaken the reproduction and despatch of this issue.

Issues will, however, continue to be assembled in Manchester and copy for the Spring 1986 issue should reach me by 28 April 1986. This may mean that the copy has to be posted up to 14 days in advance of the deadline, a feat which some members rarely achieve so that this issue contains some items intended for the Spring issue which only arrived after the copies had been despatched.

Mamoru Nomura apologises for having nothing to contribute to this issue of the Newsletter but announces the '4th Polymer Microspheres Symposium, Japan' to be held 6-8 November, 1986 sponsored by six learned societies: Bob Fitch is to be a Plenary Lecturer and any other Group members or their colleagues who plan to visit Japan or East Asia at that time are invited to contact Dr Nomura who would be able to arrange for them to participate in the Symposium also.

An updated List of Polymer Colloids Group Members is included in this Newsletter.

A. S. Dunn

List of Members of the Polymer Colloids Group
(Revised July 1985)

2

Circulation outwith North America (19)

1. Dr D.C.Blackley, London School of Polymer Technology, The Polytechnic of North London, Holloway, London N7 8DB, England.
2. Dr F. Candau, CNRS Centre des Recherches sur les Macromolécules, 6 rue Boussingault, 67085 Strasbourg Cedex, France.
3. Dr W.A.B.Donners, DSM Research & Patents, P.O. Box 18, 6160 MD Geleen, Holland.
4. Dr A. S. Dunn, Department of Chemistry, UMIST, P.O. Box 88, Manchester M60 1QD, England.
5. Dr J.W.Goodwin, School of Chemistry, University of Bristol, Cantock's Close, Bristol, BS8 1TS, England.
6. Dr F.K.Hansen, Dyno Industrier A/S, Lillestrøm Fabrikker, Svelleveien, P.O. Box 180, 2001 Lillestrøm, Norway.
7. Dr T.W.Healy, Department of Physical Chemistry, University of Melbourne, Parkville, Victoria 3052, Australia.
8. Dr J.Iyklema, Laboratory for Physical and Colloid Chemistry, Agricultural University, De Dreijjen 6, 6703 BC Wageningen, Holland.
9. Dr S. Muroi, Coating Materials Laboratory, Asahi Chemical Industry Co. Ltd., 2-1 Samejima, Fuji-City, Shizuoka, Japan.
10. Dr D.H.Napper, Department of Physical Chemistry, The University of Sydney, Sydney, New South Wales 2006, Australia.
11. Dr M. Nomura, Department of Industrial Chemistry, Fukui University, Fukui, Japan.
12. Dr R.H.Ottewill, School of Chemistry, University of Bristol, Cantock's Close, Bristol, BS8 1TS, England.
13. Dr C. Pichot, C.N.R.S. Laboratoire des Matériaux Organiques, B.P. 24, 69390 Vernaison, France.
14. Dr D.G.Rance, I.C.I. plc, Petrochemicals and Plastics Division, P.O. Box 90, Wilton, Middlesborough, Cleveland TS6 8JE, England.
15. Dr P.J.Stenius, Ytkemiska Institutet, Box 5607, S-114 86 Stockholm, Sweden.
16. Dr J. Ugelstad, Institutt for Industriell Kjemi, Norges Tekniske Høgskole, 7034 Trondheim-NTH, Norway.
17. Dr A. Vrij, Riksuniversiteit Utrecht, van't Hoff Laboratorium, Padualaan 8, 3584 CH, Utrecht, Holland.
18. Dr A. Watillon, Université Libre de Bruxelles, Service de Chimie Analytique et Minérale, 50 av. F.D.Roosevelt, Bruxelles 5, Belgium.
19. Dr V.I.Yeliseyeva, Institute of Physical Chemistry, Academy of Sciences of the U.S.S.R. Leninsky Prospekt 51, 117312 Moscow, U.S.S.R.

117312, МОСКВА.

ЛЕНИНСКИЙ ПР., 51, ИНСТИТУТ ФИЗИЧЕСКОЙ

ХИМИИ АН СССР.

ИРСА. ЕЛИСЕЕВА В.И.

СССР

List of Members of the Polymer Colloids Group
(Revised July 1985)

North American Circulation (22)

1. Dr P. Bagchi, Research Department, Eastman Kodak Co., Chemical Division, Kodak Park B-81, Rochester, N.Y. 14650, U.S.A.
2. Dr D.R.Bassett, Technical Center, Union Carbide Corporation, South Charleston, West Virginia 25303, U.S.A.
3. Dr E.A.Collins, Diamond Shamrock Corp., P.O. Box 318, Painesville, Ohio 44077, U.S.A.
4. Dr M. Croucher, Xerox Research Centre of Canada, 2480 Durwin Drive, Mississauga, Ontario, Canada, L5L 1J9
5. Dr M.S.El-Aasser, Department of Chemical Engineering, Whitaker Laboratory No. 5, Lehigh University, Bethlehem, Pennsylvania 18015, U.S.A.
6. Dr R.M.Fitch, S.C.Johnson & Son Inc., Racine, Wisconsin 53403, U.S.A.
7. Dr J.S.Dodge, B.F.Godrich Co., Chemical Division Technical Center, Avon Lake, Ohio 44012, U.S.A.
8. Dr A.E.Hamielec, Department of Chemical Engineering, McMaster University, Hamilton, Ontario, Canada L8S 4M1.
9. Dr A. Klein, Department of Chemical Engineering, Whitaker Laboratory No. 5, Lehigh University, Bethlehem, Pennsylvania 18015, U.S.A.
10. Dr I.M.Krieger, Olin Building, Case-Western Reserve University, Cleveland, Ohio 44106, U.S.A.
11. Dr C.-C. Lin, Division of Chemical Engineering, Department of Chemical Engineering & Chemistry, New Jersey Institute of Technology, 323 High Street, Newark, New Jersey 07102, U.S.A.
12. Dr I. Piirma, Institute of Polymer Science, University of Akron, Akron, Ohio 44325, U.S.A.
13. Dr J.L.Gardon, Sherwin-Williams Co., 11541 South Champlain Avenue, Chicago, Illinois 60628, U.S.A.
14. Dr G.W.Poehlein, School of Chemical Engineering, Georgia Institute of Technology, Atlanta, Georgia 30332, U.S.A.
15. Dr A. Rembaum, Jet Propulsion Laboratory, California Institute of Technology, 4800 Oak Grove Drive, Pasadena, California 91103, U.S.A.
16. Dr R.L.Rowell, Department of Chemistry, University of Massachusetts, Amherst, Massachusetts 01003, U.S.A.
17. Dr F.L.Saunders, Dow Chemical Co., Central Research, 1712 Building, Midland, Michigan 48640, U.S.A.
18. Dr W.B.Russel, Department of Chemical Engineering, Princeton University, Olden St., Princeton, NJ 08544, U.S.A.
19. Dr V.T.Stannett, Department of Chemical Engineering, Box 5035, North Carolina State University, Raleigh, North Carolina 27607, U.S.A.
20. Dr J.W.Vanderhoff, Emulsion Polymers Institute, Sinclair Laboratory No. 7, Lehigh University, Bethlehem, Pennsylvania 18015, U.S.A.
21. Dr T.G.M. van de Ven, Pulp and Paper Building, Department of Chemistry, McGill University, 3420 University Street, Montreal PQ, Canada, H3A 2A7.
22. Dr D.C.Sundberg, Department of Chemical Engineering, Kingsbury Hall, University of New Hampshire, Durham, New Hampshire 03824, U.S.A.

9 AUG 1985 ³ Recd

IMPERIAL CHEMICAL INDUSTRIES PLC
PETROCHEMICALS AND PLASTICS DIVISION
RESEARCH AND TECHNOLOGY DEPARTMENT
WILTON CENTRE

POLYMER COLLOID GROUP ANNUAL MEETING, TILTON NH - 9 JULY 1985

Present:

D Bassett, D C Blackley, F Candau, J W Dodge, M El-Aasser, R M Fitch,
I M Krieger, R H Ottewill, I Piirma, G Poehlein, D G Rance, R L Rowell,
F Saunders, P Stenius, J W Vanderhoff, Th van der Ven, R Wessling

The Polymer Colloid Group Meeting took place on 9 July 1985 at Tilton NH with 17 members present. The main business was to discuss the arrangements for the 1986 Polymer Colloids Conference at Racine, Wisconsin. It was agreed that this meeting should take the form of an Advanced Study Workshop which should have as its objective the formulation of a status note on the future research direction in the area of Polymer Colloids. The participation of the meeting is to be kept to 60 people to include members of the Group together with invited contributors. A letter concerning selection of participants, lecture/workshop themes and other organisational details has been circulated to members by Professor Mohamed El-Aasser. El-Aasser is applying for funding from NSF, NATO and member industries involved in the Polymer Colloid Group.

Other meetings for 1986 are as follows:

ACS Meeting, Symposium on Emulsion Polymerisation, New York, 13-18 April

60th Colloid and Surface Science Symposium; Emulsion Polymers and Emulsion Polymerisation: Fundamental Studies and Applications, Atlanta GA, 15-18 June

A further NATO-ASI on Polymer Colloids was proposed for 1988 in Strasbourg, France. Dr Francoise Candau agreed to be local host; she will initially book a local conference centre for 120 people for 2 weeks during July 1988. Professor Ron Ottewill was appointed Chairman for this ASI, Dr Derek Rance as co-Chairman.

New nominations for membership of the group were considered and as a result the following were elected:

Professor W B Russel Princeton University Dept of Chemical Engineering Olden St Princeton NJ 08544 USA	Dr W A B Donners DSM Research & Patents PO Box 18 6160 MD Geleen THE NETHERLANDS	Dr M Croucher Xerox Research Centre of Canada 2480 Dunwin Drive Mississauga Ontario CANADA L5L 1J9
---	--	--

The next Polymer Group meeting will be held at Racine, July 1986.

D G RANCE
Analytical and Polymer Science Group

RT/DGR/PH
6 August 1985

4

ANNOUNCEMENT
AND
CALL FOR PAPERS
SYMPOSIUM ON
"EMULSION POLYMERIZATION"

COSPONSORED BY:

DIVISION OF POLYMERIC MATERIALS SCIENCE AND ENGINEERING
AND
DIVISION OF COLLOID AND SURFACE CHEMISTRY
AMERICAN CHEMICAL SOCIETY MEETING
APRIL 13-18, 1986
NEW YORK

Please submit a Letter-of-Intent to participate in the Symposium as soon as possible by writing to either of the chairpersons. The ACS 200-Word Abstract forms and the preprint paper will be mailed upon request.

