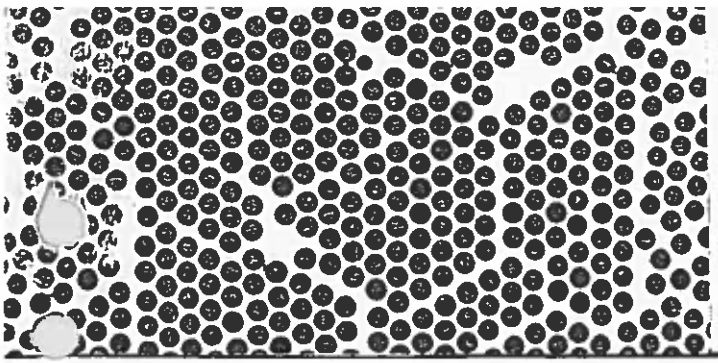

IPCG

INTERNATIONAL POLYMER COLLOIDS GROUP

SEPTEMBER, 1987

VOLUME 18 6 NOV Recd NUMBER 2

NEWSLETTER

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IPCG

INTERNATIONAL POLYMER COLLOIDS GROUP

LIST OF MEMBERS
(Revised August 1987)

North American Circulation

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2.	Dr. M. Croucher	Xerox Research Centre of Canada, 2660 Speakman Drive, Mississauga, Ontario, Canada, L5K 2L1
3.	Dr. J. S. Dodge	B.F. Goodrich Co., Chemical Division Technical Center, Avon Lake, Ohio 44012, USA
4.	Dr. M. S. El-Aasser	Department of Chemical Engineering, Whitaker Laboratory No. 5, Lehigh University, Bethlehem Pennsylvania 18015, USA
5.	Dr. A. P. Gast	Department of Chemical Engineering, Stanford University, Stanford, California 94305 -5025, USA
6.	Dr. R. M. Fitch	S.C. Johnson & Son Inc., Racine, Wisconsin 53403-5011 USA
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10.	Dr. R. Pelton	Department of Chemical Engineering, McMaster University, Ontario, Canada, L8S 4L1
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13.	Dr. R. L. Rowell	Department of Chemistry, University of Massachusetts, Amherst, Massachusetts 01003, USA
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18.	Dr. V. T. Stannett	Department of Chemical Engineering, Box 5035, North Carolina State University, Raleigh, North Carolina 27607, USA
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23.	Dr. M. Winnik	Department of Chemistry, University of Toronto, Ontario, Canada, M5S 1A1
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Rest of the World Circulation

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 Macromolecules, 6 rue Boussingault, 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 160, 2001 Lillestrøm, Norway
7.	Dr. T. W. Healy	Department of Physical Chemistry, University of Melbourne, Parkville, Victoria 3052, Australia
8.	Dr. H. Kast	BASF A.G., Polymer Forschungs Laboratorium, D-6700, Ludwigshafen, West Germany
9.	Dr. J. Lyklema	Laboratory for Physical and Colloid Chemistry, Agricultural University, De Dreijen 6, 6703 BC Wageningen, Holland
10.	Dr. S. Muroi	Coating Materials Laboratory, Ashai Chemical Industry Co. Ltd., 2-1 Samejima, Fuji-City, Shizuoka, Japan
11.	Dr. D. H. Napper	Department of Physical Chemistry, The University of Sydney, Sydney, New South Wales 2006, Australia
12.	Dr. M. Nomura	Department of Industrial Chemistry, Fukui University, Fukui, Japan
13.	Dr. R. H. Ottewill	School of Chemistry, University of Bristol, Cantock's Close, Bristol, BS8 1TS, England
14.	Dr. C. Pichot	CNRS Laboratoire des Materiaux Organiques, B.P. 24, 69390 Vernaison, France
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 te Utrecht, van't Hoff Laboratorim, Postbus 80.501, Padualaan 8, 3508 TB, Utrecht, Holland
18.	Mr. J. Waters	ICI plc, Paints Division, Wexham Road, Slough, S12 5DS, England
19.	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.

FROM THE EDITOR'S DESK

A Change of Editor

As will already be apparent, the Newsletter has suffered a change in Editor. Sandy Dunn, who contributed so much to the past success of the Newsletter, had decided to retire as Editor and I have taken over the responsibility for collating your contributions. This change was ratified by the Group meeting at Tilton in early July.

It would be most remiss of me if I did not immediately pay glowing tribute to Sandy Dunn's many contributions to the activities of the International Polymer Colloids Groups. Sandy, has, of course, achieved international recognition for his scientific contributions to polymer colloids. But his contributions to polymer colloids have gone far beyond that. As Editor of the Newsletter over many years, Sandy has provided much of the glue (anti-dispersion force) that has held the group together between meetings, given that its members are dispersed widely over Mother Earth and so can only meet irregularly. The thanks of all members, both past and present, are thus extended to Sandy for his outstanding efforts on behalf of IPCG; our best wishes are also extended for his future book writing activities as well. We look forward to reading the fruits of your labours.

New Members

Seven new members were elected to IPCG at the Tilton Annual Business Meeting: welcome to Alice Gast, Bob Pelton, Koichi Takamura, Peter Sperry, Ron Uschold, Julian Waters and Chip Zukoski. Long may your contributions appear in the Newsletter. Former members whose names were removed because of their changed circumstances or failure to contribute are: Rance (resigned), Lin, Watillon, Bagehi, Collins and Gardon.

Conferences

The 6th Gordon Research Conference on Polymer Colloids, organized by Ron Ottewill, has come and gone. To judge from the reaction of its participants, it was an outstanding success. Well done Ron! Mohamed El-Aasser was elected Vice-Chairman of the 7th Gordon Conference, which Irja Piirma will organize in 1989. He will chair the 8th Gordon Conference

The Third NATO Advanced Study Institute will be held in Strasbourg from 3-15 July, 1988, under the Directorship of Ron Ottewill. Previous ASIs were held in Trondheim (1975) and Bristol (1982). Francoise Candau has kindly agreed to be the local organizer so we can be assured of the best intellectual and physical fare. It is intended to publish the proceedings of the Institute in book form.

1989 is also going to be a busy year for conferences: that biennial event, the 7th Gordon Conference, has already been mentioned. In addition, the Chemical Societies of the Pacific Basin countries (USA, Japan, China, Canada, Australia, New Zealand, Mexico, Korea, etc.) (PAC-CHEM) will be holding a meeting in Honolulu in December, 1989 at which there will be 4 sessions on the general theme of *'Polymer Colloids, Micelles and Vesicles.'* Melvin Croucher and myself will be involved in its organization. Please contact me if you wish to be on the mailing list for possible participants at a conference on a sun drenched island paradise in the blue Pacific at a time when the Northern Hemisphere is shrouded,as is its wont, in ice, sleet, snow and rain (and that's on its good days).

Finally, if you are organizing, or know of, a conference relevant to IPCG, please advise me of all details so that I can publicize it in the Newsletter.

Minutes of AGM, Revised Membership List and Rules of Membership

Please find attached all the above, suitably updated.

Book Reviews

I would like to include in the Newsletter reviews of books that would be of interest to our members. So when you come across a new book relevant to polymer colloids, please write a review of it for the Newsletter and forward it to me.

Miscellaneous Notes

Vivian Stannett will contribute to the next Newsletter a summary of his work on the inverse emulsion polymerization of vinyl pyrrolidone. Per Stenius' contribution arrived too late for inclusion in the last Newsletter and it so has been held over until this one.

Bob Fitch has kindly taken over the distribution of the Newsletter for North American members. Thanks be to Bob (and S. C. Johnston) for their munificence. I am forwarding the Rest of the World copies via an airmail courier.

Date for Next Newsletter

Contributions for the next Newsletter should be forwarded to me by AIRMAIL by 30 April 1988.

D. H. Napper
Editor

MINUTES of the ANNUAL BUSINESS MEETING of the POLYMER COLLOIDS GROUP held at Tilton School, Tilton, New Hampshire on Wednesday 8th July 1987 at 5 p.m.

Present: Dave Bassett, Francoise Candau, Melvin Croucher, Jim Dodge, Sandy Dunn, Mohamed El-Aasser, Bob Fitch, Jim Goodwin, Don Napper, Ron Ottewill, Irja Piirma, Bob Rowell, Ritchie Wessling (vice Frank Saunders), John Vanderhoff, Theo van de Ven (15).

Membership: It had always been understood that members should resign if they were no longer active in the field and Derek Rance had done so. Academic members were required to provide a contribution (which could be quite brief and which, in any case, should not be excessively long - normally not more than three A4 pages typed single spaced) to each of the semi-annual issues of the Newsletter. The reminder sent in September had stimulated most delinquents into action but Lin had not contributed at all in the last 5 years and Watillon had never done so although Dr Stone-Matsui had attended meetings from time to time. Industrial members were expected to contribute to the Newsletter whenever possible and to attend meetings but little had been seen of Bagchi, Collins, or Gardon in recent years although Ed Collins continued to participate in the Lehigh Short Courses both in America and Europe. . Because it was essential that the Group should not become too large in order than the burden of its administration might not be excessive, it was decided that the membership of these five should be terminated but that Bagchi should be asked to nominate at successor at Eastman Kodak who was actively working in the field. Sandy Dunn would write to them to inform them of this decision.

It was noted that it was desirable that major latex manufacturers should be represented in the Group by a member of their staff who was active in the field who could reproduce his copy of the Newsletter for internal circulation if desired. The following nominations were accepted unanimously: the members indicated were to inform the candidates of their election orally. Sandy Dunn would write later forwarding a copy of the Group's History and Rules, List of Members, and Spring 1987 Newsletter.

Gregg Alms	E.I.du Pont de Nemours & Co Polymer Products Dept., P.O. Box 1217, Building 21, Parkersburg, West Virginia 26102.	(Rowell)
Alice Gast	Department of Chemical Engineering Stanford University, Stauffer 111, Stanford, California 94305	(Goodwin)
Bob Pelton	Department of Chemical Engineering McMaster University, Hamilton, Ontario, Canada, L8S 4L7	(Goodwin)
Koichi Takamura	Polysar Ltd Vidal St. South, Sarnia, Ontario, Canada, N7T 7M2	(van de Ven)
Peter Sperry	PRM Pioneering Research Rohm & Haas Co. 727 Norristown Road, Springhouse, Pennsylvania 19477	(Napper)
Julian Waters	ICI plc Paints Division, Wexham Road, Slough, SL2 5DS, England.	(Dunn)

Chip Zukoski 110 Mitchem (Rowell)
University of Illinois,
Urbana,
Illinois 61801

Newsletter. Funds for the production of the Rest of the World Edition were practically exhausted but Don Napper was prepared to take on the Editorship and the distribution to the Rest of the World: this would be by Air Courier which was nearly as fast as by Air Mail but much cheaper. Ron Ottewill would continue to have reminders sent out to members 6 weeks prior to the issue deadline: these would emphasise that copy must be sent to Australia by Air Mail. Ritchie Tessling said that Frank Saunders planned to retire within the next 18 months and would like some one else to take over the North American distribution. Bob Fitch said that S.C.Johnson & Son could do this from any mutually convenient date.

Programme. Ron Ottewill had had confirmation by telephone that NATO funds for an Advanced Study Institute to be held in Strasbourg 3 - 15 July 1989 had been approved although the amount would not be known until the documents arrived. He had had to prepare the application at short notice to meet the deadline. The Organising Committee had been named as Ottewill (U.K. - Director), Candau (France - Local Organiser), Rowell (USA), and Ugelstad (Norway). It was agreed that the proceedings should be published but it was noted that the publishers favoured by NATO made little effort to promote their publications although their production was technically satisfactory. NATO funding would only suffice for about 85 participants but this could be increased by seeking industrial support which, it was hoped, might amount to £ 10 000. It was agreed that the Institute should be publicised widely in the first instance by a note in the next Newsletter and by direct mail to the Gordon Conference participants: prospective industrial participants required as long notice as possible to obtain company approval for a fortnight's absence. Detailed decisions on which meeting rooms should be reserved etc. were remitted to the Organising Committee.

It was noted that Mohamed El-Aasser had been elected Vice-Chairman of the 7th Gordon Conference in 1989 and would be Chairman for the 8th Gordon Conference in 1991.

Ron Ottewill said that a R.S.C. Faraday Division General Discussion on 'Colloid Stability' would be held in Bristol in either April or September 1990. The 59th A.C.S. Colloid and Surface Science Symposium would be held at Lehigh in June 1990. A decision would have to be made later as to which of these events would have the largest number of Group members present and would therefore be the optimum site for the 1990 Annual Business Meeting.

It was hoped that it might prove possible to hold a meeting in Australia in 1992: this might be an American-Australian Exchange Conference organised through the N.S.F.

The meeting closed at 6.05 p.m.

THE POLYMER COLLOIDS GROUP

History

The Polymer Colloids Group was founded at a meeting at Lehigh University on 27 September 1971 at which were present Bob Fitch (then at the University of Connecticut), Irv Krieger (Case-Western Reserve), Ron Ottewill (Bristol), Gary Poehlein (then at Lehigh), John Vanderhoff (Lehigh), and David Williams (then at the City College of the City University of New York). They decided to invite six other academics active in the field to join the Group and Sandy Dunn (UMIST), Don Napper (Sydney), Alan Robertson (McGill), Vivian Stannett (North Carolina), and Tom Wallace (Rochester) agreed to do so.

