A good time was had by all the 73 participants who were able to attend
the N.A.T.O. 'Polymer Colloids II' Advanced Study Institute in Bristol
although not all of these were able to be present for the whole time.
In addition to those present at the Annual Meeting (the minutes of which
appear on a later page) Derek Rance and Per Stenius were there for the
second week.

The 1983 Annual Meeting will take place during the Fourth Gordon Research
Conference on 'Polymer Colloids' which will be held at Tilton School,
Tilton, New Hampshire, 11-15 July 1983.  The programme will need to be
complete by early January so any suggestions should be made to the
Chairman, John Vanderhoff, or the Vice-Chairman, Ritchie Essling (at the
Dow Chemical Co., Midland, Michigan) without delay.  Intending participants
who write to Dr Alexander M. Cruickshank, Gordon Research Conferences,
Pastore Chemical Laboratory, University of Rhode Island, Kingston,
Rhode Island 12881 would receive the details as soon as these are available
although the Chairman will circulate these to Group Members.

There were 120 participants at the Plastic and Rubber Institute's
two-day 'Emulsion Polymers' Conference in London in June.  The book
containing the preprints of the 20 papers presented (excluding the Main
Lectures by Vanderhoff and Tadros) can be purchased from the P.R.I.
(11 Hobart Place, London, SW1W 0HL) for £16.

Mohamed El-Aasser is organising Special Session 2 on 'Colloid Research'
at the American Institute of Chemical Engineers 76th National Meeting,
March 27-31, 1983 at Houston, Texas.  The outline programme for the Meeting
appears in the June 1982 issue of 'Chemical Engineering Progress'.
Registration information from A.I.Ch.E. Meetings Dept., 345 E.47th St,
New York, NY 10017, Telephone (212) 705 7320.+

Ron Ottewill chairs the Organising Committee for the Royal Society of
Chemistry Faraday Division's 76th General Discussion on 'Concentrated Colloidal
Dispersions' which is to be held at Loughborough University, 14-16 September
1983.  Particle-particle interactions will provide the main theme.  Details
will be available in due course from Mrs Y.A.Fish, The Royal Society of
Chemistry, Burlington House, London, W1V 0BN.

Some members of the Group attended a Symposium on Emulsion Polymerisation
held in Leipzig, East Germany in 1980.  The papers presented appear in
English, German, or Russian in Acta Polymerica (formerly 'Faserforschung und
Textiltechnik')32 (1981) [7 & 10].  A further Symposium is likely to be held
there in the autumn of 1984.

A meeting on emulsion copolymerisation under the auspices of the
C.N.R.S. is to be held in France in March or April 1984.

The detailed programme for the 2nd Polymer Microspheres Symposium
Japan appears as Nomura's contribution to this Newsletter.

+The detailed programme for the Special Session appears on a page
preceeding Members' contributions

MINUTES of the ANNUAL BUSINESS MEETING of the POLYMER COLLOID GROUP held on Wednesday 30th June 1982 at 8.15 p.m. in the T.V. Lounge of Hiatt Baker Hall, Bristol.

Present: D.R.Bassett, D.C.Blackley, A.S.Dunn, M.S.El-Aasser, R.M.Fitch, J.W.Goodwin, A.E.Hamielec, I.M.Krieger, R.H.Ottewill, I.Piirma, G.W.Poehlein, R.L.Rowell, J.Stone-Masui and A Watillon, J.W.Vanderhoff, T.G M. van de Ven. H.Kawaguchi represented M. Nomura (17)

Future arrangements. The next meeting would be held during the 4th Gordon Research Conference on Polymer Colloids which was scheduled for Tilton School, New Hampshire, July 11-15, 1983 with John Vanderhoff as Chairman and Ritchie Wessling as Vice-Chairman.

Mohamed El-Aasser drew attention to the Polymer Colloid Symposium which was to be held during the A.I.Ch.E. Meeting at Houston, Texas 27-31 March, 1983 and Haruma Kawaguchi said that John Ugelstad and Alan Rembaum were to be the guest speakers at the '2nd Polymer Microspheres Symposium, Japan' which was to be held at Fukui, 11-13 November 1982. Offers of Short Contributions in English from any Group members able to be present would be welcome. A Symposium on Emulsion Copolymerisation was to be held in France in July 1984 under the auspices of the C.N.R.S.

Theo van de Ven was asked to look into the possibility of holding a future meeting of the Group in Canada possibly in conjunction with the Canadian Polymer Forum.

Membership. A Vrij (University of Utrecht) and Alan Rembaum were elected to membership. It was agreed that the C.N.R.S. group should be represented and Mohamed El-Aasser subsequently ascertained that Christian Pichot would be the representitive. W.A.B.Donnors of D.S.M. had expressed interest in membership but election was deferred until after the 1983 Gordon Conference which he would be invited to attend. As agreed last year John Vanderhoff would now approach Gerhard Reinisch. Goren has now left the N.S.F. and it was agreed that his associate membership and that of David Williams should now be terminated.