Deadline for Abstracts: October 1, 1985

Deadline for Preprints: November 1, 1985

CHAIRPERSONS FOR THE SYMPOSIUM

Dr. I. Piirma
Department of Polymer Science
The University of Akron
Akron, OH 44325
Telephone: (216) 375-7504

Dr. Mohamed S. El-Aasser
Emulsion Polymers Institute
Department of Chemical Eng.
Sinclair Lab, Bldg. #7
Lehigh University
Bethlehem, PA 18015
Telephone: (215) 861-3598

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

by Françoise CANDAU

RADICAL COPOLYMERISATION OF WATER-SOLUBLE MONOMERS IN INVERSE MICRO-
EMULSION (Z. Zekhnini)

The purpose of the present investigation was twofold. The first goal was to extend the microemulsion polymerisation process described in the previous reports to the synthesis of water-soluble copolymers such as poly(acrylamide-co-acrylates) which are widely used in a large number of applications. The second goal was to increase the solid contents of the final latex particles.

Our results show that an optimization of the process depends critically on the nature of the oil forming the continuous medium and on the emulsifier blend. The stability of microemulsions is also function of the sodium acrylate content in the comonomer feed. Addition of monomers increase considerably the microemulsion region in the phase diagram due to the surface-active properties of these components.

Very stable fluid and clear latexes containing large sodium acrylate-acrylamide concentrations (~25%/overall composition) and relatively low emulsifier contents (~10%) have been prepared by polymerisation in microemulsions stabilized by nonionic surfactants. The optical transmittance of the latexes were measured by turbidimetry and their particle size by photon correlation spectroscopy. The dimensions of the particles ($d \approx 60\text{nm}$) decrease with increasing acrylate content or emulsifier concentration.

The microstructure of the copolymers was determined by ^{13}C NMR (in collaboration with Dr. F. Heatley, Manchester University, U.K.) which enabled us to analyze the monomer sequence distribution and to compare it

There are reasons for believing that graft copolymers of hydrophobic rubbery polymers, such as natural rubber, and hydrophilic monomers, such as the lower hydroxyalkyl acrylates and methacrylates, will have interesting and useful technological properties. We have recently investigated the polymerisation of four such hydrophilic monomers in natural rubber latex, the intention being to prepare latices in which a proportion at least of the contained polymer is graft copolymer.

The four hydrophilic monomers we have used are 2-hydroxyethyl acrylate, 2-hydroxypropyl acrylate, 2-hydroxyethyl methacrylate, and 2-hydroxypropyl methacrylate. As a group, these four monomers provide interesting variations in both hydrophilicity and reactivity. The grade of natural rubber latex used was a so-called "substage" concentrate. This type of concentrate is prepared by a process in which the latex is first creamed and is then diluted with water and centrifuged. The concentrations of non-rubber constituents in this type of concentrate are rather less than those which are present in conventional once-centrifuged concentrate. This type of natural rubber latex was chosen in order that the amounts of non-rubber substances available to inhibit or otherwise complicate the polymerisation reaction would be reduced.

We have found that the polymerisation of all four monomers proceeds smoothly at room temperature and pH 9 if a redox system comprising potassium persulphate and sodium metabisulphite is used to initiate the reaction. Initially problems were encountered because the latex tended to become colloidal destabilised under the joint influence of the water-soluble monomers and the enhanced ionic strength associated with the addition of the components of the initiation system. However, by reducing the amount of initiator and also adding sufficient sodium dodecyl sulphate as a colloid stabiliser, it has been found possible to maintain colloid stability in reaction systems which contain up to 40% by weight of hydrophilic monomer on the rubber. The indications are that, of the four monomers investigated, 2-hydroxyethyl methacrylate is least prone to cause problems of colloid destabilisation when polymerised in natural rubber latex using the potassium persulphate/sodium metabisulphite redox initiation system.

Under the conditions used, all four monomers can be polymerised to complete conversion. As expected, the two acrylate monomers polymerised much faster than did the two methacrylate monomers. An interesting feature of the polymerisation of the methacrylate monomers is that, although the reaction proceeds fairly rapidly to about 50% conversion, the reaction thereafter proceeds much more slowly to complete conversion. The rates of polymerisation of the hydroxyethyl and hydroxypropyl esters appear to be similar under the conditions used.

Providing that the latex has been stabilised by the addition of sodium lauryl sulphate, and the level of redox initiator is sufficiently low, the products of the reactions are stable latices which resemble the initial natural rubber latex in appearance. Attempts have been made to separate the polymeric component of these reaction products into hydrophilic homopolymer, natural rubber, and graft copolymer. Degrees of grafting, defined as the weight fraction of hydrophilic monomer which is present in the graft copolymer, range from about 40% to nearly 80%. They appear to correlate inversely with the hydrophilicity of the monomer. Efficiencies of grafting, defined as the weight fraction of polymerised hydrophilic monomer which is present in the form of graft copolymer, range from about 50% to about 80%. Again they appear to correlate inversely with the hydrophilicity of the monomer.

from
Wim A.B. Donners
DSM, Research and Patents
P.O. Box 18, 6160 MD GELEEN
The Netherlands

30 SEP Recd

THE MICROSTRUCTURE OF POLY (VINYLALCOHOL). (F.F. VERCAUTEREN).

Poly (vinylalcohol) (PVOH) and poly (vinylalcohol-co-vinylacetate) (PVOH-Ac) are widely used in industry, e.g. in emulsion and suspension polymerisation. These polymers show a very complex behaviour, and it has been indicated (1) that structural irregularities may play a role in this. We studied a 99.4 % hydrolysed PVOH, M_n 105 kg mole⁻¹ by ¹³C 50 MHz NMR in H₂O/D₂O (3 : 1) solution to which a few % of isopropanol was added. In fig. 1 the 20-50 ppm region of the spectrum is shown, which includes the methylene carbon resonances of CH₂ groups in head-to-head/tail-to-tail sequences for which the formula is also shown in fig. 1.

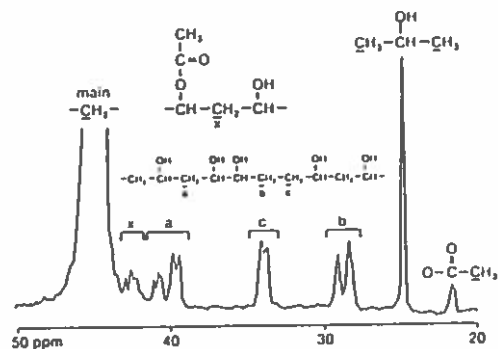


Fig. 1.

From this formula it is obvious that the intensity of the a, b and c peaks should be equal. This can only be achieved if the peak at 40.8 ppm is also assigned to the a carbon. This assignment has never been made before, although Ovenall's spectra (2) show sufficient resolution to reveal the presence of this peak. The fact that the intensities of the a, b and c carbon resonances are equal is direct proof for the correctness of Flory and Leutner's prediction (3) that a head-to-head linkage must necessarily be followed by a tail-to-tail bond. Apart from some fine structure the a and b carbon resonances both consist roughly of two peaks of unequal intensity. We propose this to be due to the asymmetry of the 1,2 glycol structure.

with statistical models. The sodium acrylate content in the comonomer feed was varied from 10 to 60% and the degree of conversion from 4 to 100%.

The average copolymer composition is shown to be independent of the degree of conversion and the sequence monomer distribution analyzed from triad proportions conforms to Bernoullian statistics within experimental error. The reactivity ratios of both monomers are therefore close to unity, a significant difference from the reported literature values obtained for copolymers prepared in solution or inverse emulsion ($r_A \sim 0.3$, $r_M \sim 0.95$). This difference can be attributed to the microenvironment which exerts a great influence on the free radical copolymerisation of acrylamide with ionogenic monomers, as shown by numerous studies. Our results confirm a polymerisation process by nucleation and interparticular collisions rather than by monomer diffusion through the continuous medium.

REFERENCES

- F. CANDAU, C. HOLTZSCHERER, S. CANDAU, "Characterization in inverse polyacrylamide latices by quasi-elastic light scattering" in Physical Optics of Dynamic Phenomena and Processes in Macromolecular Systems. B. Sedláček Ed., W. de Gruyter, Berlin, N.Y. p. 397 (1985).
- C. HOLTZSCHERER, S. CANDAU, F. CANDAU, "Modification of polyacrylamide microlatices by using a seeding procedure", in "Surfactants in Solution", K. Mittal et P. Bothorel Eds., (in press).

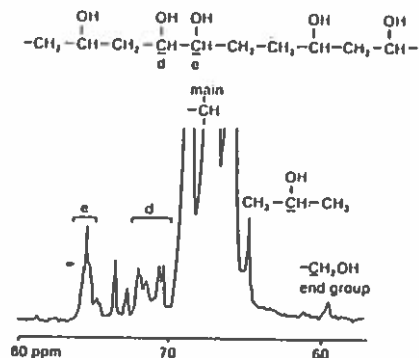


Fig. 3

In fig 3 some tentative assignments are given for the e and d carbons. In this same region also the resonance of the quaternary carbon at the branch-point of a nonhydrolysable branch is expected, which will always be included in the determination of the methine intensity by simple integration. In principle this problem might be solved by spin echo J-modulated experiments to discriminate between CH and quaternary carbons. Even then the limited accuracy of the method is a problem. We prepared 10 PVOH-Ac samples by reacytation of the same PVOH, and found for the CH/CH₂ ratio a standard deviation of 4.5 % although all polymers had the same amount of branching. The spectra used had a quality similar to those in ref 1. If for example a PVOH sample would have an amount of branching of 5 %, its determination by the method of ref 1 would lead to an error of 100 %. Further details will be published in 'Polymer'. The work is now extended to the NMR characterisation of PVOH-Ac's, and the solution behaviour of PVOH in aqueous systems.

References

1. A.S. Dunn, S.R. Naravane, Brit. Polym J., 12, 75 (1980)
2. D.W. Ovenall, Macromolecules, 17, 1458 (1984)
3. P.J. Flory, F.S. Leutner, J. Polym. Sci, 3, 880 (1948)

Recent publications (copies available on request)

A.P. Pijpers, W.A.B. Donners, Quantitative determination of the surface composition of acrylate copolymer latex films by XPS (ESCA)
 J. Polym. Sci. Polym. Chem. Ed., 23 (1985), 453

W.A.B. Donners, L.G. Peeters, D.A. Pons, A. Abel, Characterisation of acrylate latices by potentiometry and spectrophotometry. Makromol. Chem. Suppl. 10/11 (1985), 297.