Annual Meetings

Meeting	Date	Venue	Chairman/Director
1st Microsymposium	16-17 June 1970	Lehigh	
2nd Microsymposium	29-30 June 1973	Lehigh	
3rd Microsymposium	June 1974	Bristol	
1st NATO Advanced Study Institute	July 1975	Trondheim	Bob Fitch
4th Microsymposium	17-18 June 1976	Lehigh	
1st Gordon Research Conference	21-26 Aug. 1977	Plymouth, N.H.	Irv Krieger
A.C.S. 'Polymer Colloids II'	10-15 Sept. 1978	Miami Beach	Bob Fitch
2nd Gordon Research Conference	2-6 July 1979	Tilton	Gary Poehlein
54th Colloid and Surface Symposium	15-18June 1980	Lehigh	
3rd Gordon Research Conference	12-17 July 1981	Tilton	Bob Fitch
2nd NATO Advanced Study Institute	26 June-8 July 1982	Bristol	Gary Poehlein
4th Gordon Research Conference	11-15 July 1983	Tilton	John Vanderhoff
Chemical Institute of Canada	3-6 June 1984	Montreal	Theo van de Ven
5th Gordon Research Conference	8-12 July 1985	Tilton	Ritchie Wessslin
NATO-Wingspread Advanced Research	30 June-4 July 1986	Racine, WI	Bob Fitch
6th Gordon Research Conference	5-10 July 1987	Tilton	Ron Ottewill
3rd NATO Advanced Study Institute	3-15 July 1988	Strasbourg	Ron Ottewill
7th Gordon Research Conference	1989		Irja Piirma

As at July 1987, the Group had 44 members, 19 in the U.S.A., 6 in Canada, 5 in England, 10 in other European countries (including 1 in the USSR), 2 in Australia, and 2 in Japan.

RULES

Because of the international membership, the organisation of the Group is informal. Administrative expenses are, so far as possible, borne by Members' Institutions in turn because the high cost of transmitting small amounts of money to foreign countries makes an annual membership subscription impracticable.

Membership is by invitation from the Annual Meeting of the Group. The Group aims to have at least one Member from each research group which is active in the field who has shown interest by attendance at meetings. Members are required to resign if they should cease to be active in research in the field.

Members keep in touch by attending the Annual Meeting (now normally in conjunction with a larger meeting) whenever possible and through the Newsletter circulated twice a year. Academic members are required to contribute to each issue of the Newsletter: failure to do so without good cause may result in the termination of membership. Industrial members should contribute to the Newsletter whenever possible. Nesletter contributions should be typed single-spaced on A4 (21 x 30 cm) paper suitably for xeroxing and should not normally exceed three pages (including any figures). The Newsletter is for private circulation only and contributions do not constitute publications. Members may reproduce copies to facilitate circulation within their own research group. Items appearing in the Newsletter which have not been published subsequently may be cited as 'private communication' provided that the author's consent has been obtained. Members should list the titles and references of any papers they have published during the preceeding 6 months in their Newsletter contributions and circulate preprints or reprints when they have sufficient copies available.

POLYMER COLLOID GROUP NEWSLETTER

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

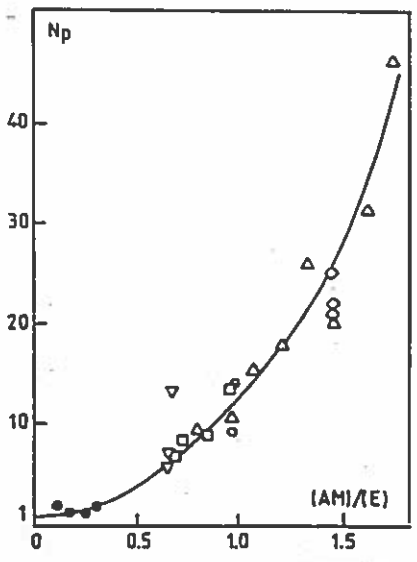
F. CANDAU

POLYMERIZATION OF ACRYLAMIDE IN NONIONIC MICROEMULSIONS : CHARACTERIZATION OF THE MICROLATICES AND POLYMERS FORMED

(C. Holtzscherer, J.P. Durand, F. Candau, Colloid and Polym.Sci. in press)

Free radical polymerization of acrylamide was carried out in nonionic microemulsions formed of water, an isoparaffinic oil, Isopar M and a blend of nonionic emulsifiers : a sorbitan sesquioleate and a polyoxyethylene sorbitol hexaoleate (HLB of the mixture : 9.3)). The size and the stability of the latex particles formed after polymerization were studied as a function of monomer, emulsifier and electrolyte concentration. High emulsifier and high monomer contents favor the obtention of high molecular weight polyacrylamides.

An important parameter, characteristic of the polymerization mechanism, is the average number of macromolecules N_p contained in a latex particle. An estimate of this number can be made from the volume of the particle and from the molecular weight of the polymer. An universal behavior relating the particle size and the number of macromolecules per particle to the acrylamide/emulsifier weight ratio could be established (see figure). Note that the limiting case corresponding to one single polymer molecule can be reached by using inverse AOT microemulsions. This behavior makes possible the selection of an appropriate system beforehand, according to the considered purposes.



Variation of N_p as a function of (AM)/(E) ratio ; △, ▽, ○, □, ◇ : nonionic series ; ● AOT series

Application of the Cohesive Energy Ratio Concept (CER) to the formation of polymerizable microemulsions (C. Holtzscherer and F. Candau, Colloids and Surfaces, submitted for publication)

The cohesive energy ratio concept (CER) developed by Beerbower and Hill for the stabilization of emulsions has been extended to microemulsions. The CER concept allowed us to predict the most suitable emulsifiers and oils for the production of polymerizable microemulsions. For example, a blend of non-ionic surfactants (sorbitan sesquioleate and poly(oxyethylene) sorbitol hexaoleate) was found to be very efficient for the microemulsification of an aqueous solution of acrylamide in an isoparaffinic oil Isopar M. Under these conditions, microemulsion polymerization leads to stable uniform polyacrylamide microlatexes (d_v0.1 m) which can be useful for industrial applications.

Publications

C. Holtzscherer, S. Candau and F. Candau : "Modification of polyacrylamide microlatices by using a seeding procedure" in "Surfactants in Solution" (K. Mittal et P. Bothorel Eds) Plenum Press, N.Y. 6, 1473 (1986)

F. Candau, "Microemulsion Polymerization" Encyclopedia of Polymer Science and Engineering (Mark-Bikales-Overberger-Menges, Eds) 9, 2nd Edition, 718, John Wiley & Sons (1987)

F. Candau, Z. Zekhnini and J.P. Durand "Copolymerization of acrylamide and sodium acrylate in microemulsions" Progress Colloid & Polym.Sci., 33 (1987)

THE DOW CHEMICAL COMPANY

MIDLAND, MICHIGAN 48674

ABSTRACT

TAPPI 1987 POLYMERS, LAMINATIONS AND COATINGS CONFERENCE

Development of New Waterborne Laminating Adhesive Systems

A. C. Makati, Dow Chemical Company, Designed Latexes & Resins, 1604 Building, Midland, MI 48674

Waterborne laminating adhesive systems that can bond plastic substrates are becoming important to the laminating industry because of environmental and economical considerations. This paper reviews the fundamentals of adhesive lamination, performance requirements of adhesives, and approaches to develop waterborne laminating systems. Proper design of these systems requires consideration of wetting, interfacial adhesion, lamination efficiency, and polymer rheology. Research to understand the fundamentals of the above critical parameters, polymer synthesis and formulation technology has led to the development of new waterborne laminating adhesive systems.

Controlling Coating Gloss Through Control of the Shrinkage During Structure* Consolidation

D. I. Lee, Dow Chemical Company, Designed Latexes & Resins, 1604 Building, Midland, MI 48674

When coating colors are applied onto paper substrates, they undergo many changes such as coating penetration through large pores, drying by surface evaporation, dewatering through the substrates causing structural changes, binder migration, shrinkage, etc. These changes affect the final coating properties. Among these interrelationships, this talk will discuss the aspect of shrinkage in relation to coating opticals, especially coating gloss, by examining the effects of binder level and coating solids on the optical properties of clay/latex coatings on plastic films. Then, some ideas of controlling coating gloss through control of the shrinkage during drying will be presented.

*Presented at a panel discussion on coating structure for the 1987 TAPPI Coating Conference, May 1987.

THE DEPENDENCE OF VISCOSITY ON COMPOSITION IN LATEX - SURFACTANT - THICKENER SYSTEMS

by

Oswald U. Anders

Dow Chemical USA. DL&R; Michigan Div. Applied Science and Technology Laboratories

ABSTRACT

Latexes are typically employed in formulations with various additives. The latter almost invariable contain surfactants and thickeners as constituents. An understanding of the behavior of the above basic systems, i.e. those containing no additional additives, should thus constitute a data base of value to many applications of latexes. in various areas of application. The rheology or viscosity profile of the formulations is often a significant consideration for specific applications as in paints, caulks, paper coating, adhesives and inks.

Preliminary data identified the presence of viscosity maxima at a certain concentration of surfactant. This seemed to apply for formulations made up of the same materials and identical surfactant/thickener ratios (S/T), but varying relative amounts of the two additives to the latex. It was also found that at low shear rates such maxima were less pronounced, thus indicating differences in the shear thinning rates as function of composition.

The present effort was intended to verify and further elucidate this finding, and develop techniques for the evaluation of the rheological behavior of such formulations. It was also intended to elucidate some of the mechanisms of interaction that affect the rheological characteristics of such systems.

The experimental effort was restricted to three component systems of three different latexes. The latter were specifically synthesized for the project. The three latexes comprised two of equal composition but different particle size, and two of different composition and equal particle size (within experimental limits). The study was also restricted to systems containing a sodium lauryl sulfate surfactant and a polyacrylate thickener with the two latter present at three different ratios i.e. 0.067, 0.09 and 0.11 at different total amounts relative to the latex.

DSM

DSM RESEARCH

Contribution to the Polymer Colloids Group Newsletter

From: W.A.B. Donners
DSM Research
P.O. Box 18
6160 MD GELEEN
THE NETHERLANDS

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

Kinetic measurements have been performed on MAA/MMA 80/20 systems in the presence of PEO of various molar masses. In all experiments the amount of EO expressed in moles was equal to the total amount of moles of monomer. PEO molar mass 20,000 and 10,000 retard the polymerization to the same extent. PEO molar mass 2,000 retards the polymerization significantly less whereas the presence of PEO molar mass 1,000 does not lead to any retardation. Nevertheless the final particle size of MAA/MMA 80/20 latices prepared in the presence of PEO molar mass 1,000 is significantly larger than the blank. The only explanation can be that PEO molar mass 1,000 is incorporated in the particles by complexation. The finding that PEO molar mass 1,000 does not influence the kinetics shows that there is no coagulation of primary particles through complexation probably because the PEO molecules are too short.
These results fit very well with earlier experimental results that showed that bimodal particle size distributions were obtained in MAA/MMA 80/20 systems with low concentrations of PEO 20,000 and 1,500 but not with PEO 600.
Further work will be directed towards low acid recipes.

UMIST

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Chemistry Department,
Dr A. S. Dunn

Emulsion Polymerisation of p-tert butyl styrene

Before returning to India, Dr Satpathy made a preliminary study of the emulsion polymerisation of p-tert-butyl styrene which suggests that this monomer would be worthy of a more detailed investigation. It differs from styrene mainly in its solubility in water is much lower and the glass transition temperature of the polymer is much higher (134 ^{o}C compared with 81 ^{o}C). One might expect its solubilisation in micellar solutions of surfactants to be similar, but this remains to be proved. However, under the same conditions, it (Fig.1) polymerises at much the same rate as styrene from which it may be inferred that the values of k_p are similar if a similar number of latex particles are formed, although this point, too, remains to be established. Herein it probably differs from o-methyl styrene and di-o-methyl styrene which Gerrens & Köhnlein studied (Z. Electrochem. 64 (1960) 1199) which were found to have lower values of k_p because of steric hindrance. These monomers also have a lower solubility in water than styrene and figure in Gershberg's well known correlation (Proc. A.I.Ch.E.-I.Chem.E. Joint Meeting, London (1965) 4 (Part 3)) of the emulsifier exponent of the rate of emulsion polymerisation in Interval II with the solubility of the monomer in water. This exponent was found to be 0.6 as for styrene as required by the Smith-Ewart theory in which this exponent arises simply because the surface area of a latex particle is proportional to r^2 whilst its volume is proportional to r^3. The usual explanation of the more water-soluble monomers having a lower value of the emulsifier exponent is the participation of aqueous phase polymerisation in parallel with polymerisation in the latex particles. However Gershberg's presentation of the results fails to bring out the point that Gerrens & Köhnlein actually found the emulsifier exponent of the number of latex particles (which must also be 0.6 in the Smith-Ewart theory) to be 0.8. In a case in which latex particles were nucleated exclusively from monomer solubilised in micelles to form latex particles which did not subsequently coalesce (as might be found for a sufficiently insoluble monomer with a high enough T_g at high emulsifier concentrations) one might expect N (and consequently R_p) to be proportional to the concentration of micellar emulsifier and, indeed, in the case of