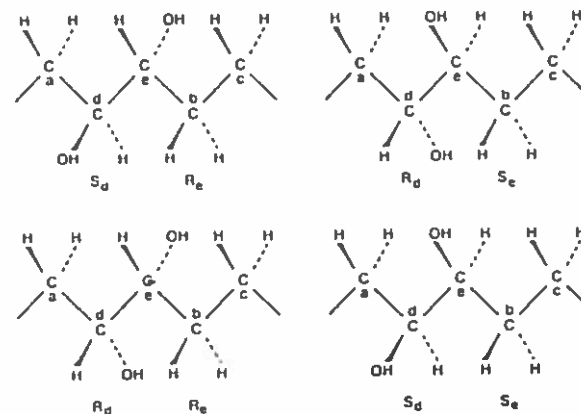


Fig. 2

As indicated in fig 2, four stereochemically different structures can be formed, which can be divided in two enantiomeric pairs (R_dS_e and S_dR_e vs R_dR_e and S_dS_e). Enantiomers are expected to have the same NMR spectrum, the two enantiomeric pairs however will show a different spectrum. Because of steric hindrance the formation of the R_dR_e and S_dS_e structure will be less favoured, and therefore we propose the low field peaks in the a and b resonances to be due to these structures. The splitting of the c carbon resonance is less pronounced, as expected, because the c carbon is further apart from the asymmetric 1,2 glycol bond.

We also studied the use of ¹³C NMR to determine the amount of branching by the method indicated in (1). This method was found to be unsuitable for various reasons. The method relies among other things on the determination of the total CH₂ and CH intensities. The integration range used in (1) for the CH₂ intensity is too limited to include the resonances from the b and c carbon, from the CH₂OH (branch) chain endgroup, from the carbon next to the carboxyl carbon in a hydrolysable side chain (calculated shift 29 ppm) and from the CH₂OAc (branch) chain endgroup expected at about 6.4 ppm upfield from the main CH peak. Extension of the integration region can correct this. The situation for the total methine intensity is more difficult.

8 OCT Recd

Electrokinetic measurements on plugs and dispersions of positively charged monodisperse polystyrene particles

The electrokinetic experiments about which we reported in Newsletter vol. 15, no. 1 have been extended to positively charged polystyrene particles. These have been prepared according to the recipe of Goodwin et al. (Colloid & Polymer Sci. 257, 61 (1979)), using azo-N,N¹-dimethylene isobutyramidine hydrochloride as the initiator. Depending on the ionic strength during the preparation, particle diameters ranged between 609 and 873 nm, and maximum surface charge densities, σ_0 , between 0.14 and 0.44 C.m⁻². Goodwin et al. reported already that the surface charge density is pH-dependent. This effect is also apparent in our data on electrophoretic mobilities, which in a 10⁻³ M KBr solution dropped from 6 x 10⁻⁸ to 4 x 10⁻⁸ m² v⁻¹ s⁻¹ in the pH-range 4 - 10. Given the pH and the ionic strength of the solution, the electrophoretic mobilities appear to be rather insensitive to the maximum values of the surface charge density.

ζ -Potentials calculated from the electrophoretic mobilities compare very well with those inferred from streaming currents obtained on plugs of the same samples, as exemplified in fig. 1. This figure shows that the maximum in the ζ -potential as a function of ionic strength that is so familiar for negatively charged latices, is also observed for positively charged particles. The occurrence of this maximum has been interpreted in various ways, one of them relating it to the presence of a layer of polyelectrolyte chains on the particle surfaces, the thickness of which varies with the ionic strength. Therefore, it

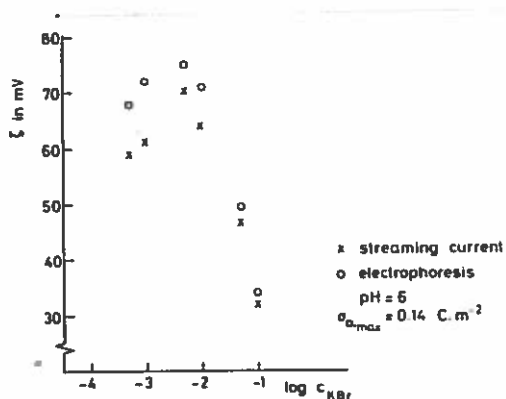


Figure 1

30 SEP Recd

by

Archie Hamielec

1. McMaster Institute for Polymer Production Technology (MIPPT)

Search for sponsor companies for the Institute (\$15,000 US/year for a minimum of 3 years) is coming to an end. To date, 17 companies located in the USA, Europe and Canada have joined the Institute. It is now felt that the staff and facilities of MIPPT can adequately service 20 companies.

2. Bulk copolymerization of p-methyl styrene and comonomers styrene, methyl methacrylate and acrylonitrile.

Extensive experimentation on the kinetics of the free radical copolymerization of p-methyl styrene and comonomers styrene, methyl methacrylate and acrylonitrile with financial support from Mobil Chemical Co., Edison, N.J. has recently been done. A kinetic model using the free volume theory to account for diffusion-controlled termination and propagation is in reasonable agreement with experimental data (conversion, M_n and M_w versus time in a batch reactor).

Two publications are in press.

3. Microsuspension polymerization of acrylamide and acrylamide/sodium acrylate.

The polymerization rate of acrylamide and acrylamide/sodium acrylate in commercial reactors during apparent runaway conditions is controlled by injecting pulses of O₂/N₂ into the reactor (air stop). Experiments are being done to investigate the effect of O₂ on polymerization rate during pulse injections of O₂/N₂.

4. Emulsion polymerization of vinyl acetate using partially hydrolyzed poly (vinyl acetate) as stabilizer.

Batch and semi-batch emulsion polymerizations are being done to investigate the extent of grafting of PVAc on to the stabilizer and the control of particle size distribution.

5. Polymerization of sodium acrylate with crosslinking monomers and the evaluation of these polymers as water absorbents.

Work is in progress, but it is too soon to report on results.

Some of the work reported herein is being done in collaboration with Dr. J.F. MacGregor, and Dr. J.L. Brash.

diffuse layer. In the quantitative interpretation a few nagging problems remain unsolved: the Cole-Cole plots indicate a spread of relaxation times although the particles were homodisperse and for a quantitative agreement with the theory (J. Lyklema, S.S. Dukhin and V.N. Shilov, *J. Electroanal. Chem.* **143** (1983), 1) a higher surface charge is needed than is found by conductometric or potentiometric titration.

Adsorption of Polypeptides on Latices and other Colloids

A paper on the conductometric titration of (9.0) latices with polylysine by B.C. Bonekamp and J. Lyklema has been submitted for publication to *J. Coll. Interfac. Sci.*

was considered appropriate to study the effect of adsorbed polyelectrolytes on the electrokinetic effects. As the polyelectrolyte, samples of polyglutamic acid (PG) of various degrees of polymerization and $pK \sim 5.2$ were chosen.

Fig. 2 not only demonstrates that adsorbed PG, with a degree of polymerization of 380, reverses the sign of the electrokinetic charge, as could be expected, but also that for highly charged PG (pH 6.5 and 8.0) the maximum in the mobility, or for that matter in the ζ -potential, is featuring again. At pH 4.5 the charge on the PG molecules is much lower, so that they behave more like uncharged polymers. The resulting loops and tails would shift the plane of shear more outwardly, thus explaining the corresponding lower electrophoretic mobility. The lower sensitivity of the conformation of adsorbed polymers to variations in the ionic strength as compared to that of polyelectrolytes, possibly explains the shallower maximum for PG 380 at pH 4.5 as well.

This data seems to support the idea that the maximum in the ζ -potential as a function of ionic strength observed for bare polystyrene particles, is related to the presence of polyelectrolyte entities on their surface.

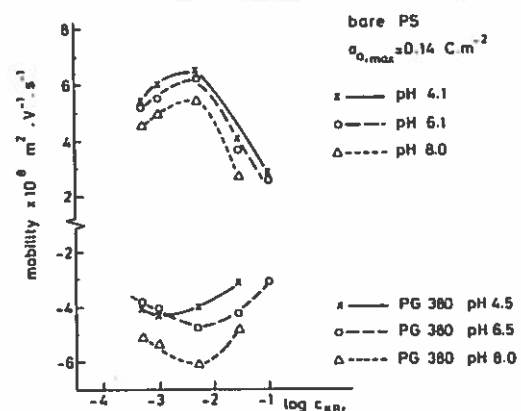


Figure 2

Other studies in the field of polymer colloids

A paper reviewing the state of the art of dielectric measurements on polystyrene latices by J. Lyklema, M.M. Springer, S.S. Dukhin and V.N. Shilov has been accepted for publication by *J. Electroanal. Chem.* In this paper it is unambiguously shown that the dielectric increment at low frequency is dominated by polarisation of the diffuse part of the double layer and not by polarisation of bound (Stern) ions. The Stern-layer is continually short-circuited by the

15
TERMINATION RATE COEFFICIENTS IN METHYL METHACRYLATE

POLYMERIZATIONS

30 SEP Recd

Mathew J. Ballard^v, Donald H. Napper and Robert G. Gilbert*

School of Chemistry, University of Sydney, N.S.W. 2006,
Australia

David F. Sangster

CSIRO Division of Chemical Physics, Lucas Heights Research
Laboratories, Private Bag 7, Sutherland, N.S.W. 2232,
Australia

Synopsis

It is shown that, by observing the kinetics of the seeded emulsion polymerization of methyl methacrylate with and without added chain transfer agent, and using γ -radiolytic initiation, it is possible to examine separately the effects of the length of the growing chain and of the weight fraction of polymer on the termination rate coefficient. Studies using this technique confirm predictions that chain entanglement causes translational diffusion to be the rate-determining termination event for growing chains of lower molecular weight, while the rate-determining termination event for growing chains of higher molecular weight is "residual": the annihilation encounter being caused by excess chain end mobility of two growing chains in a viscous medium. The data show unambiguously that free volume theories which do not incorporate the molecular weight of the growing chain are inapplicable to this system.

16
Entry Rate Coefficients in Emulsion Polymerization Systems

By Ian A. Penboss

Wattyl Paints, P.O. Box 464, Blacktown, NSW 2148, Australia

AND

Robert G. Gilbert* and Donald H. Napper

School of Chemistry, University of Sydney, Sydney, N.S.W.
2006, Australia

Abstract

A detailed theory is presented for the rate coefficient for entry of free radicals into latex particles in emulsion polymerization systems; this yields an expression for the radical capture efficiency. It is shown that the first-order rate coefficient for entry into a latex particle (ρ) can be accurately represented as $\rho = \rho_A + \alpha k_f$, where ρ_A is the rate coefficient for entry of free radicals arising directly from initiator, α is a "fate parameter" giving the relative importance of re-entry and hetero-termination of desorbed free radicals, k_f is the exit rate coefficient and \bar{n} is the average number of free radicals per latex particle. Expressions for ρ_A and α in terms of the rate coefficients for the component aqueous phase mechanisms are also presented, including the dependence on the concentration of initiator and number density of latex particles. This theory is applied to extensive data on the seeded emulsion polymerization of styrene; this is a typical non-polar monomer, for which capture efficiencies are commonly low. The data fitting includes an extensive sensitivity analysis. An excellent fit to the data is obtained, whence rate coefficients for the individual aqueous phase processes may be deduced. It is concluded for this system either that entering free radicals are colloidal in nature and/or that the entering oligomeric free radical must displace a surfactant molecule from the surface of the particle. Expressions enabling one to calculate ρ (and thus the capture efficiency) for use in modelling studies of non-polar monomers are presented.

of the emulsifying system (anionic, nonionic or mixtures) as well as the monomer feed composition was investigated in order to well control the seed latex. In a second step, it is studied how the seed latex (particle size, final conversion), the initial monomer feed composition and the monomer addition rate affect the structural and colloidal characteristics of the final latexes.

3 - Kinetic studies in styrene-methyl acrylate emulsion copolymerization
(W. RAMIREZ)

A kinetic study was achieved for the emulsion copolymerization of the styrene (S) - methylacrylate (MA) system with SDS as emulsifier and $K_2S_2O_8$ as initiator system. Copolymer and azeotropic compositions confirm the simulation predictions derived from the program taking into account the actual reactivity ratios and partition coefficient of each monomer in the organic and aqueous phases. Instantaneous and overall conversion, average copolymer composition, particle size and number evolution were investigated, as well as the average number of radicals per particle. After preparing monodisperse copolymer latexes via different processes, their colloidal characteristics are currently studied, mainly in order to get informations on the particle morphology.

4 - Emulsifier-free copolymerization of styrene and butyl acrylate in the presence of functional comonomers (Jean-Luc GUILLAUME)

Batch emulsifier-free copolymerizations of styrene (S) and butyl acrylate (B) have been performed for a S/B ratio = 50/50 in the presence of two types of functional comonomers (sodium methacrylate (MA) or potassium sulfopropylmethacrylate (SPM) and two initiators (potassium persulfate or 4-4' azobiscyano pentanoic acid (AZO)). When using the AZO/MA system results in the formation of polymer particles with only surface carboxylic end groups. The particle size of the final latexes can be adjusted with the MA concentration, provided the polymerization is carried out at pH 6.5. However, the higher MA concentration, the sooner the polymerization levels off in conversion. With the $K_2S_2O_8$ /SPM system, particles bearing only sulfate and sulfonate groups are produced and the polymerization is

1 - Emulsion polymerization of styrene in the presence of zwitterionic surfactants (H. ESSADDAM)

Kinetics of emulsion polymerization of styrene using $Na_2S_2O_8$ as initiator and in the presence of various sulfonated-type zwitterionic surfactants (prepared in the lab) were investigated as a function of different parameters ; the results were compared with those obtained with the SDS-emulsified polymerization. The particle nucleation mechanism was found to be greatly dependent upon the CMC of the surfactant. In the case of surfactant having high CMC (such as 2.4 g/l to 70°C, similar to that of SDS (3 g/l)) the mechanism is predominantly micellar-type provide the emulsifier concentration is above the CMC. With surfactants having low CMC (0.1 g/l), homogeneous nucleation plays a major role even at concentrations above the CMC. Polymerizations were found to be slow and not completed in the acidic ph range, whereas a basic pH results in a high conversion and the formation of monodisperse latexes. The addition of mono or divalent electrolytes affects the particle size of the latexes, except if the amount of emulsifier is high enough to fully cover the resulting particles. Experiments were also performed to test the stabilizing efficiency of these zwitterionic emulsifiers at high solids content.

2 - Preparation of semi-continuous emulsion copolymers of acrylonitrile with alkyl acrylates (L. SABATIER)

After a preliminary study on (acrylonitrile-n-butyl acrylate) batch emulsion copolymerizations, the current work is mainly directed on the synthesis of emulsion copolymers via a semi-batch technique. An (acrylonitrile-n-butyl acrylate) seed latex is previously prepared at a 20% solids content, then a preemulsified monomer mixture (acrylonitrile-ethyl hexyl acrylate) is continuously added to reach 50% solids content. At first the influence

I. Piirma

1. Work carried out by Mukesh Jain

In the past we have reported results in emulsion polymerization with some polyoxyethylene type nonionic surface active materials such as the Emulphogenes, the Tritons and the Igepals. We found that with some of these materials, and at polymerization temperatures higher than 40°C, (in some cases even below that) the starting emulsions in these polymerizations were not always of the oil-in-water type but rather multiple water-in-oil-in-water, or even water-in-oil emulsions. These emulsions changed back to oil-in-water during the polymerization when the monomer phase decreased. In the course of these polymerizations, and as a result of these emulsion changes in the system, we saw two constant rate regions in the conversion vs. time curves and a bimodality in the latex particle size distribution.

A similar study has now been carried out with the Pluronic polyols. These are commercially available nonionic surfactants, chemically ABA block copolymers with polyoxyethylene-polyoxypropylene blocks produced by BASF Wyandotte. The monomers we used in these studies were styrene and methyl methacrylate.

In styrene polymerizations conducted at 60°C, the Pluronic polyols in the HLB range of 13 to 16 showed also bimodality in the particle size distribution and two constant rate regions in the conversion-time plots. More detailed experiments with Pluronic polyol P84 (HLB 14) showed increased solubility of the surfactant in styrene and a decreased solubility, in water at higher temperatures. Hence, the partition of the surfactant between the two phases changed with temperature, creating different starting emulsions at different temperatures. The accelerated rate started at about 40% conversion concomitantly with a large increase in the number of particles. It is obvious from these results that the initial observations made with Emulphogene BC-840 are not unique for this surfactant but applies to all nonionic surface active materials in a certain HLB range, and does not exclude the polymeric surfactants.

2. Synthesis of a few polymeric custom designed polymeric amphipathic materials is continuing, but the polymerization results so far are too sketchy to report.

complete. In that case, the particle size of the final latexes is smaller than with the previous system and 40% of the SPM is fixed on the particle surface, instead of 20% with MA. In both cases, a too high functional monomer concentration results in the latex destabilization caused by the formation of a large amount of polyelectrolytes. Kinetic studies indicate that most of the functional monomer is incorporated into the particle surface during the last 30% conversion of the polymerization. A tentative explanation of such a behaviour is discussed based on the existence of two polymerization loci in the latex system.

5 - Microstructure study in styrene-n-butyl acrylate emulsion copolymers by ¹³C-NMR spectroscopy (M.F. LLAURO-ARRICADES - C. PICHOT - J. GUILLOT - L. RIOS - M.A. CRUZE - C. GUZMAN-C) (Abstract of a paper submitted for publication in POLYMER).

A detailed study of the sequence distribution in styrene (S)-n.butyl acrylate (A) emulsion copolymers is reported by using ¹³C-NMR spectroscopy. From the interpretation of the spectra of the homopolymers and copolymers, the assignment of the carbonyl (A) and quaternary (S) carbon atom resonances has been carried out, which allows a quantitative estimation of the compositional triad distributions in the copolymers. Results were found to be in relatively good agreement with calculated triad fractions deduced from a simulation program taking into account the actual reactivity ratios and type of emulsion process.

radical movements, is controlled by chain transfer to monomer. In this case, \bar{X}_n in the 25x25x25 lattice cube is calculated to be 30.

Random walk calculations (Monte Carlo simulations) were carried out for a number of free radicals and these results were averaged to obtain $\rho(z)$. Figure 3 shows the results of these Monte Carlo computations. Clearly, in this case, free radicals are not uniformly distributed in the particle volume. The calculated $\rho(z)$ is a decreasing exponential function (Poisson distribution). In addition, it can be observed that the averaged $\rho(z)$ is less scattered as the number of random walk simulations increases from 10 to 28. Figure 4 shows similar calculations for a 40x40x40 cube in which the scaled \bar{X}_n is 124. The solid line represents the least square best fit of $\rho(z)$ by an exponential function (Equation 1) based on 43 simulations.

$$\ln \rho(z) = -1.4259 - 4.3787 z \quad (1)$$

Free radical distribution functions such as $\rho(z)$ can be incorporated into kinetic models for emulsion polymerization to improve predictions of reaction rate and grafting efficiencies etc. These calculations will also lead to a better qualitative understanding of the development of non-uniform morphologies in the polymer particles.

DISTRIBUTION OF FREE RADICALS IN A LATEX PARTICLE DURING EMULSION POLYMERIZATION

3 OCT Reed

by

Chorng-Shyan Chern & Gary W. Poehlein
School of Chemical Engineering
Georgia Institute of Technology
Atlanta, GA 30332-0100

Most kinetic treatments of emulsion polymerization are based on an assumption that free radicals are uniformly distributed within the particles. This is not likely to be true in many cases because the hydrophilic initiator end groups will tend to remain near the particle surface.

We have developed a very preliminary model for estimating the average radial distribution of free radicals with radius. The remainder of this paper presents a brief outline of our initial computations.

A cube which is subdivided into volume units equivalent to one monomer molecule is used to represent the latex particle. The cubic geometry is chosen for the first model because it is simpler than that of a sphere. The error introduced by the edge and corner effects should be less with increasing the number of volume units in the cube. Figure 1 illustrates a core-shell polymer particle and the corresponding cubic lattice distribution. One goal of this research will be to calculate the distribution function of free radicals within the latex particles, $\rho(z)$ --- $z = 0$ at the particle surface and $z = 1$ at the particle center.

The preliminary calculations have involved the simulation of free radical movement by propagation reaction with monomer within the cubic lattice. The first step is to place dead polymer molecules at a specified volume concentration in the cube. This is done in a random manner and thereafter each site in the lattice contains either a monomer molecule or a polymer chain segment. The second step then involves the random placement of a free radical on a surface site which contains a monomer molecule. Thereafter the free radical is allowed to move, in a random manner, to other adjacent sites which contain monomer. This polymerization movement of the growing polymer chain (free radical) is continued until a specified degree of polymerization is achieved or until the free radical is completely surrounded by sites filled with dead polymer segments.

The first calculations were based on simulation of a polymer particle with a diameter of 4,000 via a cube containing 25 lattice sites on each edge of $(25)^3$ total sites. Figure 2 shows the scaling calculations used to simulate a styrene polymerization in which the end of chain propagation, and hence free

Figure 1

APPLICATION OF MONTE CARLO METHOD IN STYRENE/POLYBUTADIENE EMULSION POLYMERIZATION

$$\bar{N} = \bar{N}_C + \bar{N}_S$$

$$\bar{N}_S = \bar{N} (1 - k_t/k_p) \int_0^{R_0 - R_C} \rho(z) dz / \int_0^{R_0} \rho(z) dz + \bar{N} (k_t/k_p) \phi_0$$

\bar{N} CAN BE OBTAINED FROM THE RELATIONSHIP OF THE RADICAL BALANCE BETWEEN THE POLYMER PARTICLE AND AQUEOUS PHASE.