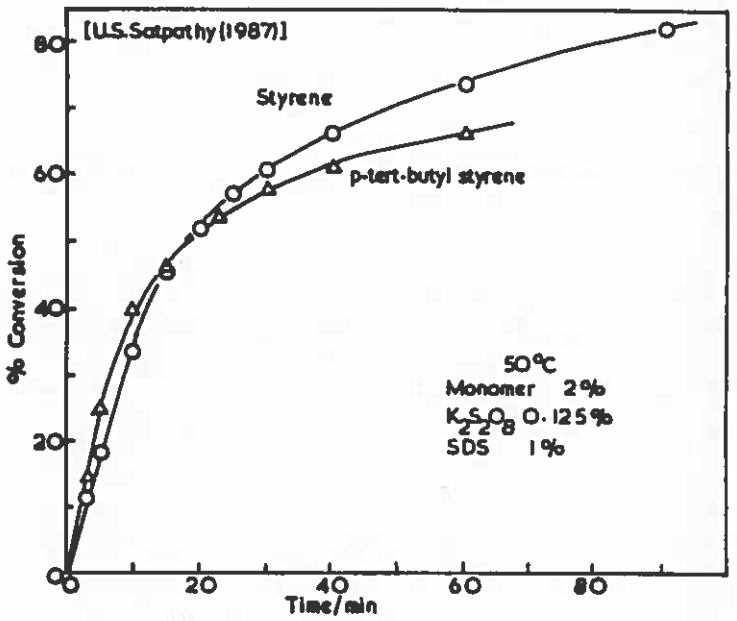
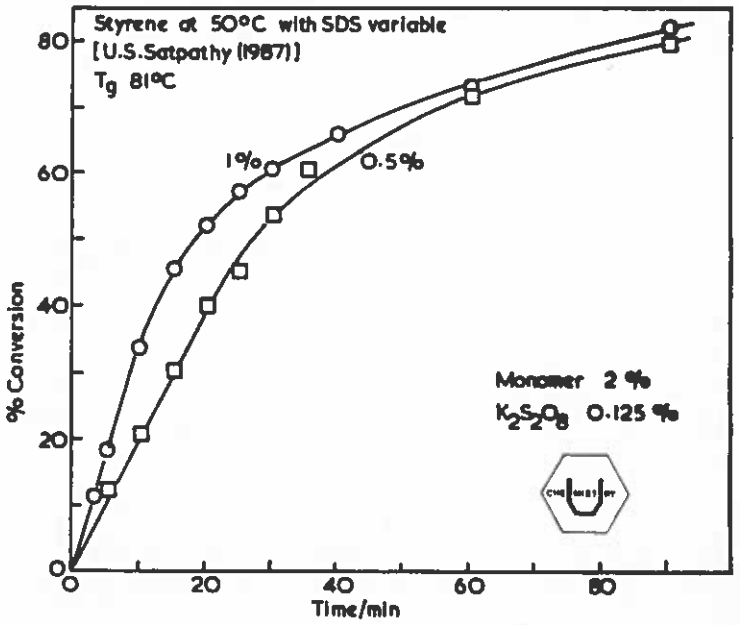
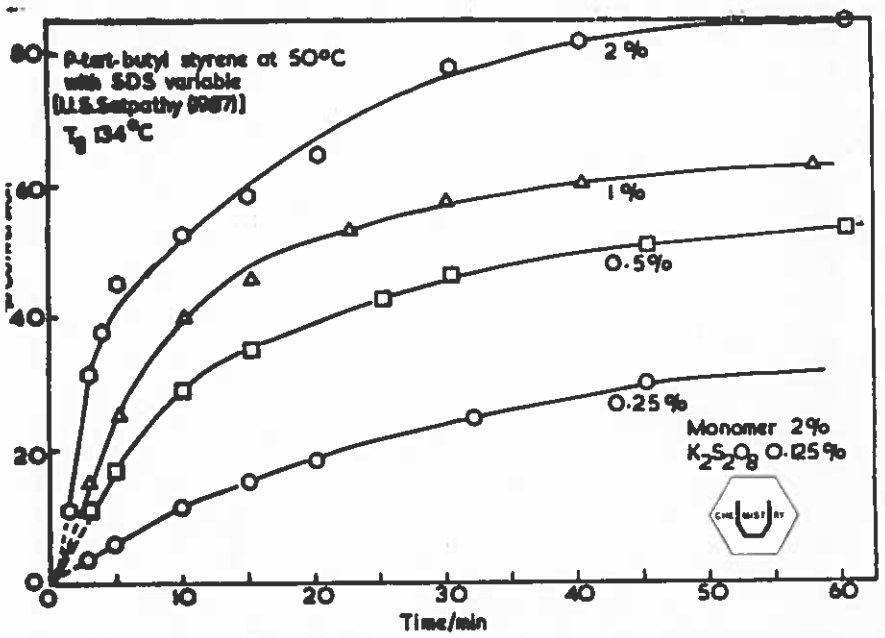


Fig. 1

styrene when the emulsifier was varied in a homologous series, it was the concentration of micellar emulsifier which turned out to be significant (cf. Dunn & Al-Shahib in Fitch ed. 'Polymer Colloids II') although the emulsifier exponent was less than 1.0. The value of the emulsifier exponent may actually be an index of the tendency of the primary latex particles to coalesce!

Fig. 2 and 3 show that the form of the conversion-time curves at different emulsifier concentrations is quite different for styrene and tert-butyl styrene. The probable reason for this is that monomer-swollen polystyrene latex particles can coalesce and thereby attain a sufficiently high coverage of the particle surfaces with emulsifier to keep the latex stable and permit high conversions to be attained at the lower emulsifier concentrations whereas the higher T_g of tert-butyl styrene may restrict coalescence so that surface charge density decreases as particle size increases so that the latex coagulates at the lower emulsifier concentrations limiting the conversion which can be attained.





Figs. 2 and 3

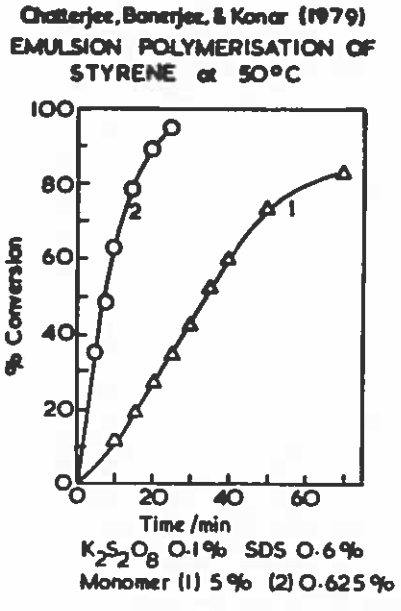


Fig. 4

The monomer/water phase ratio is not usually considered to be an important factor in emulsion polymerisation but Fig. 4 reproduces a remarkable results published (though without comment) by Chatterjee, Banerjee, & Konar (J. Polym. Sci. Polym. Chem. Edn. 17 (1979) 2193)

At a constant emulsifier concentration, the rate of emulsion polymerisation of styrene is much higher at a very low monomer/water ratio (0.625%: the monomer is in micellar solution initially) than when a more normal phase ratio (5%) was used. Dr Satpathy was able to reproduce Curve 1 exactly but not Curve 2 although he did find a higher rate at the low phase ratio. The rate observed at the low phase ratio was sensitive to stirring speed whereas that at the normal phase ratio was not. It seems that at the low phase ratio there was just about enough emulsifier to stabilise all the primary latex particles and an emulsifier exponent of 1.0 might be found under these conditions although the particles were not so stable that some coalescence could not be induced by stirring.

Contribution to the Polymer Colloids Group Newsletter

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

Emulsion Polymers Institute, Lehigh University
Bethlehem, Pennsylvania 18015, U.S.A.

The titles of our current research projects are given in the enclosed Contents of our Graduate Research Progress Reports, No. 28, July 1987. Copies of any of these reports can be obtained by contacting Ms. Debra Nyby at the above address. Summaries of recent progress in several research areas are presented here.

I. Large-Particle Size Polymer Particles

A. Formation of Uniform Nonspherical Particles (H.R. Sheu)

The mechanism of formation of uniform non-spherical latex particles has been proposed based on thermodynamics and the experimental observation of phase separation in swollen and polymerized latex particles. The latter was demonstrated using 5.2 μm crosslinked polystyrene seed particles. Both swelling (toluene) and polymerization (styrene) studies illustrated this domain separation, which initially occurs as the temperature is raised from ambient to polymerization conditions (70°C). Polymerization causes increased separation. Elastic and interfacial contributions to minimizing the free energy are, therefore, greater than the mixing energies. Conditions for reducing phase separation are defined by examining how to minimize chemical potential differences between the monomer in the particles and aqueous phase. These include: (a) a small monomer/polymer swelling ratio; (b) a seed with a low cross-link density and small size; (c) a low polymerization temperature and others. Mr. H.R. Sheu recently presented some of this work at the ACS Meeting in New Orleans (PMSE Vol. 56, 922 (1987))

B. Dispersion Polymerization (Y.Y. Lu)

The mechanism of dispersion polymerization of styrene in ethanol, (producing 4 μm monodisperse particles) is being examined with emphasis on the polymerization taking place in the continuous phase. It was previously concluded that both the continuous phase and the polymer particles were sites of significant polymerization. Molecular weight analysis of the soluble polymer recovered from the ethanol/styrene continuous phase early in a reaction (particle nucleation begun) show polymer of molecular weight 3000 (wt. average) or a degree of polymerization of 29. This is believed to be near the critical chain length for precipitation of the growing radical (under the conditions of 20% styrene, 80% ethanol). This value is expected to decrease as monomer is depleted from the ethanol phase (decreasing the solvency) as a result of consumption by polymerization. A paper has been submitted to the J. of Polymer Sci., describing some of this work.

II. Miniemulsions

A. Mass Transfer Coefficients in Co-polymerization (V. Rodriguez)

Initial attempts at measuring the mass transfer coefficients of monomers (styrene and methylmethacrylate) between droplets of separately prepared miniemulsions and the aqueous phase using a 2 chamber diffusion cell were unsuccessful because of the large resistance of the membrane separating the two miniemulsions. Another approach has been attempted which has yielded values in the range of $1.1\text{-}1.6\text{X}10^{-5}$ cm/sec for MMA and $0.9\text{-}2.1\text{X}10^{-5}$ for styrene. These are subject to some uncertainty resulting from the assumption of the initial droplet size of the miniemulsion droplets (200nm) which is not known precisely (and is not monodisperse). The method used to obtain these data is the following. The basic principle is to obtain the relative concentrations of the monomers in the droplets by analyzing the composition of the copolymers formed by fast UV initiated polymerization. Two separate miniemulsions of monomers A and B are prepared, one containing a water-insoluble UV photoinitiator, and the other a water-insoluble inhibitor. The two miniemulsions are mixed for varying periods of time and then polymerized to a low conversion (<0.5%) in a cell designed for exposure to UV radiation (40 sec). The copolymer formed is recovered and its composition determined by IR. The copolymer composition is related to the relative monomer concentrations in the initial droplets containing the UV initiator by using the Mayo-Lewis copolymer equation. Experiments are run for each combination of monomers and photoinitiator/inhibitor. The overall mass transfer coefficients were calculated from the rate of transport of monomers, the concentration gradients and the interfacial area of the droplets. Characterization of the droplet size distributions is planned.

B. Continuous Polymerization in a Tubular Reactor (S. Adamec)

Vinyl acetate/butyl acrylate miniemulsions have been polymerized using a tubular (plug flow) reactor. This process takes advantage of the high stability of the miniemulsions and serves to check the performance of such a reactor. Recent results indicate conversions lower than predicted from batch data (70% vs 90%). The reasons for this are unclear and currently being investigated. Polymer characterization is also in progress.

III. Preparation of Rocket Propellants by Emulsification (T. Hawkins)

A model emulsion propellant is being developed having a high internal phase content (eutectic salt mixture, 75%) and the required physical properties of a solid rocket propellant. A potassium iodide-sodium iodide-urea eutectic mixture has been selected having met the necessary requirements for the model eutectic salt mixture:(1) melt temperature <50°C; (2) non-detonable; (3) inexpensive; and (4) anhydrous. A hydroxy-terminated polybutadiene, R45-HT (Sartomer), was chosen initially as the binder, while several isocyanates are being evaluated to effect curing. The emulsifier system necessary to produce the "water-in-oil emulsion" continues to be evaluated; a Span 85/Tween 85 mixture has given stable emulsions which can be cured at 60°C. These cured systems are now being characterized in terms of their physical properties.

Abstracts* of Papers Presented at the ACS Meeting,
New Orleans, August 1987

Microemulsion Polymerization of Styrene

J.W. Vanderhoff, J.S. Guo and M.S. El-Aasser

Initiation of polymerization in styrene oil-in-water microemulsions by water-soluble potassium persulfate or oil-soluble 2,2'-azobis-(2-methylbutyrolitrile) at 70°C gave stable latexes which were bluish and less translucent than the original microemulsions. The polymerization rates were not constant, but increased to a maximum and then decreased. The latex particle size distributions were broad (5-40 nm) and the average sizes were larger than the 3.65-nm average size reported for similar microemulsions. The weight-average molecular weights were high, $1\text{-}2\times10^6$. The maximum polymerization rate and number of particles varied with the 0.47 and 0.40 powers of potassium persulfate concentration, and the 0.39 and 0.38 powers of 2,2'-azobis-(2-methylbutyronitrile) concentration, respectively, consistent with the 0.40 value expected for Smith-Ewart case 2. Microemulsion polymerizations of styrene-toluene mixtures at the same oil-water phase ratio gave slower rates and lower weight-average molecular weights but the same size distribution as styrene alone. The mechanism proposed comprised initiation and polymerization in the microemulsion droplets.

Sulfonated Latex Particles as Acid Catalysts for the Continuous Inversion of Sucrose

J.H. Kim, M.S. El-Aasser, A. Klein and J.W. Vanderhoff

Sulfonated polystyrene latex particles were used as acid catalysts in the continuous inversion of sucrose at 50-70°C. The particles (surface charge 168 ueq/g) were confined in a stirred reactor with a semipermeable membrane; sucrose solution was pumped in and product solution was pumped out. The catalytic activity of the particles was unchanged after 20 days continuous use. Variation of particle size (0.13 and 0.42 μm) and stirring rate showed that internal and external mass transfer was not a controlling factor. The kinetics were pseudo-first-order; the rate constant at 70°C was 2.30/N-min as compared with 0.07/N-min for macroporous sulfonated ion-exchange resin; the apparent activation energy was 111 kJ/mole as compared with 121 kJ/mole for the homogeneous acid-catalyzed reaction. The faster rate was attributed to the very great surface area, high charge density, and lack of internal diffusional resistance of the latex particles. The proposed mechanism comprised adsorption of sucrose on the particle surface, followed by inversion and desorption of product.

*These papers appear in Proceedings of the ACS Division of Polymeric Materials: Science and Engineering, Vol. 57, 1987

Particle Nucleation in Vinyl Acetate-Butyl Acrylate Miniemulsion Copolymerization

J. Delgado, M.S. El-Aasser, C.A. Silebi and J.W. Vanderhoff

Fluid, opaque conventional or macroemulsions are prepared using low concentrations of anionic emulsifier and comprise droplets of 1-10 μm diameter. Viscous, translucent microemulsions are prepared using high concentrations of anionic emulsifier-alcohol mixtures and comprise droplets of 10-100 nm diameter. Fluid, opaque miniemulsions are prepared using low concentrations of anionic emulsifier-alkane or fatty alcohol mixtures and comprise droplets of 100-200 nm diameter. Vinyl acetate-butyl acrylate miniemulsions were prepared using sodium hexadecyl sulfate-hexadecane mixtures and copolymerized in batch. The number of particles nucleated was smaller, the rate of copolymerization was slower, and the amount of vinyl acetate incorporated into the copolymer was slightly lower than in conventional emulsion copolymerization. The hexadecane stabilized the droplets against coalescence by diffusion. The major locus of particle nucleation was the stable submicroscopic monomer droplets, in contrast to the aqueous phase (homogeneous nucleation) for conventional emulsion copolymerization.

Recent Publications

"Morphology and Grafting Reactions in Core/Shell Latexes", M.P. Merkel, V.L. Dimonie, M.S. El-Aasser and J.W. Vanderhoff, J. Polym. Sci.: Part A: Polym. Chem., 25, 1219 (1987).

"Process Parameters and Their Effect on Grafting Reactions in Core/Shell Latexes", M.p. Merkel, V.L. Dimonie, M.S. El-Aasser and J.W. Vanderhoff, ibid, 25, 1755 (1987).

"A Polymer Thin-Film Technique to Study the Micromorphology of Core/Shell Latexes", O.L. Shaffer, V.L. Dimonie, M.S. El-Aasser, J.W. Vanderhoff, J. Polym. Sci.: Part A: Polym. Chem. 25, 2593 (1987).

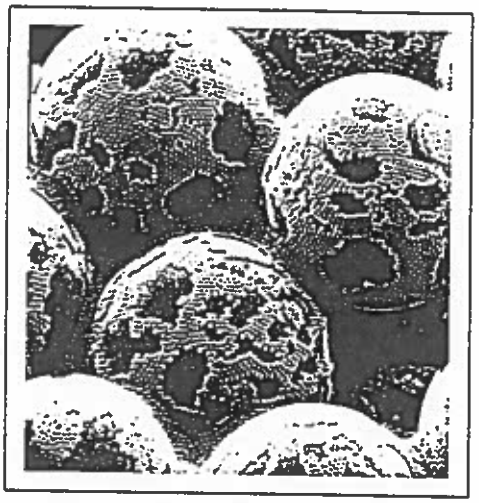
The Emulsion Polymers Institute's 19th Annual Short Course "Advances in Emulsion Polymerization and Latex Technology" will be held at Lehigh on June 6-10, 1988. The European Short Course will be given August 22-26, 1988.

EMULSION POLYMERS INSTITUTE

Graduate Research Progress Reports

No. 28

July 1987



Lehigh University

Bethlehem, Pennsylvania

CONTENTS

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STANFORD, CALIFORNIA 94305-5025

DEPARTMENT OF CHEMICAL ENGINEERING

Contribution to Polymer Colloids Newsletter
Current Research Projects - Alice P. Gast
September 1987

1. The Adsorption of Polymers on Colloidal Particles
with Kookheon Char (jointly advised with C. W. Frank)

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

Summary: This is primarily an experimental project aimed at elucidating the mechanisms of polymer adsorption onto colloids, a subject of great technological importance in coatings, inks and magnetic storage media. The system under study is a water soluble polymer, poly(ethyleneoxide), with pyrene groups attached to the ends. The pyrene fluorescence provides a probe of end-to-end distance and chain end mobility. There are many unresolved questions in polymer adsorption that we intend to address, including the conformation of polymers on small highly curved surfaces, the displacement of polymers from surfaces by chains of differing molecular weight, and the effect on conformations of specific chemical interactions with a surface such as hydrogen bonding, hydrophobic attractions and electrostatic interactions.

Publication: Macromolecules, 1987, 20, 1833.

2. The Adsorption of Block-Copolymers from Micellar Solution
with Mark R. Munch

Goal: To determine the equilibrium and kinetic adsorption behavior of amphiphilic polymer molecules adsorbing from microphase separated solutions.

Summary: The adsorption of amphiphiles onto solid surfaces is complicated by their surface activity and tendency to associate into micelles. Interesting physical problems involving amphiphilic molecules arise in many situations including emulsification, detergency, homogenization of polymer blends and colloidal stabilization. The key question we wish to resolve is the mechanism by which these molecules attach themselves to interfaces when already existing in small stable domains known as micelles. We are modeling the phase behavior and adsorption equilibrium of this system with a mean-field model. Our experimental apparatus is designed to measure the rate of adsorption of polymers at a solid-liquid interface by a new noninvasive technique based on the principles of integrated optics. We are first investigating an interesting class of polymers with long nonpolar tails and a small polar head group.

Two publications submitted to Macromolecules.

3. The Dynamics of Colloidal Crystallization
with Ioannis Monovoukas

Goal: To determine the mechanisms of nucleation and growth of volume-filling entropically driven crystals of a model colloidal suspension.

Summary: The scientific interest in the crystallization process is high from both fundamental and technological perspectives. While many scattered observations of the order-disorder transition exist, we aim to quantify the equilibrium phase diagram and determine the dominant mechanisms of nucleation and growth of these crystalline systems. We are particularly interested in the transitions between stable cubic structures in these systems. Our approach involves the synthesis characterization and careful purification of suspensions of sub-micron polymer latices carrying charged groups on their surfaces. With the screened coulombic repulsion we have a means of controlling the range and magnitude of the interactions and thereby controlling our position on the phase diagram. We investigate the crystal structure via visible light diffraction monitoring crystallite lattice type, orientation, and size. We study the crystal growth process as a function of distance from the phase boundary or degree of saturation.

4. Field-Induced Aggregation In Suspensions
with Paul M. Adriani

Goal: To model the structure and resulting macroscopic properties of suspensions in external fields.

Summary: The presence of an external field can cause aggregation in suspensions such as magnetic media and electrorheological fluids. The field produces an anisotropic distribution of particles resulting in anisotropic physical properties such as dielectric constant, elastic modulus and viscosity. Our main objective is to be able to predict these properties from a fundamental theory. We model the particle-particle interactions in this suspension as dipolar interactions and find the proper reduction of the multibody problem to an equivalent two-body form. We then employ the statistical mechanics of dipolar particles in fields to determine the microstructural arrangement of particles in the suspension and the resulting phase behavior (where aggregates are considered phase domains). We use a perturbation to the quiescent structure to determine the response to flow and from the resulting stresses can calculate rheological properties of these suspensions. The results of such calculations for the high frequency dynamic viscosity and elastic shear modulus are shown in figures 1 and 2. The figures show the dramatic increase in the elastic modulus upon increasing dipole strength. The much smaller increase in the dynamic viscosity indicates its relative insensitivity to the interaction potential between particles. Many interesting statistical thermodynamics questions arise in systems with external fields and we intend to investigate the nature and properties of the field-induced phase transitions and phase domains.

Elastic Shear Modulus

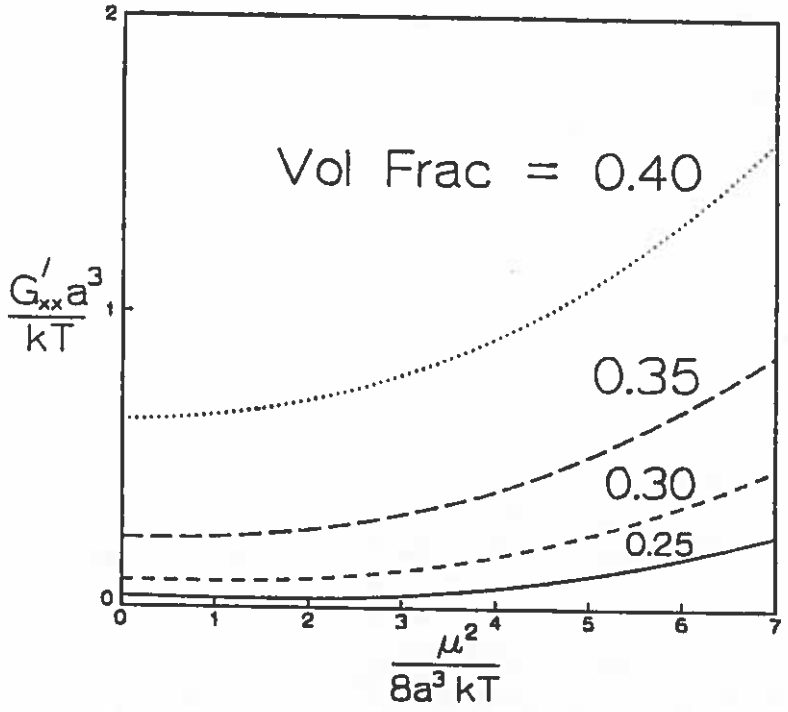


FIGURE 1

Dynamic Viscosity

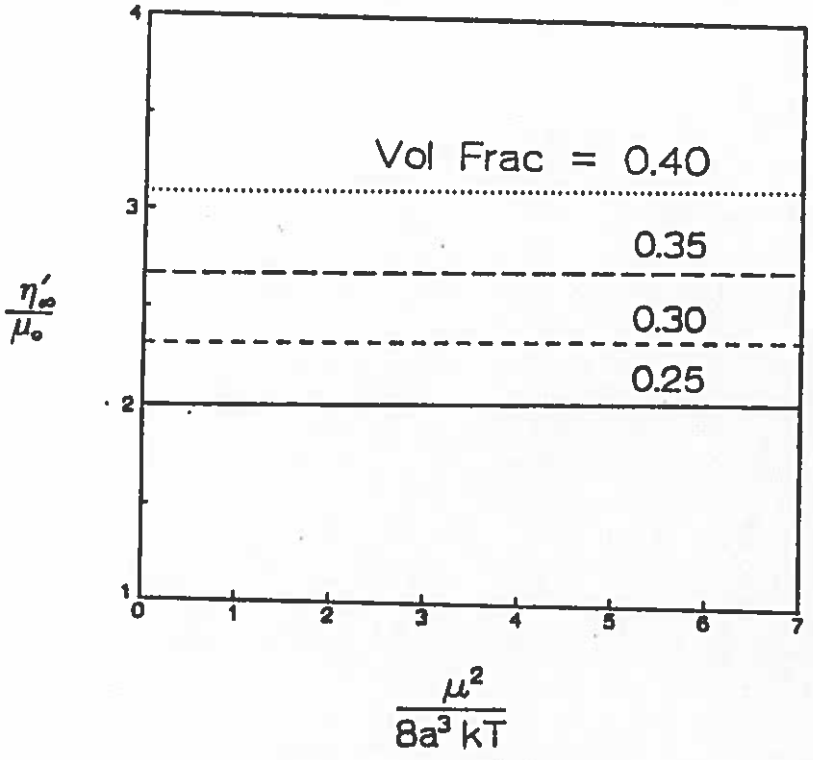


FIGURE 2

Contribution to the Polymer Colloid Group Newsletter.

The use of polymer latices as adsorbents in protein adsorption studies.

A. Elgersma, W. Norde and J. Lyklema
Agricultural University
Laboratory for Physical & Colloid Chemistry
De Dreijen 6
6703 BC Wageningen

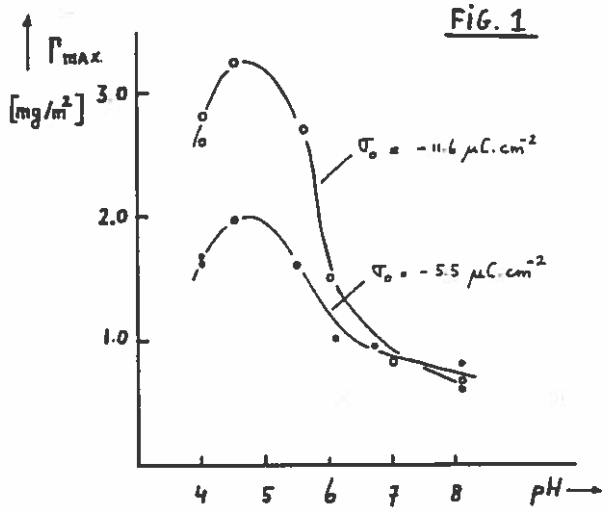
To study protein adsorption on polymeric materials, latices have great advantages compared to macroscopic surfaces. Latices are often more well-defined and due to their large specific surface area simple depletion methods can be used to determine the adsorbed amount of protein. Our method avoids marking the protein with an extrinsic label that might affect structural properties of the protein and possibly cause a different adsorption behaviour.
By adjusting the initiator and the polymerization conditions the electrochemical characteristics of the latex surface can be controlled. Thus, both negatively and positively charged latex (having a surface charge that is constant over a wide pH-range) are used for protein adsorption studies.

In fig. 1 the maximum adsorbed amount (=plateau value of the adsorption isotherm) of Bovine Serum Albumine (BSA) is plotted as a function of pH for two polystyrene latices with different surface charge densities. Around the isoelectric point (iep) of BSA, maximum adsorption takes place at both latices. This maximum adsorption is higher for the higher charged latex. Around the iep of BSA, the conformational stability of the protein is a maximum due to the zero net charge on the molecule. For pH values above the iep of BSA adsorption also occurs, although adsorbent and adsorbate have the same charge sign. At pH = 7-8 the adsorption is about the same on both latices, indicating that the surface charge is not any longer a determinating factor in BSA adsorption.

Electrokinetic measurements yield information on the colloidal stability of the latices (coated with a protein layer). Colloid stability of coated latices is, for example, of great importance for diagnostic test systems.
In fig. 2 the electrophoretic mobility (U/x) is plotted as a function of the amount of BSA adsorbed on negatively charged PS-latices at different pH-values. U/x decreases with increasing adsorbed amount. This decrease is steeper for the less negative latex and the more positive protein (lower pH).
Arrows indicate flocculation.