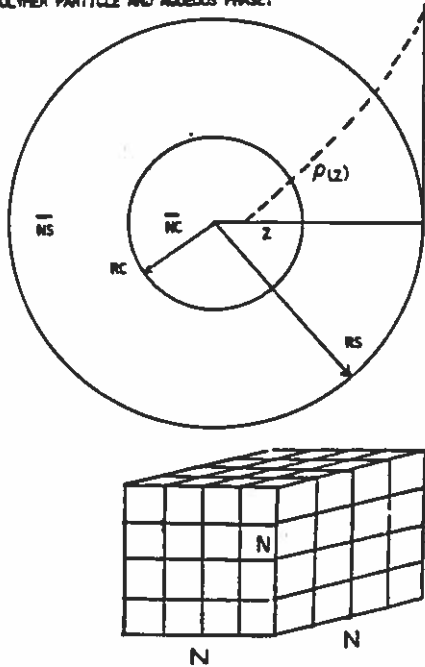


Figure 3

25X25X25 CUBIC PARTICLE

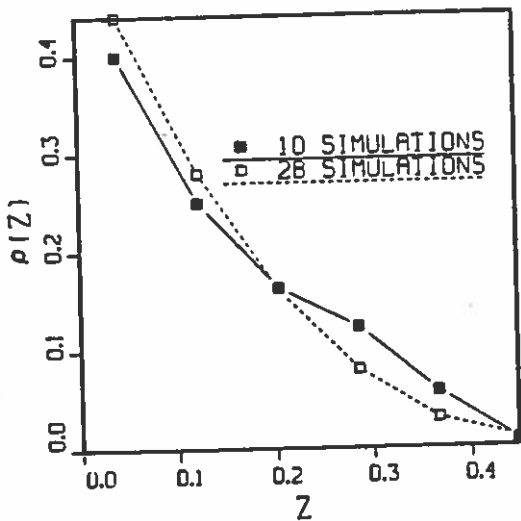


Figure 2

A CUBIC MODEL POLYMER PARTICLE

DIAMETER OF A STYRENE MOLECULE = 14.8 Å
 DIAMETER OF A POLYMER PARTICLE = 4,000 Å

VOLUME OF A CUBE WHICH CAN ONLY CONTAIN ONE STYRENE MOLECULE
 = (14.8 E-10)³ = 3.24 E-27 m³

VOLUME OF A POLYMER PARTICLE
 = 1/6 π (400 E-9)³ = 3.35 E-20 m³

DEGREE OF POLYMERIZATION

ASSUME CHAIN TRANSFER PROCESSES CONTROL THE CHAIN LENGTH OF THE POLYMER CHAIN FORMED IN THE EMULSION POLYMERIZATION SYSTEM.

At 60°C, k_t/k_p = 5 E-5.

THEREFORE, $\bar{X}_n = 1/(k_t/k_p) = 2 E4$

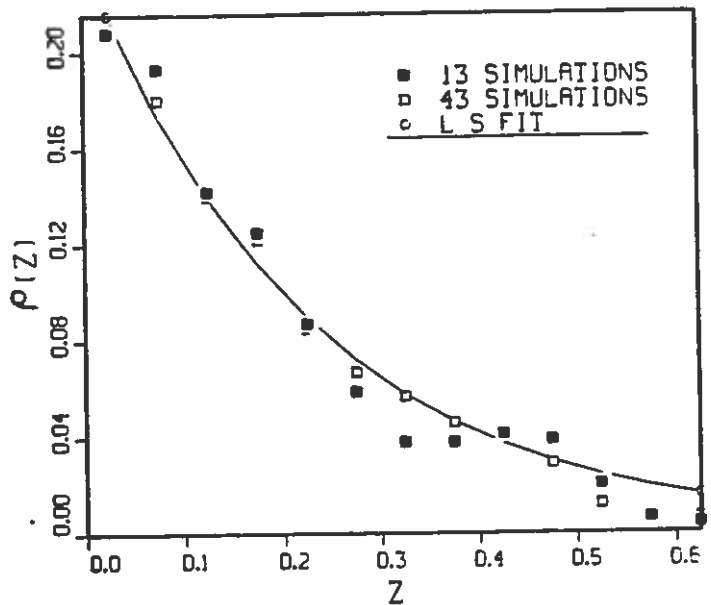
\bar{X}_n IN A 25 X 25 X 25 CUBIC MODEL POLYMER PARTICLE IS

$$\frac{3.35 E-20 / 3.24 E-27}{25 \cdot 25 \cdot 25} = \frac{2 E4}{\bar{X}_n}$$

$\bar{X}_n = 30$

Figure 4

40X40X40 CUBIC MODEL PARTICLE



R.E. Marganski* and R.L. Rowell⁺
Department of Chemistry
University of Massachusetts
Amherst, MA 01003

8 MAY Rec

After settling, the pH of the supernatant was measured. The dispersion was stirred at fast speed for two minutes then reduced to slow speed during a run while samples were withdrawn by pump from the instrument sample tube.

Microelectrophoresis measurements. Electrophoretic mobility was measured with a Pen Kem 3000 automated electrokinetics analyzer (6). The instrument has a van Gils type eight μ l silica sample chamber with permanently bonded palladium electrodes, all mounted in a thermostated water jacket. Particles are illuminated with a 2 mW He-Ne laser and their image is projected onto the surface of a precision rotating radial grating. Electrophoretic movement causes a frequency shift in the light transmitted through the grating as compared to a reference detector. A Rockland 512/s narrow-band real time fast Fourier transform analyzer then computes the frequency spectrum from the individual contributions of the light scattered from many particles in order to obtain a representation of the electrophoretic mobility distribution based on the average of sixteen spectra. The average mobility may be computed from the distribution and is also obtained independently by a frequency-tracker in the instrument. Focusing at the stationary layer is under automatic control.

Although the electrophoretic motion may be qualitatively observed through a microscope, the standard procedure is to conduct all experimental work using the keyboard of an interfaced personal computer. An extensive software is provided to handle the tedious experimental checks required for microelectrophoresis (3) as well as to provide storage, retrieval and display of all data and results using a varied computer graphics package.

In a typical measurement a volume of about 5 ml is drawn into the apparatus, most of which is used to rinse the cell. Distilled water was loaded into the chamber between all measurements. The instrument automatically corrects for electrode polarization and Joule heating by setting the limits on the power, voltage and current applied. The measured electrophoretic mobility is an average of several measurements giving a standard error and accepted only after a field-reversal cross-check for true microelectrophoresis.

Results and discussion

Dependence of average mobility on pH. The pH dependence of the average electrophoretic mobility of the alumina is shown in Figure 1. It is clear that hydrogen ion acted as a potential determining ion. There is zero mobility or an isoelectric point at pH 9.4. At higher pH the alumina is negative while at lower pH it is positive. The mobility shows a maximum negative value of $-3.3 (\mu\text{m/s})/(\text{V/cm})$ at pH 11.0 followed by a decrease. At low pH a near constant mobility of $+5.4 \pm 0.3 (\mu\text{m/s})/(\text{V/cm})$ is attained near pH 6 and extends to the lowest pH measured at 1.79.

Isoelectric point. We have included our determination of the iep along with reports from previous investigators summarized in Table 1. We have arranged the data in order of increasing pH.

Table 1. Isoelectric point of aqueous alumina dispersions

pH(iiep)	Method	Investigators	Reference
6.7	Electrophoresis	Dobias, Spurny & Freudlova	7
8.4	Electrophoresis	Johansen & Buchanan	8
8.6-8.8	Streaming potential	Johansen & Buchanan	9
9.0	Electrophoresis	Wakamatsu & Mukai	10
9.1	Streaming potential	Robinson	11
9.1	Electrophoresis	Yopps & Fuerstenaue	4
9.4	Streaming potential	Modi & Fuerstenaue	5
9.4 \pm 0.2	Electrophoresis	This work	

Introduction

We selected α -alumina as a model system for studies of the role of the electrophoretic mobility in the stability of pigment and latex dispersions. The importance of the electrophoretic mobility had arisen in other work from our laboratory on latex dispersions (1) and aqueous coal slurries (2).

The dependence of the electrophoretic mobility on pH leads directly to the isoelectric point (iep), a useful property in describing an oxide surface (3). We found a wide variation in the iep of alumina as determined by previous investigators so that one goal of the present work was a re-determination of the iep.

Previous investigations have yielded only the dependence of the mean mobility on pH. In the present work we have employed the latest state-of-the-art instrumentation embodied in a fully computer-controlled apparatus that allows characterization of the full range of the electrophoretic mobility distribution which may in general arise from both a distribution in particle size as well as from a distribution in surface charge.

Experimental

Materials. The powder was 99.0% pure recrystallized α -alumina, designated Alcoa Standard Grade T-61 and supplied by the Whittaker, Clark and Daniels Corporation, South Plainfield, NJ. It had been dry ground and sieved 95%, -325m (44 μ m). Photomicrographs showed that most of the particles were smaller than 10 μ m. Impurities listed in the unpurified reagent were SiO₂ (0.1%), Fe₂O₃ (0.2%), Na₂O (0.1%) and CaO (0.07%). A pycnometric determination of the density gave 3.95 g/cc.

The alumina was leached overnight in concentrated HCl, washed with distilled water until the filtrate showed no change in pH and stored under double distilled water until ready for use. Prior to preparation of the dispersion, the alumina was filtered, washed and then dried at 120°C for 24 hours. This procedure has been shown to give reproducible results by Fuerstenaue et al. (4,5) and gave reproducible results in our work. Leaching eliminated impurities of small magnetic grains which were visible on magnetic stir bars used with dispersions prepared from untreated alumina.

The water was distilled a second time from the laboratory distilled water supply using a Corning AG-1b all Pyrex glass still. Certified ACS grade NaOH and HCl were obtained from Fisher Chemical Company. All glassware was scrupulously cleaned with chromic acid at the beginning of the work. The glassware was then filled with distilled water and allowed to stand for a few days in order to leach out chromic ions adsorbed on the glass. Thereafter, glassware was thoroughly rinsed with warm water, then with distilled water and allowed to drain and dry.

Dispersion preparation. One hundred ml of double distilled water, with the pH adjusted to the preliminary value, were added to clean polyethylene bottles containing 0.2000 g purified, dried alumina giving a final concentration of 0.2 wt.%. The use of plastic containers avoided the possibility of silica contamination found to occur in basic solutions in glass containers (3). The contents were stirred at fast speed for three minutes and then allowed to settle overnight at 25°C in a thermostated water jacket.