Currently, these experiments are extended to include adsorption of monoclonal immunoglobulins and the competition of IgG with BSA.

FIG. 1


Γmax
[mg/m²]
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2.0
1.0
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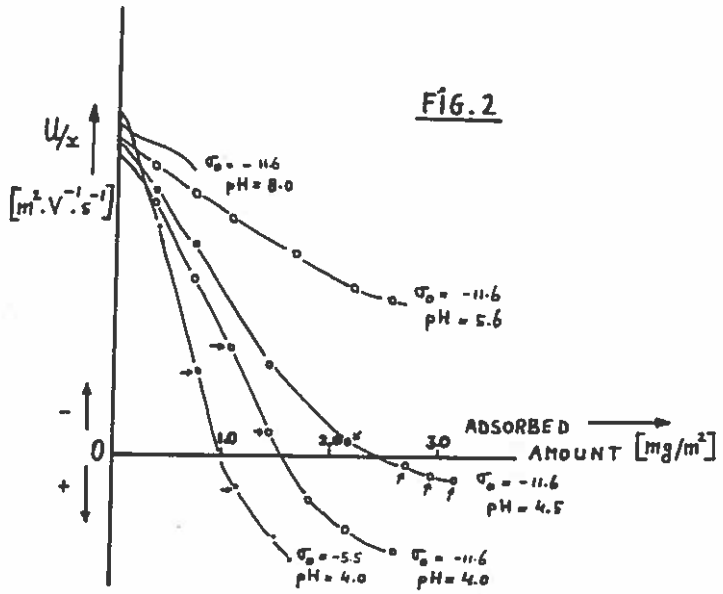
σ₀ = -5.5 μC.cm⁻²
4
5
6
7
8
pH

FIG. 2


U/x
[m².V⁻¹.s⁻¹]
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pH = 8.0
σ₀ = -11.6
pH = 5.6
-
0
+
1.0
2.0
3.0
ADSORBED AMOUNT [mg/m²]
σ₀ = -11.6
pH = 4.5
σ₀ = -5.5
pH = 4.0
σ₀ = -11.6
pH = 4.0

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POLYMER COLLOIDS AT THE UNIVERSITY OF SYDNEY

Reporter: D. H. Napper

Termination Events in Emulsion Polymerization

It has long been assumed that the free radical termination processes that occur in emulsion polymerization are identical with those operative in bulk systems. Whether or not this assumption is correct remains to be established experimentally. There are theoretical reasons why there may be differences for some monomers but these have yet to be conclusively demonstrated.

Notwithstanding the above it can be asserted unequivocally that the k_t values reported in the literature (or the *Polymer Handbook*) for low conversion bulk systems (typically in the range 10^7- 10^8 $dm^3\ mol^{-1}\ s^{-1}$) are *irrelevant* to conventional emulsion systems. The latter always contain, say, 30-50% preformed polymer and the presence of this polymer, *of necessity*, reduces the value of k_t markedly. There are, of course reports in the literature of the fitting of experimental data for emulsion systems over a wide range of conversions using the zero-polymer k_t results from bulk systems. This success in global fitting can be misleading; the models used always contain sufficient adjustable parameters to ensure that an erroneous value for k_t can be compensated for by adjusting the values of other unknown parameters.

Emulsion polymerizations provide useful systems for exploring termination processes because they can be readily switched on by γ-radiolysis of the aqueous dispersion medium. Removal of the system from the γ-ray source allows the relaxation process (often principally bimolecular termination events) to be studied directly. Such studies show, without exception, that values of k_t of order 10^2-10^5 $dm^3\ mol^{-1}\ s^{-1}$ are appropriate for emulsion systems. These are between two and six orders of magnitude smaller than the values reported for zero-polymer bulk systems.

Why are the values of k_t so small for emulsion systems? The basic reason resides, of course, in the presence of preformed polymer and the effects that this exerts on the mobility of the growing polymer chain ends. If the growing polymer chains are sufficiently entangled then their centre-of-mass diffusion is retarded or prevented almost completely. In such cases, residual termination becomes the principal termination mechanism. Residual termination is termination whereby the growing chain ends are placed in close proximity, and so can undergo termination, as a result of propagational events. Termination and propagation are thus intimately connected in most emulsion polymerization processes.

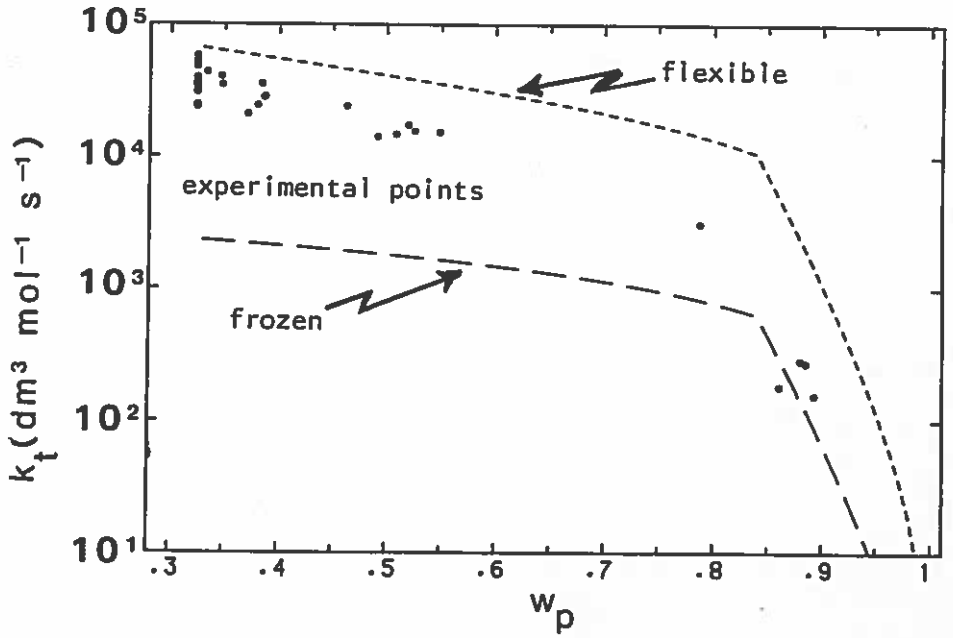
Greg Russell and Bob Gilbert have developed a simple but elegant theory to describe the upper and lower bounds for the values of k_t if residual termination is operative. Their starting point is the classical Smoluchowski theory for diffusion controlled bimolecualr termination processes Two extreme cases are envisaged dependent upon chain flexibility: the first, a lower bound, is that of the completely rigid chain; the second, an upper bound, is that of a chain end that is flexible beyond the last entanglement node. Their theory predicts that the residual termination rate coefficient should lie in the range

$$4\pi k_p C_M a^2 \sigma/3 \leq k_t(res) \leq 8\pi k_p C_M a^2\ j_c^{1/2}/3$$

where k_p = propagation rate coefficient, C_M = monomer concentration in the latex particles, a = rms end-to-end distance per square root of the number of monomer units, σ = Lennard-Jones diameter of a monomer molecule and j_c = entanglement spacing of the polymer. There are, alas, no adjustable parameters here, all parameters being experimentally determinable.

The predictions of the theory are compared with the results of experiment for the emulsion polymerization of methyl methacrylate at 50°C in the figure below. It is apparent that the experimental data for methyl methacrylate lie between the upper and lower theoretical limits. For low weight fractions of polymer (w_p), the value of k_t (res) corresponds to that predicted for a flexible chain; as w_p increases, so k_t (res) decreases until it reaches the value predicted for a frozen chain. This occurs near to the glass transition point (w_p = 0.84). Beyond that point, the value of k_t(res) drops significantly as k_p decreases. The decrease in k_t (res) thus appears to arise from three causes: first, a reduction in C_M due to consumption of monomer by polymerization; second, a decrease in the flexibility of the chain end; third, a decrease in k_p due to propagation becoming diffusion controlled. These changes in k_t(res) are presumably responsible for the observed Trommsdorff effects in emulsion polymerization of methyl methacrylate.

The theory works remarkably well for polystyrene emulsion polymerizations as well. As I reported in the last Newsletter, that system is far more complex since there is more than one bimolecular termination process operative. Mary Adams has now succeeded in unravelling these differences between styrene and methyl methacrylate.



Polymer Colloids at the University of Sydney - contd.

Pulbication List

1. I. A. Maxwell, D. H. Napper and R. G. Gilbert, J. Chem. Soc. Faraday Trans. I 83, 1449-1467 (1987)

'Emulsion Polymerization of Butyl Acrylate'

2. I. A. Penboss, R. G. Gilbert and D. H. Napper, J. Chem. Soc. Faraday Trans. I 82, 2247-2268 (1986)

'Entry Rate Coefficients in Emulsion Polymerization Systems'

3. M. J. Ballard, D. H. Napper, R. G. Gilbert and D. F. Sangster, J. Polymer Sci. A Polym. Chem. 24, 1027-1041 (1986)

'Termination Rate Coefficients in Methyl Methacrylate Polymerizations'

4. M. J. Ballard, R. G. Gilbert, D. H. Napper, P. J. Pomery, P. W. O. Sullivan and J. H. O'Donnell, Macromolecules 19, 1303 (1986)

'Propagation Rate Coefficients from ESR Studies of the Emulsion Polymerization of Methyl Methacrylate'

5. S. J. McCarthy, E. E. Elbing, I. R. Wilson, R. G. Gilbert, D. H. Napper and D. F. Sangster, Macromolecules 19, 2440 (1986)

'Seeded Heterogeneous Polymerization of Acrylonitrile'

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DEPARTMENT OF CHEMICAL ENGINEERING

J. POLYM. SC., POLY CHEM. TO APPEAR

Polystyrene and Polystyrene-butadiene Latexes Stabilized by Poly (N-isopropylacrylamide)

R. H. PELTON,* *Pulp and Paper Research Institute of Canada, 570 St. John's Blvd., Pointe Claire, Quebec, Canada H9R 3J9*

Synopsis

Latexes stabilized by poly(N-isopropylacrylamide) (polyNIPAM) were prepared by polymerizing NIPAM in the presence of polystyrene and polystyrene-butadiene latex or by styrene emulsion polymerization in the presence of NIPAM/In 0.01 *M* $CaCl_2$ polyNIPAM stabilized latexes exhibited critical flocculation temperatures in the range 32–35°C, which is approximately equal to the lower critical solution temperature of polyNIPAM in water. Partial substitution of NIPAM with some acrylamide (AM) gave higher flocculation temperatures. Coagulation studies with cleaned latex indicated that the polyNIPAM or polyNIPAM-co-AM polymer chains were anchored to the latex particle surfaces.

CENTRE NATIONAL DE LA RECHERCHE SCIENTIFIQUE

LABORATOIRE DES MATÉRIAUX ORGANIQUES

CONTRIBUTION TO POLYMER COLLOID GROUP NEWSLETTER
FROM
LABORATOIRE DES MATERIAUX ORGANIQUES (CNRS)
SUBMITTED BY C.PICHOT

1)COLLOIDAL PROPERTIES OF ZWITTERIONIC-STABILIZED POLYSTYRENE LATEXES: (C.GRAILLAT_B.DUMONT)

It was early shown that polystyrene latexes having a narrow size distribution could be prepared in a relatively large range of particle size(from 40 nm to 800 nm) when using various amphoteric sulfobetaine surfactants.With the dodecyl-dimethyl ammoniopropane sulfonate(CMC=7.3 mmole.l^{-1}), low particle size(around 40 nm) were obtained with a PSD definitively narrower than with SDS.Larger particles were obtained with the N-N dimethyl octadecylammonio-3 sulfopropylethane acetamide exhibiting lower CMC(0.018 mmole.l^{-1}).Work is currently investigated to have a better knowledge of the surface-active properties and stabilizing power of those zwitterionic surfactants.Studies are carried out to precisely examine:i)the dynamic of adsorption onto cleaned-PS latexes as a function of the type of surfactant;ii)the electrophoretic mobility and rheological behavior of the corresponding zwitterionic-stabilized PS latexes.

2)CHARACTERIZATION OF EMULSION COPOLYMER PARTICLES PREPARED IN THE PRESENCE OF A NONIONIC FUNTIONAL MONOMER. (P.CHRISTOU-C.BONARDI)

Extensive work has been recently investigated to study the location of the N-hydroxylmethyl acrylamide(NMA) in copolymer latexes of butyl acrylate with styrene or MMA and its influence on the ultimate properties of the corresponding films.Several techniques have been used to characterize the distribution of the functional monomer as a function of the conversion or the polymerization process,either directly from TEM,QELS,ESCA ,soap titration and ^{13}C NMR or undirectly through the determination of mechanical properties(under static or dynamic regimes).All the results seem to indicate that NMA (which is highly water-soluble)is slightly copolymerized but is rather fixed onto the particle surface as hydrosoluble chains(physically adsorbed or covalently-bound).

3)RECENT PUBLICATIONS AND THESIS

* Computer simulation of emulsion copolymerization processes for monomers of different water solubility.J.GUILLOT in *"Polymer Reaction Engineering"Ed. K.H.Reichert, W.Geiseler.Hütig & Wepi Verlag, 147, 1986.*

* Characterization of the particle surface and morphology in vinyl acetate-butyl acrylate emulsion copolymers-Effect of the polymerization pathway.X.Z.KONG,C.PICHOT,J.GUILLOT in *Colloid Polymer Sci.265, 1, 1987*

* Inverse emulsion polymerization of acrylamide:II-Synthesis and characterization of copolymers with methacrylic acid.V.GLUKHIKH,C.GRAILLAT,C.PICHOT in *J.Polym Sci Polym Chem Ed.25, 1127, 1987*

* Functionalization of Butyl acrylate-MMa copolymer latexes by the N-hydroxy methyl acrylamide. Thesis P.CHRISTOU- *Lyon ,July 1987*

* Functionalization of a PS latex with the bis 2 chloroethyl-itaconate. Thesis F.LEVY- *Lyon, September 1987*

Newsletter Contribution
from The University of Akron

by I. Piirma
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1. Synthesis of vinyl aclohol-vinyl gallate copolymer by Gary Jialanella (paper accepted by Polymer Bulletin)

An amphipathic copolymer was synthesized via a transesterification reaction of poly(vinyl alcohol) and methyl gallate. These copolymers exhibit unique characteristics possessed by the gallate group which can function as a chelating agent where it complexes with metal ions in solution. This ability to complex with metal ions offers some interesting and useful characteristics to the latex or dispersion stabilized with this amphipathic copolymer. Metal complexes can exhibit a variety of different colors, depending on the concentration of the components, solvents, types of solvent, pH and temperature. For example, it has been found that a solution of ferric chloride in the presence of the gallate chelating group in different conditions exhibit thermochromism and solvochromism, with color changes from yellow, orange-brown, green, blue, violet or black.