⁺ Author to whom correspondence should be addressed.

*Present address: E.I. Du Pont De Nemours & Company, Chemical and Pigments Dept., De Lisle Plant, P.O. Box 430, Pass Christian, MS 39571.

9. Johansen, P.G. and Buchanan, A.S., *Australian J. Chem.* **10**, 392 (1957).
10. Wakamatsu, T. and Mukai, S., *A.I. Ch. E. Symp. Ser. No. 150*, **71**, 81 (1975).
11. Robinson, M., Master's Thesis, U. California, Berkeley, 1962.
12. Marganski, R.E., Ph.D. Thesis, University of Massachusetts, Amherst, 1984.

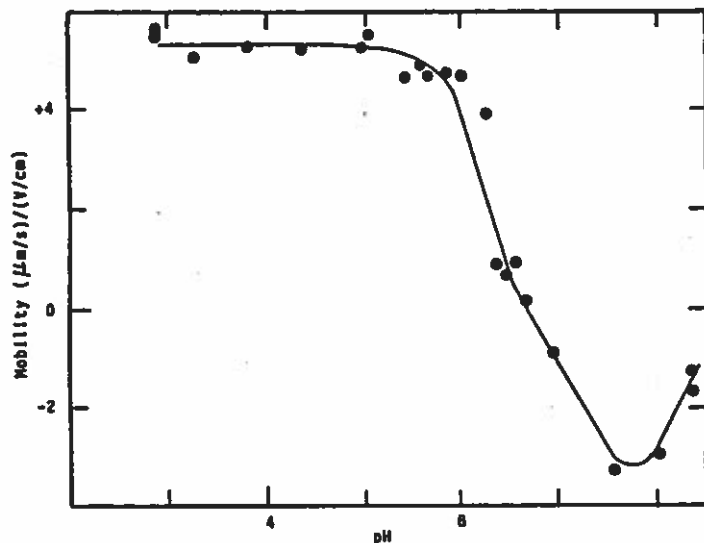


Figure 1. Dependence of the average electrophoretic mobility on pH for dilute aqueous alumina dispersions at 30°C.

Dobias et al. (7) leached their alumina samples for 5 minutes in 6N HCl, washed then dried the samples at 120°C and finally stored the dried samples. The low iep suggests that their procedure did not give a completely hydrolyzed surface.

It is also possible that the methods of Johansen and Buchanan (8,9) likewise did not allow sufficient time for equilibrium to be reached. Their alumina sample contained a 0.94% silica impurity as well.

Yopps and Fuerstenau (4), Modi and Fuerstenau (5), and Robinson (11) all used samples that had been aged in water. Since our results for alumina aged in water for one month are in close agreement with the latter workers, we conclude that a sample aged in water is required for an equilibrated surface, presumably in a highly hydroxylated state. The handling and storage of alumina by Wakamatsu and Mukai (10) was not given.

Electrophoretic mobility distribution (emd). To our knowledge, the Pen Kem System 3000 is the first instrument capable of providing a meaningful measure of the electrophoretic mobility distribution. Since the dispersions in this work were only 0.2 wt.%, the flocculation was negligible. Therefore, the particle size distribution and light scattering convolution factors were constant so that the pH dependence of the electrophoretic mobility distribution can be attributed to differences in the surface charge density at the alumina surface.

In Figure 2 we show representative emd for pH 1.8, 4.8 and 12.8. The emd showed systematic changes with pH not unlike work that was reported earlier for an aqueous dispersion of coal (2).

Breadth of the electrophoretic mobility distribution (bemd). The breadth was calculated by integrating the electrophoretic mobility spectrum, normalizing the area to one and taking the limits between which 90% of the observed mobility occurred. The baseline was determined by taking 5% of the maximum signal and establishing the rms reference. In Figure 3 we show the dependence of the breadth on pH. The data indicate points of maximum breadth (pxb) at pH 5.0 and 10.7 and a point of minimum breadth (pnb) near the iep. The diminished breadth at the extremes of pH was less than one-half the maximum value. We note that the pxb at pH 5.0 and 10.7 do not coincide with the iep at pH 9.4 where, in fact, the breadth is a minimum. Flocculation would be expected to be pronounced at the iep but in the present work flocculation was suppressed by very low particle concentration.

Explanation of the pxb in terms of the surface chemistry of the system has been considered elsewhere (12) and will be treated in a longer account of this work.

Acknowledgement

This work was supported by grants from the Atlantic Research Corporation of Alexandria, VA. Technical assistance and instrument support was provided by Pen Kem, Inc. of Bedford Hills, NY.

References

1. Ford, J.R., Rowell, R.L. and Bassett, D.R. in *Emulsion Polymers and Emulsion Polymerization*, Bassett, D.R. and Hamielec, A.E., Eds., ACS Symp. Ser. 165, Washington, D.C., 1981.
2. Marganski, R.E. and Rowell, R.L., *J. Dispersion Sci. & Tech.*, **4**, 415 (1983).
3. Hunter, R.J., *Zeta Potential in Colloid Science*, Academic Press, New York, 1981.
4. Yopps, J.A. and Fuerstenau, D.W., *J. Colloid Interface Sci.* **19**, 61 (1964).
5. Modi, H.S. and Fuerstenau, D.W., *J. Phys. Chem.* **61**, 640 (1957).
6. *System 3000 Automated Electrokinetics Analyzer*, Pen Kem Inc., 341 Adams St., Bedford Hills, NY 10507.
7. Dobias, B., Spurny, J. and Freudlova, E., *Collection Czech. Chem. Commun.* **24**, 3663 (1959).
8. Johansen, P.G. and Buchanan, A.S. *Australian J. Chem.* **10**, 398 (1957).

8 OCT Reed

NMR Characterization of Composite Latex Particles

C. J. McDonald, P. Smith, D. L. Lee, J. G. Galloway
The Dow Chemical Company, Midland, MI 48674

The morphology of latex particles have been described by thermal, mechanical, microscopic, and spectroscopic methods. Within the last few years the power of magnetic resonance spectroscopy (NMR) for characterizing polymer chain dynamics has been demonstrated. These data were developed by measurement of relaxation parameters associated with the pulsed Fourier transform experiment. If the molecular motions of a polymer chain are influenced by the way they are distributed in a composite material, then NMR spectroscopy should be able to provide additional information on morphology.

The feasibility of structure characterization by NMR has been investigated with an interpenetrating polymer network synthesized as a latex. The system consisted of a soft first stage copolymer made from n-butyl acrylate and styrene with various levels of a crosslinker present. The second stage was a homopolymer of styrene. Comparative data was obtained with differential scanning calorimetry and electron microscopy and Carbon - 13 NMR.

The NMR data took the form of line width measurements as a function of temperature. These line width data can be related to a relaxation parameter, T_2 - the transverse relaxation time, which is sensitive to molecular motions in the kilohertz range. Most often the data were obtained on a film of the latex pelletized to fit the dimensions of the NMR tube. The measurements of the NMR line width as a function of temperature were made without the benefit of magic angle spinning or other approaches normally used in the examination of solid polymers. The motion of the soft component in this composite were sufficient to observed its spectrum uniquely without the interference of the hard phase. Two parameters could be deduced from such data. At low temperature the line width broadens such that a temperature at which the spectrum collapses could be defined. At high temperature a limiting behavior was observed which could be characterized by a curve fitting procedure. Both parameter were found to be sensitive to the domain size of the hard polymer in the soft copolymer matrix varying by a much as 40 C over the limits of domain size examined. Corroborative microscopic and thermal data indicated that the NMR approach was sensitive beyond the resolving power of the other methods. Supplementary information on the influence of polymer form, phase ratio of the soft and hard components and the peak dependence of these data have been obtained.

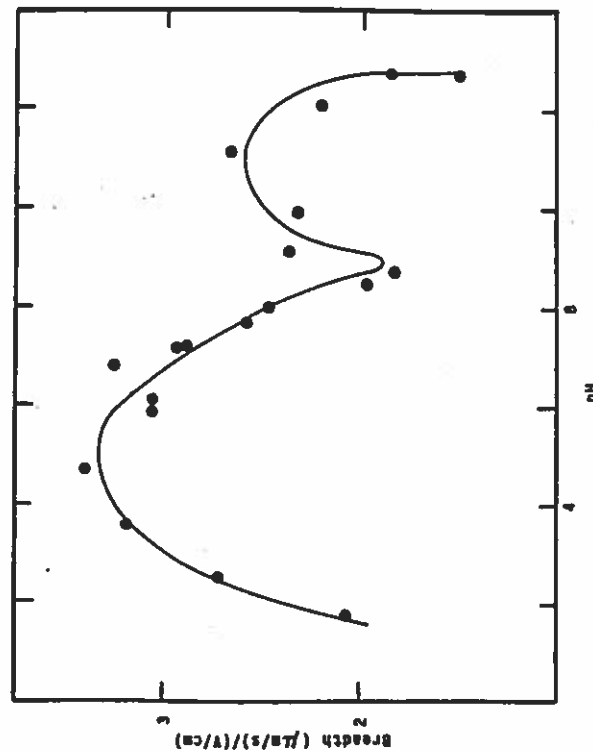


Figure 3. Dependence of the breadth of the electrophoretic mobility distribution on pH for dilute aqueous alumina dispersions at 30°C.

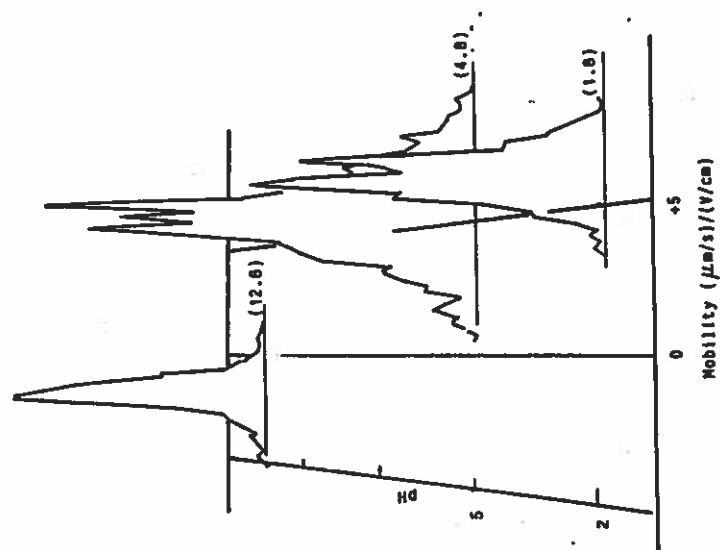


Figure 2. Electrophoretic mobility distributions at 25°C for dilute aqueous alumina dispersions at pH 12.8, 4.8 and 1.8.