2. Emulsion Polymerization with a Mixture of Ionic and Nonionic Surfactants by Hou-Hsein Chu

This is a subject that has been studied at length by so many researchers, but it still seems to provide opportunities for further investigations. In this study a proportional relationship was developed between the total particle surface area per cm^3 aqueous solution at 90% conversion (TS) and the total amount of surfactant used in polymerization. The monomer was styrene and the reaction temperature was 50°C. Two surfactants were sodium dodecyl sulfate and tridecyloxypoly(ethyleneoxy)ethanol (Emulphogene GC-840 by GAF).

The results as expected showed different characteristic stabilization capabilities between the two single surfactant systems. Values of TS of the mixed systems correlated with the summation values of both single surfactants.

The particle sizes of the polymerizations containing only nonionic surfactant were considerably larger than those in the mixed systems, indicating that only very small amounts of ionic component is needed to provide increased stability.

It was found that with a fixed concentration (by weight) of the nonionic component in the mixed surfactant the volume average particle size decreased with increasing concentration of the ionic surfactant. With a fixed concentration of the ionic component, the volume average particle size also decreased with increasing amount of nonionic surfactant in the mixture. These results are contrary to observation made by Woods et al. (J. Paint Tech., 40, 541 (1968). Their results showed particle size increase with the addition of the nonionic component The difference in the reaction conditions and chemical structure of the surfactants makes the comparison meaningless, however, and illustrates that the particle number and size obtained in emulsion polymerization is dependent on other variables besides the concentration of the surfactant and the number of micelles it creates.

COPOLYMERIZATION IN CONTINUOUS REACTOR SYSTEMS

Richard Mead and Gary Poehlein
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Copolymerization experiments with the monomer pairs styrene-methyl acrylate and styrene-acrylonitrile have been carried out in a continuous reactor system comprised of a plug-flow tube followed by two stirred tanks (Fig. 1). One of the goals of this research was to quantify radical desorption coefficients for the copolymerization reactions and to utilize rate and molecular weight data to obtain rate constants for the cross monomer transfer reactions. Preliminary results for the styrene-methyl acrylate system are presented in this communication.

Figure 2 shows typical conversion-time profiles for each of the three reactors. Figs. 3 and 4 show particle size distributions of the effluent streams from these reactors after steady-state conversions had been reached. A steady-state reactor model can be used to fit the PSD data. The adjustable model parameter is the radical desorption coefficient. Fig.5 shows how the desorption coefficient varies with MA concentration and Fig. 6 is a 3-dimensional plot of the same data with the concentrations shown for the two monomers in the polymer particles. Radical desorption increases with the amount of methyl acrylate present as would be expected. Chain transfer to MA monomer is more rapid than to styrene and the resulting free radical should have a higher water solubility.

Molecular weight and rate data can be used to calculate rate for the cross monomer transfer reactions as shown by Rudin et al (J. Polym. Sci., Poly Chem., 17, 493 (1979); 20, 1993 (1982) and 24, 2191 (1986)). This same technique, modified for the continuous reactor system, was applied to our experimental results. The values obtained for the rate constants were:

$$k_{AB} = (1.14 \pm 0.46) \times 10^{-2} \ \ell/\text{mole-sec}$$

$$k_{BA} = (0.57 \pm 0.27) \ \ell/\text{mole-sec}$$

where k_{AB} is for the reaction between an oligomeric styrene radical and MA monomer and k_{BA} is for the other cross reaction. As a reference the normal monomer transfer constants for styrene and MA are approximately 1.2×10^{-2} and 0.068 ℓ/mole-sec respectively. The values for the cross transfer constants shown above suggest that copolymer oligomeric radicals with styrene on the radical end react at about equal rates (for the transfer reaction) with styrene and methyl acrylate. The copolymer oligomeric radical terminated by an MA radical end, however, appears to react faster with styrene than with MA.

MA radicals are more reactive than ST radicals in the propagation reactions. In the copolymerization system, this results in a small value for the fraction of active oligomeric radicals that are terminated by an MA radical. Hence the total contribution of the monomer transfer reactions with MA radicals is less than might be expected based on the values of the transfer reaction rate constant.

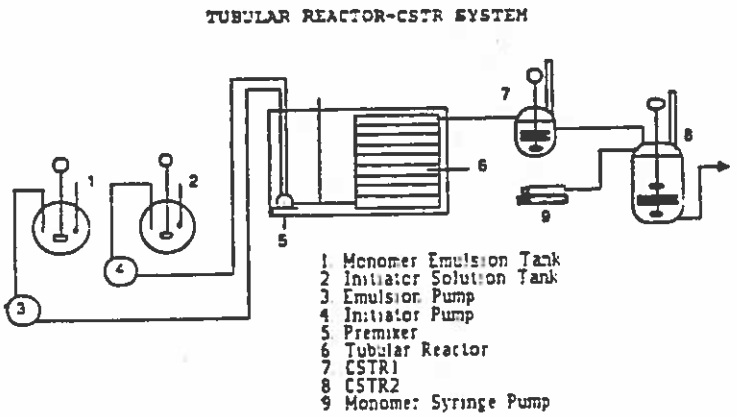


Figure 1. Experimental Continuous Reactor System Comprised of Plug-Flow Reactor and Two Continuous Stirred-Tank Reactors in Series.

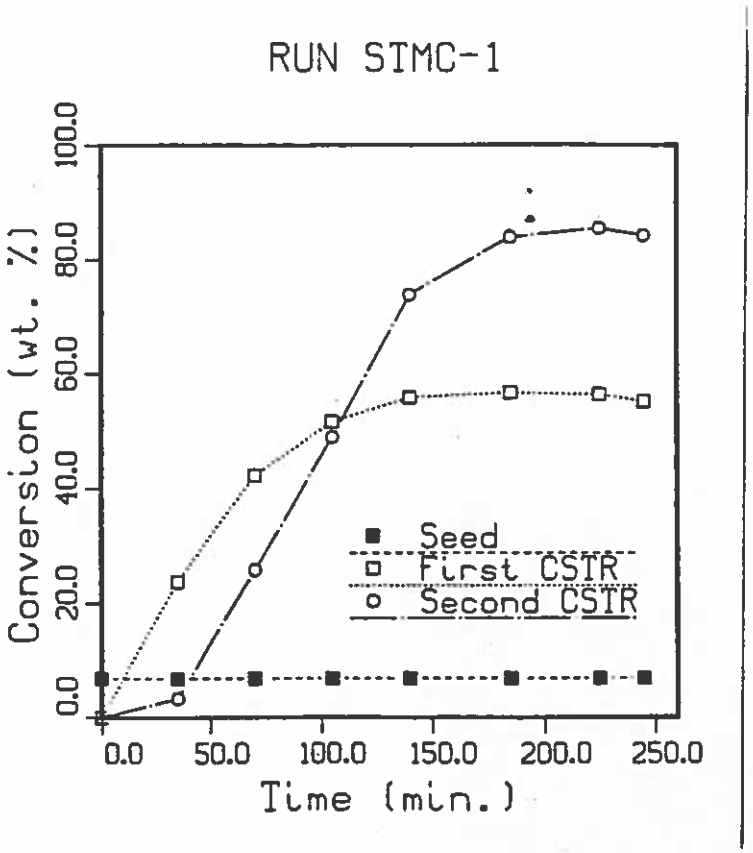
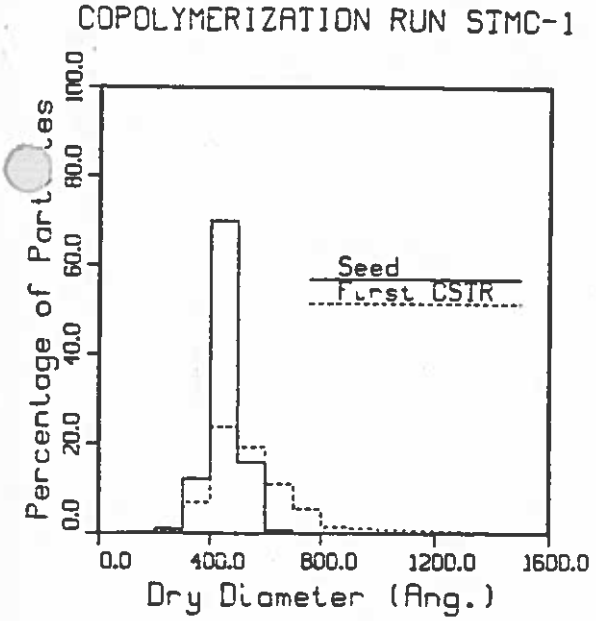


Figure 2. Conversion Transients for Styrene-Methyl Acrylate Emulsion Copolymerization Run STMC1.



ig. 3. Latex Particle Size Distributions for Seed and CSTR1 of Run STMC1.

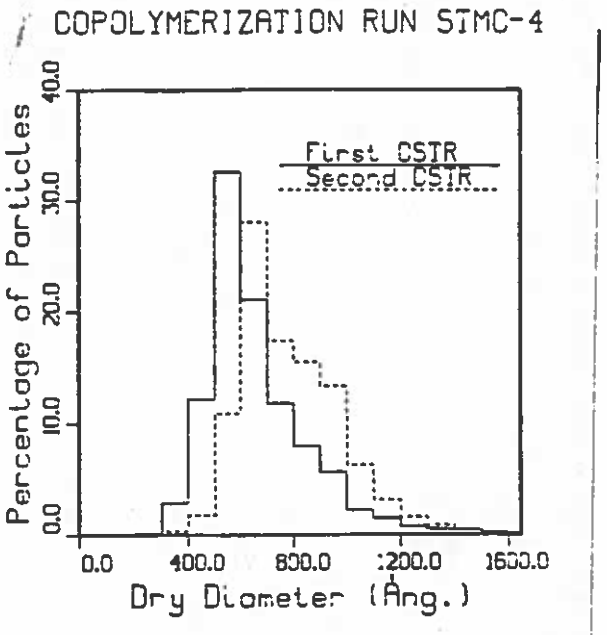
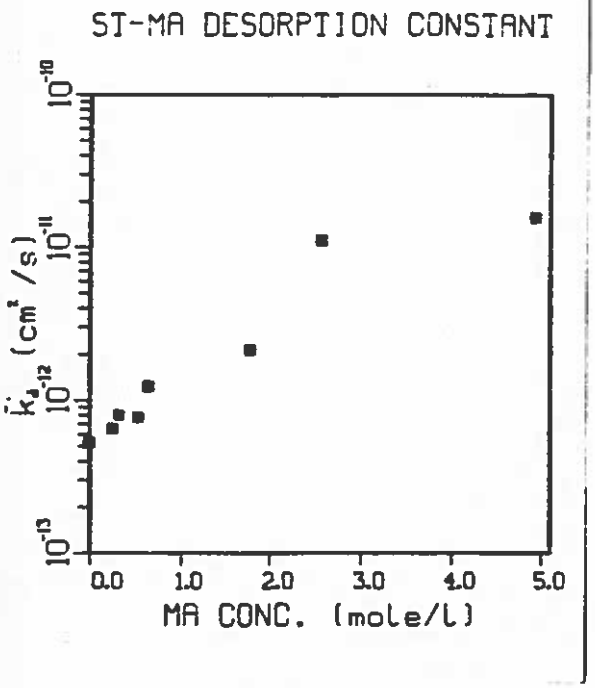


Fig. 4. Latex Particle Size Distributions for CSTR1 and CSTR2 of Run STRMC4.



ig. 5. Experimentally-Fitted Desorption Constants for Styrene-MA Emulsion Copolymerization.

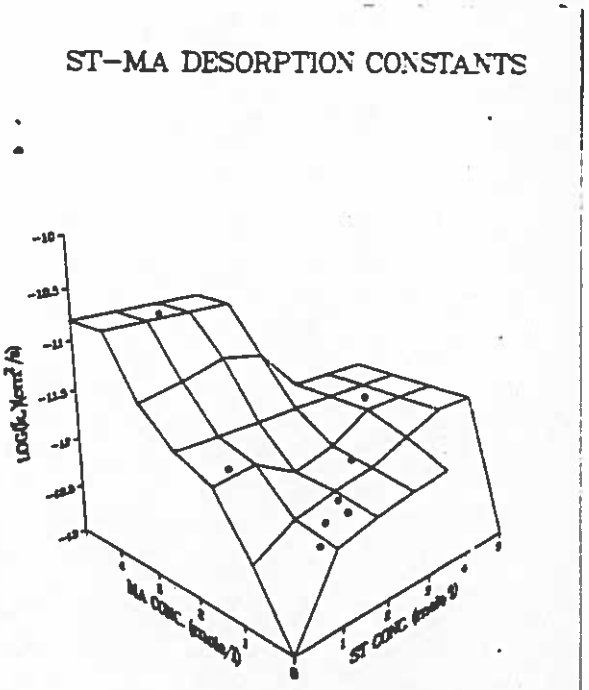


Fig. 6. Experimentally-Fitted Mean Desorption Constants for Styrene-Methyl Acrylate Emulsion Co-polymerizations.