New Development in Production and Application
of Monodispers Particles.

John Ugelstad

Institute of Industrial Chemistry - SINTEF
7034 Trondheim, Norway

Despite the fact that we for quite a long time have been preparing a great variety of highly monodisperse polymer particles in the size range 1 - 100 μm some people seem to ignore their existence. Thus, it is rather surprising to find in a brochure on space particles recently sent out by National Bureau of Standards the following citation: ----
"However the force of gravity would coagulate the 10 μm spheres into useless clumps of polystyrene and would also make them egg-shaped, rather than round. Therefore uniform spheres of this size can be produced only in the gravity-free environment of space."

I include a SEM picture (1) of 10 μm crosslinked polystyrene particles made on earth and also a histogram of these particles (2) obtained by flow cytometry with hydrodynamic focusing. The coefficient of variation in diameter is less than 0.5%.

Also I include two SEM pictures from New England Nuclear of their commercial 15 μm radioactive particles produced from our particles. The one with the highest magnification (3) confirm that the particles are smooth and that they are spherical and not egg-shaped. The other SEM of the same particles (4) showing about 1000 particles shows that there are indeed very few particles out of size.

Moreover is shown a SEM picture of 10 μm porous particles from our process used in chromatography in the so-called FPLC system from Pharmacia Fine Chemicals AB. (5).

So the so-called "useless clumps of particles" are applicable for a lot of purposes.

THE METHYLATION OF AN ACRYLAMIDE COPOLYMER LATEX

Medardo Monzon, C. J. McDonald

The Dow Chemical Company, Midland, MI 48674

The post-reaction of incorporating the reactive N-methylolacrylamide (NMA) group into a polymer latex was studied with carbon-13 nuclear magnetic resonance spectroscopy (C-13 NMR). The methylation reaction of formaldehyde with an acrylic ester-acrylamide copolymer latex in the presence of a weak base catalyst, triethylamine, introduced NMA in yields of 70% when using an equimolar stoichiometry of the reagents. The derivatized latex was capable of undergoing crosslinking reactions which enhanced the wet tensile strength of the original polymer by 700%.

Kinetics, equilibria, and type of base catalysis were characterized for this reaction using a polymer similar in composition to the oligomers found in the serum phase of the latex. The water soluble components present in the latex serum were separated using an ultrafiltration method. Their composition, average molecular size and concentration were determined by C-13 NMR spectroscopy, size-exclusion chromatography and gravimetry.

The formation of the N-methylolacrylamide derivative is best described as a general base catalyzed process, first-order in the catalyst and in each of the reagents. The reaction exhibits a reversible equilibrium evidenced by a decrease in conversion to the N-methylol derivative with dilution.

Interacting Magnetic Composites with a Superparamagnetic Latex*

O. Kwon, J. Solc, and G. Rabold, Central Research-Specialty Products Laboratory, The Dow Chemical Company, Midland, MI 48674

New magnetic composites, one component of which is a superparamagnetic latex, exhibit new effects and offer a new concept of magnetic material development.

The superparamagnetic latexes are ultrafine magnetic particles ($\sim 200 \text{ \AA}$) permanently encapsulated in submicron polymer spheres by emulsion polymerization.¹ When the superparamagnetic latexes surround the coercive particles in a magnetic composite, the resultant coercivities, as a function of composition, show dramatic deviations from a simple mixing rule. It is attributed to a short-range interaction of the superparamagnetic particles close proximity to the coercive particles.

Dynamic properties in the rf and microwave frequency ranges are substantially modified, too. In fact, we find a large loss synergism and variation of low spectra effected by the intimate mixing of the magnetic composite.

1. J. Solc, U.S. Patent No. 4,421,660 (1983).

* Presented at the International Conf. on Magnetism
San Francisco, Aug. 1985

Our work at Institute of Industrial Chemistry, SINTEF and Dyno has been concentrated around different variations in processing monodisperse particles. The coefficient of variation in size of special particle types is as said less than 0.5%.

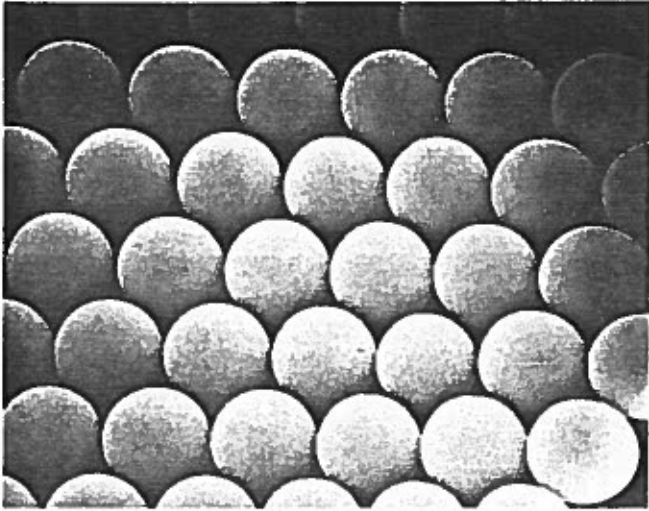
Two of the most interesting applications of the particles where an intense research is going on for the moment are:

- 1) Use of monodisperse particles as magnetic holes.
- 2) Use of monodisperse particles for dynamic studies of clustering and ordering in two dimensional systems.

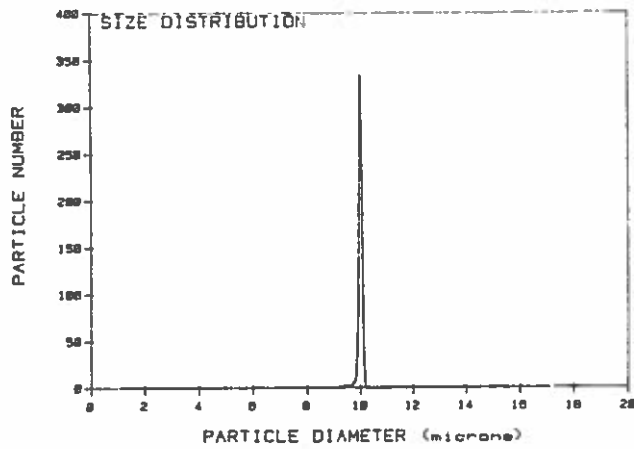
This work was initiated by dr. Skjeltorp at IET Norway. Since his pionering work other scientists have followed up using our highly monodisperse particles. Most of this work appears in papers in physics. (Litterature list is available on request).

The magnetic hole concept of Skjeltorp combines the highly monodisperse particles in the size range 2 to 25 μm with magnetic fluid, a monodomain magnetic system which is superparamagnetic. By dispersing the pure polystyrene-divinylbenzene particles in the magnetic fluid we initially have a situation as shown on picture (6). Then by applying a magnetic field on the particles they will acquire a magnetic dipole and act as magnetic holes. One may get an interaction between the particles which may be a repulsion or an attraction depending upon the direction of the field. With the field normal to the layer of polymer particles one will get a repulsion. This causes as seen on picture (7) formation of a crystalline triangulare structure. A field parallel to the layer causes the particles to line up, picture (8).

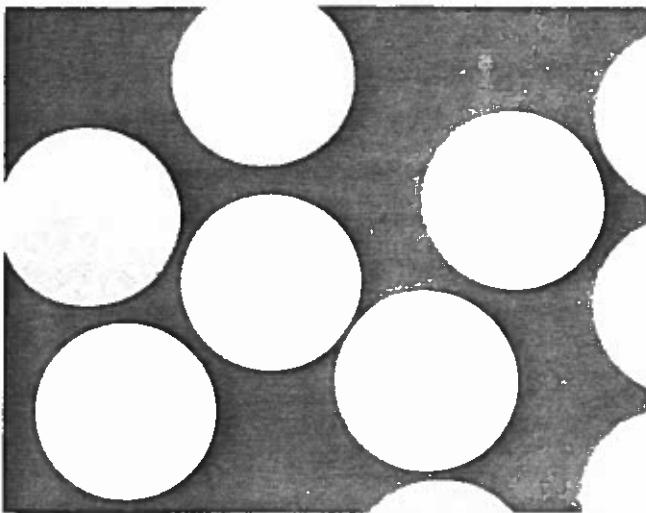
Monodisperse particles in the range 1 - 10 μm have also found application for direct observation of two-dimensional clustering and ordering. A more comprehensive study of these phenomena also including studies with non-spherical monosized particles is under way.



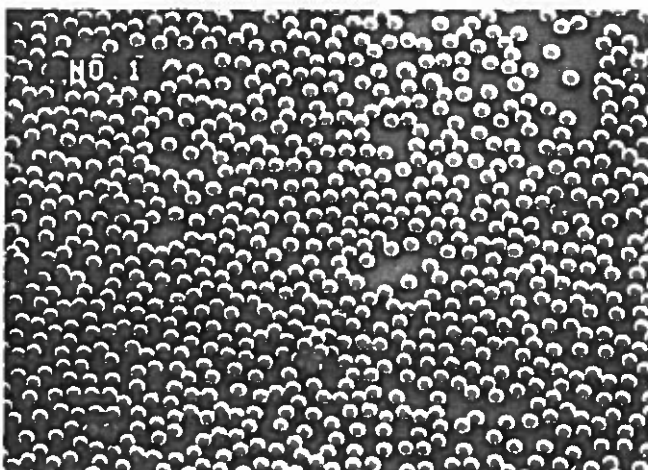
(1). SEM of 10 μm crosslinked polystyrene particles.



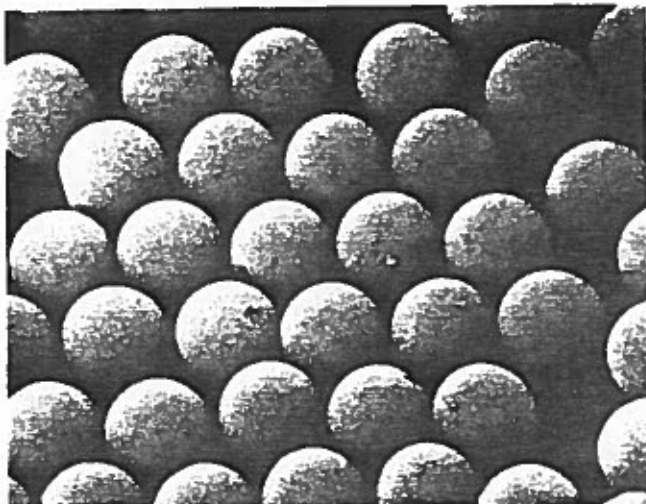
(2). Particle size distribution of 10 μm crosslinked polystyrene particles measured by Flow Cytometry. C.V. 0.5%



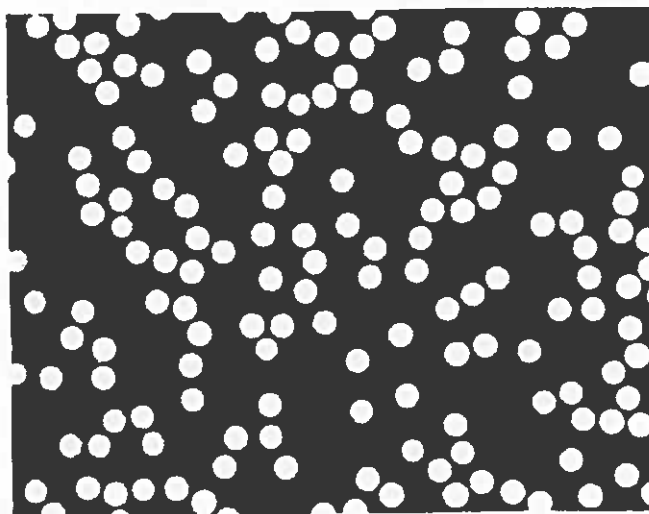
(3). SEM of 15 μm radioactive particles. (photo NEN).



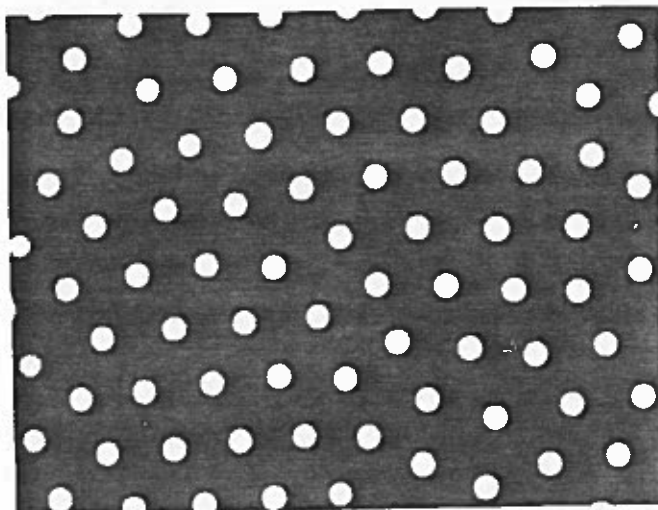
(4). SEM of 15 μm radioactive particles. (photo NEN).



(5). SEM of 10 μm porous particles for chromatography.



(6). Pictures 6-8 show optical micrographs of 25 μm PS/DVB particles in a magnetic-fluid film.
(6) with no external magnetic field applied.



(7). With an external magnetic field normal to the film.
 $H_{\perp} = 100$ Oe.



(8). With an external magnetic field parallel to the film.
 $H_{\parallel} = 100$ Oe.

38

37

Pulp and Paper Research Institute of Canada, and
Department of Chemistry, McGill University
Montreal, Quebec, Canada, H3A 2A7

3. A two-dimensional model of the flow of ordered suspensions of rods.
(J.H. Masliyah and T.G.M. van de Ven)

Analysis of creeping flow over an array of freely rotating cylinders sandwiched between two sliding parallel plates is studied using a finite difference and a least-squares numerical technique. The flow pattern was found to be very much influenced by the cylinder-to-cylinder spacing and by the gap width of the parallel plates. The shear stress on the cylinder surface and on the parallel plates was found to be a strong function of position. The viscosity of a suspension composed of an array of freely rotating cylinders was deduced from the applied shear rate and the evaluated shear stress on the parallel plates. Experimental results confirm the numerical findings. The results show that the viscosity of ordered suspensions is reduced by changing the packing from a symmetrical distribution to one in which the number of layers is reduced and the number of particles in each layer is increased. This agrees with experimental data on the flow of ordered latex suspensions by Tomita and van de Ven (JCIS, 99, 374 (1984)).

The following are abstracts of papers submitted to various journals (J. Phys. Chem., J. Colloid & Interface Sci. and Intern. J. Multiphase Flow).

1. Relaxation phenomena in suspensions of anisometric Brownian Particles
(D.S. Jayasuriya and T.G.M. van de Ven)

A general method is presented which in principle can be used to treat theoretically the relaxation of any property of a suspension that can be expressed in terms of the orientation distribution of the suspended anisometric particles. This method has been applied to various physical properties to obtain expressions relating the relaxation to rotary diffusion coefficients of spheroidal and ellipsoidal particles. Some aspects of the theory are tested by rheo-optical measurements on non-spherical polymer colloids (polystyrene-poly-tert. butyl-acrylate of approximate ellipsoidal shape (with axes of 940, 660 and 500 nm) and are found to be in good agreement with the theory.

2. Rheo-optics of suspensions of anisometric particles. III. Effects of electrolyte and particle concentration on peri- and orthokinetic particle motion. (D.S. Jayasuriya and T.G.M. van de Ven).

Rheo-optical measurements on suspensions of non-spherical latex particles yield information about the shape and size of the suspended particles which agree with those measured using electron microscopy. Interestingly, the rotation of the particles and the rotary diffusion coefficients showed a dependence on particle concentration and on the electrolyte concentration of the medium. For low concentrations, results can be explained on the basis of expansions in volume fraction ϕ of the period of rotation T and the rotary diffusion coefficient D_r :

$$T = T^0 (1 + a\phi)$$

$$D_d = D_r^0 (1 + b\phi),$$

where T^0 and D_r^0 are the values at zero concentration and a and b are the first virial coefficients. D_r^0 , a and b seem to depend on electrolyte concentration. T^0 seems to be less or not affected by salt.



co-directors

Dr. John W. Vanderhoff
Professor of Chemistry
(215) 861-3589

Dr. Mohamed S. El-Aasser
Professor of Chemical Engineering
(215) 861-3598

April 17, 1985

8 MAY Reed

TO: Polymer Colloids Group
FROM: M.S. El-Aasser on behalf of The Emulsion Polymers
Institute, Lehigh University *MICP*
SUBJECT: Contribution to April's 1985 newsletter

Apologies for not contributing to the last issue of the newsletter. A lot has happened since our last report. We will be brief.

1. The following Ph.D. Theses were completed:

- (i) "Agitation-Induced Coagulation of High-Solids Latexes", Vern Lowry, 1985.
- (ii) "Covalent Binding of Biological Macromolecules to Activated Polystyrene Latexes", Theresa Michael, 1985.
- (iii) "Adsorption and Stabilization Studies of Polymers on Latex Particles", Maqsood S. Ahmed, 1984.
- (iv) "Formation and Stabilization of Inverse Emulsion Polymers", Donna Visioli, 1984.
- (v) "Mechanism of Core-Shell Emulsion Polymerization", Deborah R. Stutman, 1984.

2. The following M.S. Theses were completed:

- (i) "Interactions Between Offset Printing Inks and Fountain Solutions during the Process of Offset Printing", Sanjay Sathaye, 1985.
- (ii) "The Effect of Initial Pressure on Coagulation during the Emulsion Polymerization of Styrene", Debra Bartsch, 1985.

3
Contribution to the Polymer Colloid Group Newsletter

117 MAY 1985

submitted by A. Vrij,
van 't Hoff laboratory of Physical and Colloid Chemistry,
University of Utrecht, Padualaan 8, 3584 CH Utrecht.

We are synthesizing already for several years silica spheres which are made lyophilic ("oil-soluble") by etherification of the surface hydroxyls with octadecylalcohol⁽¹⁾. The spheres, which are in the colloidal size range of ~20-300 nm, can be dispersed in organic solvents like cyclohexane and toluene. At very high concentrations the larger particles form "colloidal crystals"⁽²⁾ in cyclohexane. The "hairy" silica spheres show steep, short range repulsions in cyclohexane very nearly mimicking "hard spheres". It is known from computer simulations that hard spheres show a fluid-solid phase transition at ~50 volume%. (Kirkwood Alder transition). We think that our silica is a real system exhibiting this phenomenon.

The colloidal spheres may also show attractive forces when the solvent becomes poorer. Jansen found, e.g., that stearyl silica in toluene shows a phase separation below 9 °C. These new results are reported in a recent letter³⁾, where also a model is developed to describe the phase separation. The model is based on a hard sphere equation of state supplemented with a Van der Waals attractive term.

- 1) A.K. van Helden, J.W. Jansen and A. Vrij, J. Colloid Interface Sci., 81 (1981) 354.
- 2) C.G. de Kruif et al., Workshop Les Houches 1984.
- 3) J.W. Jansen, C.G. de Kruif and A. Vrij, Chem. Phys. Lett. 107 (1984) 450.

(iii) "The Slide Agglutination Assay: A Study of the Factors Affecting Sensitivity", Mark Smith, 1984.

(iv) "The Preparation of Aqueous Silicon Carbide Dispersions", Gary Carl, 1984

3. There are currently a total of twenty-seven active projects in the Institute. The latest issue of our Graduate Research Progress Reports was No. 23, January 1985. Some copies are still available. Please write to M.S. El-Aasser if you are interested in getting a copy.

4. There are (5) graduate students, Ph.D. candidates who are currently working on various aspects of "The Miniemulsion Process"; P. Abeywardena, C.D. Lack, Y.T. Choi, J. Delgado and M.P. Merkel. A review of the various activities is enclosed in two articles: (i) "Preparation of Latexes by the Miniemulsion Process" by M.S. El-Aasser to be presented at the Polymer Latex II meeting of the Plastics and Rubber Institute, May 21-22, 1985; and (ii) "Polymerization of Styrene Miniemulsions", Y.T. Choi, M.S. El-Aasser, E.D. Sudol and J.W. Vanderhoff, submitted for publication J. Polymer Sci., April 1985.

5. The 16th Annual Short Course "Advances in Emulsion Polymerization and Latex Technology" will be held at Lehigh, June 3-7, 1985; the European 8th Annual version of the course will be held at Davos, Switzerland, August 19-23, 1985.

6. The organization process of the 1986 Polymer Colloids in Racine Wisconsin has started. Enclosed is a separate correspondence on the subject. All members of the Polymer Colloids Group are urged to complete the enclosed questionnaire as soon as possible.

7. J.W. Vanderhoff, F.J. Micale and M.S. El-Aasser have received the 1984 Inventors of the Year Award from NASA for their work on the "Preparation of Large-Particle-Size-Monodisperse Latexes" on board of the space shuttles. They also received The NASA's Space Act Award for 1984 along with the graduate students who worked on the program, Drs. E. David Sudol, C.M. Tseng and Mr. A. Silwanowicz. The awards were given at a ceremony which was held at NASA Headquarters in Washington, D.C. on March 28, 1985.

MSEA/kd
enclosure