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PCG Newsletter Contribution from R.L. Rowell

Below are abstracts of two papers presented at the ACS Meeting in New Orleans covering recent work on electrophoresis and acoustophoresis. In Bruce Marlow's work, the theory of both areas was found to be self consistent when compared on a calculated zeta potential. The paper with Anna Morfesis, we found that an appropriate grouping of the electrokinetic data could lead to an extremely sensitive electrophoretic titration which is indicative of the undisturbed surface chemistry of the particle.

198. A COMPARISON OF THE ACOUSTIC AND ELECTROPHORETIC MOBILITIES OF AN EXPANDABLE-LAYER LATEX AS A PROBE OF SURFACE SHEAR, PARTICLE HYDRODYNAMICS AND DENSITY. B.J. Marlow, Pen Kem, Inc., 341 Adams St., Bedford Hills, New York 10507, and R.L. Rowell and A. Morfesis, Department of Chemistry, University of Massachusetts, Amherst, Massachusetts 01003.

Mobility as a function of pH and ionic strength, represented by conductivity, is used to construct a three-dimensional fingerprint characteristic of the surface electrochemical properties of a dilute expandable-layer latex. The plotting techniques and error limits of the algorithm used are discussed. A critical comparison is made between the mobility-plot profile from microelectrophoresis at high dilution with acoustophoresis at 10% latex by volume. The analysis includes: (1) effect of data convolution by light scattering versus particle density, and (2) comparison with different theoretical models to show hard sphere behavior, free draining expandable-layer, and density variation at large expansion. The present work is related to previous measurements on the latex by a variety of techniques.

232. MICROELECTROPHORESIS AS A PROBE OF THE SURFACE CHEMISTRY OF AN EXPANDABLE LAYER LATEX. A.A. Morfesis* and R.L. Rowell, Department of Chemistry, University of Massachusetts, Amherst, Massachusetts 01003.

Measurements of the electrophoretic mobility of an expandable layer latex have been carried out as a function of pH and ionic strength using a Pen Kem 3000 Automated Electrokinetics Analyzer. The theory of particle microelectrophoresis is reviewed and it is shown that the grouping $6\pi\eta a u_E$ can be simply related to the total charge on the particles (η is viscosity, a is hydrodynamic radius and u_E is electrophoetic mobility). Analysis of the data was carried out using previous measurements of the dependence of particle size and viscosity on pH. The results are interpreted as an ultra-sensitive electrophoretic titration showing a major end-point and a second end-point that can be "developed" by varying the ionic strength.

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Structure of a Colloidal Dispersion under Shear (N. J. Wagner)

We have recently measured two optical properties of a hard-sphere colloidal suspension under weak shear to ascertain the non-equilibrium structure of the dispersion. This structure is generated in response to the shear deformation and is anisotropic. It is this anisotropy which is reflected in an anisotropy in the macroscopic dielectric tensor for the dispersion. As the dielectric tensor can be related to the optical properties of the dispersion, the flow induced anisotropy in the structure is detected through measurements of the flow dichroism (conservative) and birefringence.

The model system used in this study was an octadecanol coated, silica suspension grown in solution by the usual techniques[1]. This system is a known hard-sphere dispersion and can be made reasonably monodisperse. It was suspended in cyclohexane, a good solvent for the octadecanol chains on the surface. Characterization of the two samples measured in these experiments by TEM gave mean radii of 49nm and 130 nm.

The instrument used to detect the dichroism and birefringence was designed by G. Fuller[2] and Rheometrics Inc. It consists of a HeNe laser source, the beam being polarized and passed through a photoelastic modulator and a quarter wave plate sequentially. The beam is then aligned down the vorticity axis of a narrow gap couette cell. The path length through the sample is approximately one inch. The transmitted beam intensity is detectd by a photodiode, which is linked to a phase lock amplifier. The device is able to measure both the magnitude of the signal and the orientation angle, and is sensitive to one part in ten billion in detecting dichroism. This enabled us to study the materials under very weak shear deformations.

In the two figures below, the magnitude of the dichroism is plotted versus shear rate for the two samples. The 49nm sample exhibits a dichroism which is linear with shear rate, a result expected in the low shear limit as the structure is linearly related to the shear rate. By increasing the

viscous forces relative to the thermodynamic forces, the structure is dominated by the viscous forces and should become independent of shear rate. The viscous forces can be increased relative to the thermodynamic forces by either increasing the shear rate or by increasing the particle size. We observed this nonlinear dependence on shear rate for the larger, 130 nm particles. These particles are linearly dichroic with shear at low shear rates but the dichroism asymptotes out at higher shear rates. The orientation angle for the 49nm particles is 45° off the velocity vector in the plane of shear, as expected for the linear regime. The 130nm particles have an orientation angle that progresses from 45° at low shear to roughly 20° at higher shear indicating the structure tends to align with the flow.

These particles are also birefringent, the 49nm particle suspension exhibits a birefringence that is linear with shear rate and has an orientation angle of 45°. The birefringence signal is two orders of magnitude larger and is a strong function of the volume fraction of the suspension. As increasing the volume fraction in a hard-sphere suspension increases the microstucture, suspensions of higher volume fractions have a stronger birefringence.

We have also incorporated the recent theoretical work of Onuki and Doi[3] with theories for the non-equilibrium microstructure of a suspension under shear[4]. Thus we can predict the optical properties of suspensions under weak shear from basic knowledge of the interparticle forces in the suspension. We can also relate the measured values of the dichroism directly to the suspension microstructure. This is being done so the dichroism measurements can be used as a test of statistical mechanical theories for the non-equilibrium structure.

[1]A. van Helden, J. Jansen, and A. Vrij, *J. Coll. Int. Sci.*, 81, 354 (1981).

[2]P. Frattini and G. Fuller, *J. Fluid Mech.*, 168, 119 (1986).

[3]A. Onuki and M. Doi, *J. Chem. Phys.*, 85, 1190 (1986).

[4]W.B. Russel and A. Gast, *J. Chem. Phys.*, 84. 1815 (1986).

FLOW DICHROISM VERSUS SHEAR RATE

Figure 1. 49nm suspension

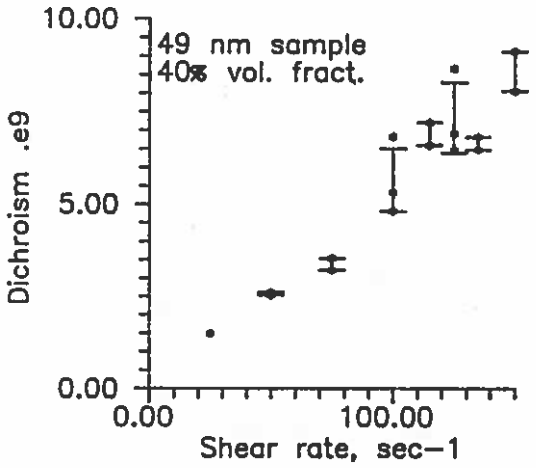
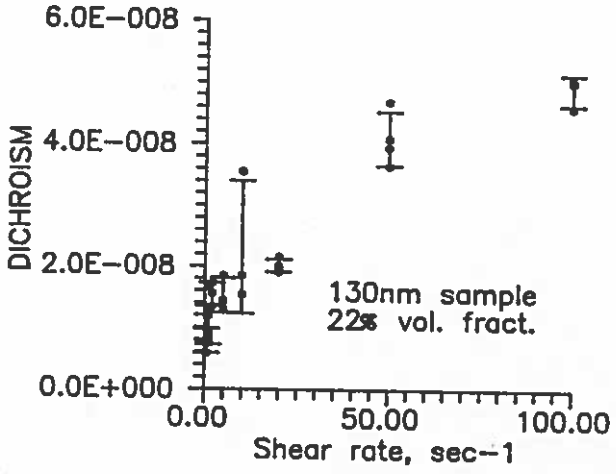


Figure 2. 130nm suspension



CONTRIBUTION TO THE POLYMER COLLOID GROUP NEWSLETTER

submitted by Per Stenius
Institute for Surface Chemistry, Stockholm, Sweden

Characterization of polymerizable surfactants

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Three different types of cationic polymerizable surfactants have been synthesized and evaluated concerning

- surface activity
- polymerization in aqueous micellar solutions/microemulsions
- stabilization and surface modification of polystyrene latex

The surfactants, being of methacrylate- or vinyl type, all show a pronounced surface activity. They form micelles in water and depending on the hydrophobic moiety, the cmc differs two orders of magnitude, 10^{-5}-10^{-3} M.

The surfactants can be polymerized in aqueous micellar solutions and in suitable cases also in microemulsions. However, the aggregation numbers in both kind of systems seem to be fairly low.

The surfactants stabilize emulsions of styrene in water, and these systems have been utilized for emulsion polymerization of polystyrene (PS). For comparison, unpolymerizable but otherwise corresponding surfactants have been evaluated as well.
In order to investigate how well the surfactant is anchored on the latex particle, the latex was washed in a serum replacement cell and the stability towards shear induced flocculation was measured as function of elution volume, figure 1. The quantity given on the X-axis (V_{out}/V_{cell}) is the total volume that passed

the cell (V_{cell}) divided by the cell volume (V_{cell} = 17 ml). As can be seen from the figure, 0.5 % unpolarizable reference surfactant is not enough in order to stabilize the latex towards shear induced flocculation. Complete <u>initial</u> stability is, on the other hand, obtained with 1 % reference surfactant. However, the stability is drastically reduced upon washing, i.e. the surfactant desorbs from the latex surface. Latex stabilized by a polymerizable surfactant exhibit a high stability even after prolonged washing. This is interpreted in terms of a permanent surface modification.

Preliminary tests show that the same results, in principal, can be obtained by first adsorbing the polymerizable surfactant on emulsier-free PS-latex and then performing a surface polymerizatio of the surfactant.

(To be presented at the ACS meeting Aug-Sept 1987 in New Orleans).

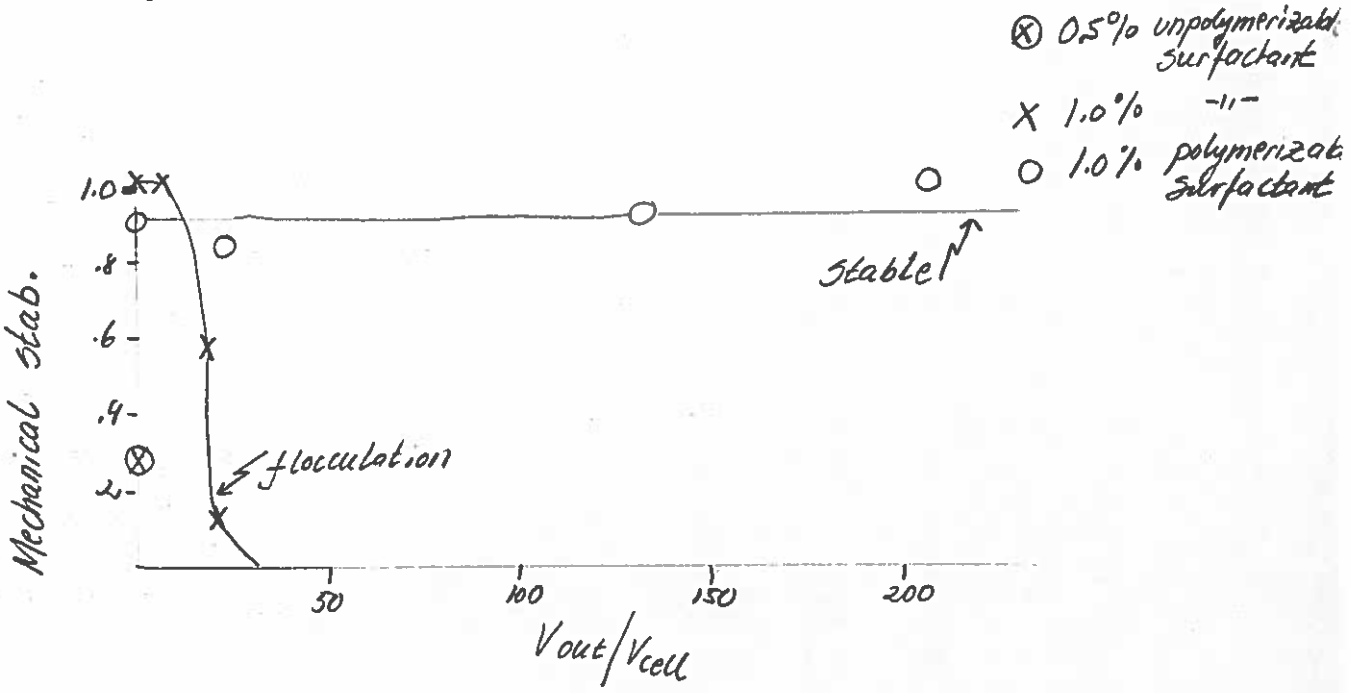

Figure 1. Stability towards shear induced flocculation (mechanical stability) of polystyrene latex as function elution volume in a serum replacement cell.

Contribution to the Polymer Colloid Newsletter submitted by A. Vrij.

DETERMINATION OF STATIC AND DYNAMIC INTERACTIONS BETWEEN MONODISPERSE, CHARGED SILICA SPHERES IN AN OPTICALLY MATCHING, ORGANIC SOLVENT.

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Abstract*

We present a light scattering study on static and dynamic interactions between monodisperse, charged silica spheres suspended in al optically matching, salt free mixture of ethanol and toluene up to volume fractions of ten per cent. The static structure factor S(K), well described by calculations in the RMSA approximation, is combined with the wave vector (K) dependent (short-time) diffusion coefficient $D_e(K)$ to give the function H(K) which represents the hydrodynamic interactions. From H(K), obtained for the first time for charged particles, we conclude that the long-range electrostatic repulsion between the spheres has a pronounced influence on the hydrodynamics of large-scale, collective particle motions, whereas small-scale single-particle diffusion is relatively unaffected.

* Chapter of the dissertation of Philipse. It will be submitted to J. Chemical Physics.

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

C. F. ZUKOSKI

Preparation of Monodisperse Silica Particles: Control of Size and Mass fraction

With G.H. Bogush and M.A. Tracy

We have extended the work of Stober, Fink and Bohn (1) to establish the ranges of reagent concentrations which result in the precipitation of monodisperse silica particles from ethanol solutions containing ammonia, water and tetraethyl orthosilicate. This work was motivated by the increasing demands for single sized oxide particles to be used as model colloids and in studies of ceramic processing technologies.

The work of Stober et al and Van Helden et al has shown that monodisperse, amorphous SiO_2 particles can be prepared using the reagents given above. -However, in these studies a limited reagent concentration range has been investigated and the results are presented in a graphical form which is difficult to read. In addition, the published recipes are limited to conditions which result in low volume fraction suspensions. This limits studies where large quantities of materials are needed. In this work we have investigated an extended range of reagent concentrations and reaction temperatures. We have also developed a seeded growth technique which can be used to prepare particles with narrow size distributions at mass fractions up to 17%.

Tetraethyl orthosilicate (TEOS) was purchased from Fisher Scientific and vacuum distilled prior to use. For each experiment the necessary amounts of ethanol, ammonium hydroxide, and deionized water (18 mega-ohm cm prepared with a Barnstead Nanopure Deionization Apparatus) were mixed in the reaction vessel and placed in a constant temperature bath. After the mixture had come to temperature, TEOS was quickly added. A series of experiments demonstrated that the final particle size and particle size distribution were not functions of the degree of agitation during the reaction.

For the seeded growth experiments, seed suspensions were prepared as described above. After the reaction had come to completion (3-8 hrs after the first addition of TEOS), TEOS and water were added to the suspension in a 1:2 mole ratio. This ratio is required as the production of one mole of SiO_2 from one mole of TEOS consumes two mole of water and produces four moles of ethanol. Additions of up to twice the number of moles of TEOS in the original recipe were repeated at 8 hour intervals for up to 10 additions.

Primarily, the effects of initial concentrations on final particle size were investigated at a reaction temperature of 25 C. Our

pproach was to hold the TEOS concentration fixed and vary the ammonia nd water concentrations in a systematic manner. The dependance of particle size on water and ammonia concentration for a TEOS concentration of 0.17 M are shown below. the TEOS concentration was varied from 0.1 to 0.5 M. Similar sets of curves as shown in Fig. 1 were found as water and NH_3 concentration were varied. All showed maxima in particle size at approximately 7 M water and 2 M ammonia. While the maximum particle size moved to higher water and ammonia concentrations as the TEOS concentration was raised, the maximum achievable size remained at approximately 800 nm for all TEOS concentrations studied.

Results gathered on over 100 sample preparations synthesized at 25° C and concentration ranges of 0.1-0.5 M TEOS, 0.5-14.0 M H_2O and 0.5-3 M NH_3 were used in the development of a correlation relating final particle size to initial reagent concentrations. The resulting expression, which has been developed to fit the experimental observations and thus contains no mechanistic information is written,

$$d = A[H_2O]^2 \exp(-B[H_2O]^{0.5}) \qquad (1)$$

with $A = [TEOS]^{0.4} (164.0 - 286.6[NH_3]^2 - 424.7[NH_3]^3)$,

and $B = 1.011 + 0.6090[NH_3] - 0.1357[NH_3]^2$,

where d is the average diameter in nanometers and the reagent concentrations are given in moles/liter. This correlation fits the data toe within about + 20% over the entire range of reagent concentrations studied. Due to the complexity of the functional dependance of particle size on reagent concentrations, a better correlation would be difficult to achieve without using an even less straight forward fitting function. However, in its present form we feel that this correlation can be useful as a predictive tool when designing reaction conditions to achieve a particular size. The curves drawn in Fig. 1 are calculated using eqn. 1. In limited experimental runs where up to 25 M H_2O were used, the correlation was found to be predictive suggesting that eqn. 1 can be used in limited extrapolations outside the range of values for which it was designed.

As a general rule, spherical particles with a narrow size distribution were achieved over the concentration ranges studied. The use of distilled TEOS was found to produce a more uniform particle morphology than using TEOS as supplied. Near the maximum achievable size for any given TEOS concentration, monodispersity was often not achieved and bimodal final particle size distributions were common.

In the range where monodispersity was achieved, we found, in agreement with van Helden et al (2), that the standard deviation expressed as a percentage of average size decreased with increasing particle size (fig. 2). Surprisingly, these results appear to follow a function which is independent of initial reagent concentrations and only dependant on final particle size.

The effect of reaction temperature on final particle properties was explored over a temperature range of 9-55 °C. Final particle

izes decreases monotonically as temperature increases (fig. 3).

While very narrow particle size distributions can be achieved with a one step process, the solids content in the resulting suspension achieves a maximum value of 3% at a TEOS concentration of 0.5M. We have found that attempts to increase weight fraction of SiO_2 by simply increasing the initial TEOS concentration results in heterodisperse particle size distributions. In order to achieve both larger particles and/or larger final mass fractions, we have developed a seeded growth technique which results in monodisperse particles at solids contents with a theoretical limit of 24%.

Seed particles were grown according to the techniques given above. The size of the seed does not influence the monodispersity of the final product and thus should be selected on the basis of the desired final size and mass fraction. TEOS and H_2O are added to the seed suspension in a 1:2 mole ratio after the seed suspension has stopped reacting. During the ensuing hydrolysis and condensation, the number of colloidally stable particles remains constant but their size increases. It was found that during seeded growth the size of the particles at the end of each addition reaction can be related to the total volume (or moles) of TEOS added to the solution by a simple expression

$$d = d_o(V/V_o)^{1/3} \qquad (2)$$

where d is the average diameter, d_o is the average diameter of the seed particles, V_o is the volume of TEOS used to produce the seed particles and V is the total moles of TEOS added to the solution (including V_o). This equation fits the experimental results very well.

The standard deviation of the particle size distribution decreases with each growth step (fig. 4) independent of the amount of TEOS added at each step. This is evident from the data in fig. 4 where in one experiment TEOS was added in increments of V_o and in a second experiment TEOS was added in increments of $2xV_o$.

These results suggest that the particle volume grows in proportion to the number of moles of TEOS added to the solution. As a result, the number of particles and the density of the particles must remain constant while they are growing. As expected for a seeded growth process, however, if the added amount of TEOS exceeds a critical value, nucleation of a second population of colloidally stable particles will occur. This critical value depends on seed size, number density and reaction temperature.

While the primary purpose of this paper has been to establish experimental conditions which result in silica particles with narrow size distribution, our studies have led us to postulate that the mechanism of particle growth is one of nucleation and aggregation which is well known to the polymer colloid community. Kinetic studies published else where (3,4) have led us to postulate that particles grow primarily through an aggregation mechanism rather than by

olecular addition. In our laboratory we are continuing to study this problem in order to establish the chemical conditions which control the rate of nucleation and stability of the particles in order to extend the technique used here to the preparation of metal oxide particles from the alkoxides of other metals.

References

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

3) Bogush, G.H., and C.F. Zukoski IV, to be published in the proceedings of the Third International Conference on Ultrastructure Processing of Ceramics, Glasses and Composites, held in San Diego, CA in February 1987.

4) Bogush, G.H., and C.F. Zukoski IV, to be published in the proceedings of Microstructures '86, held in Berkeley, CA in August 1986.

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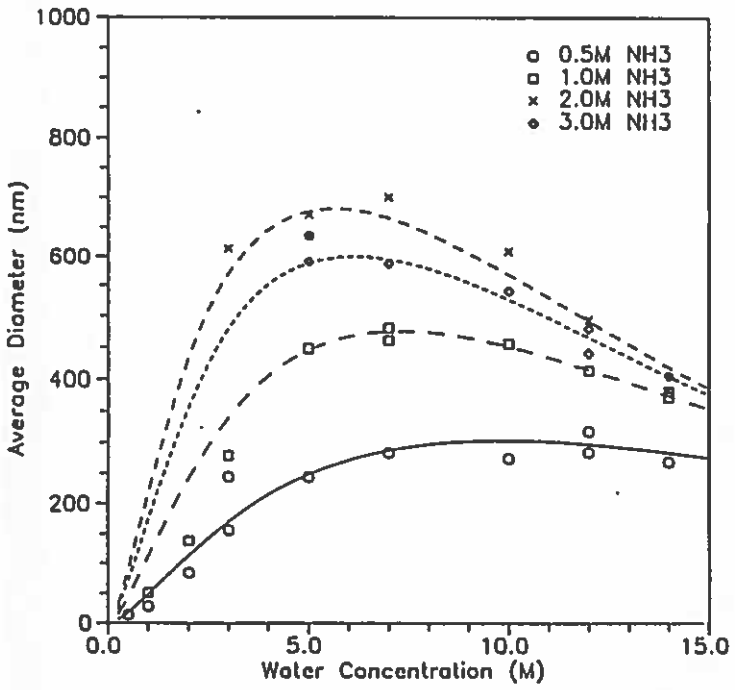


Fig. 1

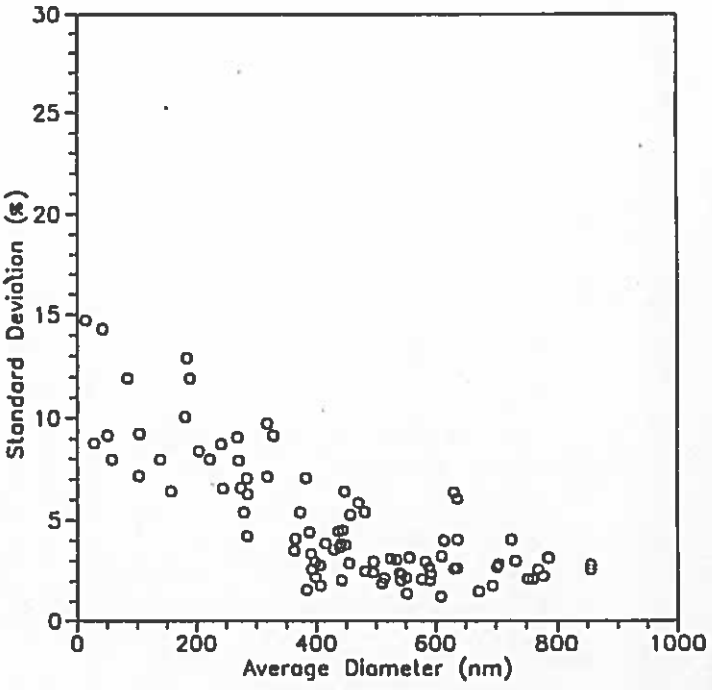
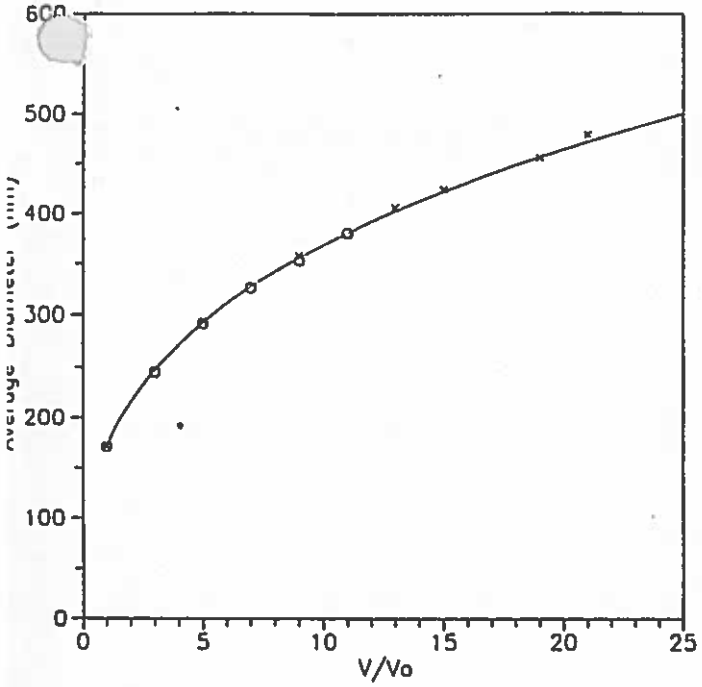


Fig. 2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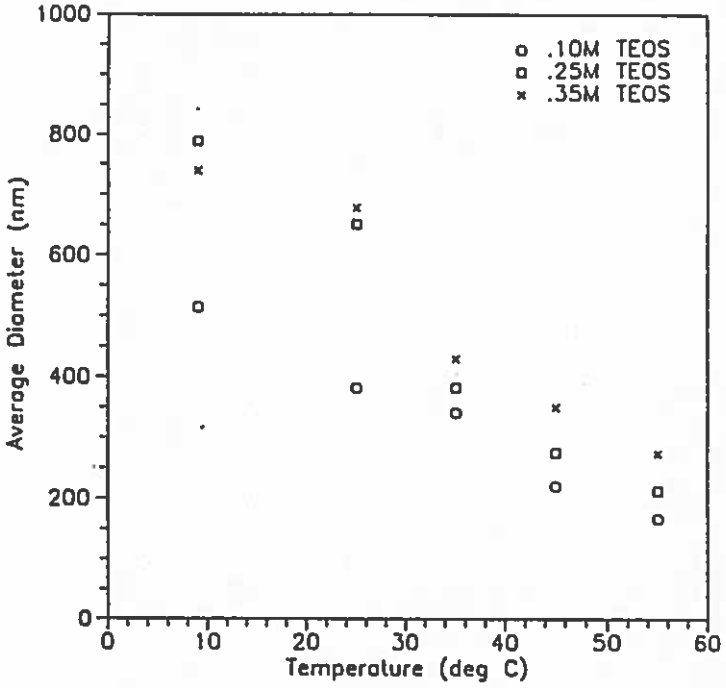
500
400
300
200
100
0
0
5
10
15
20
25
V/Vo

Fig. 3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800
600
400
200
0
Average Diameter (nm)
0
10
20
30
40
50
60
Temperature (deg C)
.10M TEOS
.25M TEOS
.35M TEOS

Fig. 4