Members expressed their thanks to Ron Ottewill and Jim Goodwin for the excellence of the arrangements they had made for the meeting in Bristol.

The meeting closed at 9.20 p.m.


CHANGE OF ADDRESS:

Professor C.-C. Lin has moved from Taiwan to:
Division of Chemical Engineering, New Jersey Institute of Technology,
323 High Street, Newark, New Jersey 07102, U.S.A.
Telephone: (201) 645-5410.

<u>List of Members of the Polymer Colloid Group</u>

(Revised July 1982)

<u>North American Circulation</u> (21)

1. Dr P  Bagchi, Research Department, Eastman Kodak Co , Chemical Division,
   Kodak Park B-31, Rochester, N.Y. 14650, U.S.A.

2. Dr D.R.Bassett, Technical Center 120-130, Union Carbide Corporation,
   South Charleston, West Virginia 25303, U.S.A.

3. Dr E.A.Collins, Diamond Shamrock Corp., P.O. Box 343, Painesville, Ohio 44077, U.S.A.

4. Dr M.S.El-Aasser, Department of Chemical Engineering, Whitaker Laboratory No.5,
   Lehigh University, Bethlehem, Pennsylvania 18015, U.S.A.

5. Dr R.M.Fitch, Department of Materials Science, University of Connecticut,
   Storrs, Connecticut 06268, U.S.A.

6. Dr J.S.Dodge, B.F.Goodrich Co., Chemical Division Technical Center,
   Avon Lake, Ohio 44012, U.S.A.

7. Dr A.E.Hamielec, Department of Chemical Engineering, McMaster University,
   Hamilton, Ontario, Canada L3S 4M1.

8. Dr A. Klein, Department of Chemical Engineering, Whitaker Laboratory No.5,
   Lehigh University, Bethlehem, Pennsylvania 18015, U.S.A.

9. Dr I.M.Krieger, Olin Building, Case-Western Reserve University, Cleveland,
   Ohio 44106, U S.A.

10  Dr C.-C. Lin, Division of Chemical Engineering, Department of Chemical Engineering &
    Chemistry, New Jersey Institute of Technology, 323 High Street,
    Newark, New Jersey 07102, U.S.A.

11. Dr S.G.Mason, Department of Chemistry, McGill University, P.O. Box 6070,
    Montreal, PQ, Canada, H A 2A7

12. Dr I. Piirma, Institute of Polymer Science, University of Akron,
    Akron, Ohio 44325, U.S.A.

13. Dr J.L.Gardon, Sherwin-Williams Co., 11541 South Champlain Avenue,
    Chicago, Illinois 60623, U.S.A.

14. Dr G.W Poehlein, School of Chemical Engineering, Georgia Institute of Technology,
    Atlanta, Georgia 30332, U.S.A.

15. Dr A  Rembaum, Jet Propulsion Laboratory, California Institute of Technology,
    4800 Oak Grove Drive, Pasadena, California 91103, U.S.A.

16 Dr A.A.Robertson, Pulp and Paper Building, Department of Chemistry, ~~Resigned~~ 9/11/82
   McGill University, 3420 University Street, Montreal PQ, Canada H A 2A7.

17. Dr R.L.Rowell, Department of Chemistry, University of Massachusetts,
    Amherst, Massachusetts 01003, U S A.

18  Dr F L.Saunders, Dow Chemical Co , Central Research, 1712 Building,
    Midland, Michigan 48640, U.S.A.

19  Dr V.T.Stannett, Department of Chemical Engineering, Box 5035,
    North Carolina State University, Raleigh, North Carolina 27607, U.S.A.

20  Dr J.W Vanderhoff, Emulsion Polymers Institute, Sinclair Laboratory No 7,
    Lehigh University, Bethlehem, Pennsylvania 18015, U.S.A.

21. Dr T G.M. van de Ven, Pulp and Paper Building, Department of Chemistry,
    McGill University, 3420 University Street, Montreal PQ, Canada H3A 2A7.

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

23. Dr A.S.Dunn, Department of Chemistry, UMIST, P.O.Box 88, Manchester, M60 1QD, England

24. Dr J.W.Goodwin, School of Chemistry, University of Bristol, Cantock's Close,
Bristol, BS8 1TS, England.

25. Dr F.K.Hansen, Dyno Industrier A/S, Lillestrøm Fabrikker, Svelleveien,
P.O.Box 160, 2001 Lillestrøm, Norway.

26. Dr N. Furlong, Department of Physical Chemistry, University of Melbourne,
Parkville, Victoria 3052, Australia.

27. Dr D.H.Napper, Department of Physical Chemistry, The University of Sydney,
Sydney, New South Wales 2006, Australia.

28. Dr S Muroi, New Product Developing Laboratory, Asahi Chemical Industry Co Ltd.,
2-1 Samejima, Fuji-City, Shizuoka, Japan.

29. Dr M. Nomura, Department of Industrial Chemistry, Fukui National University,
Fukui, Japan.

30. Dr R.H.Ottewill, School of Chemistry, University of Bristol, Cantock's Close,
Bristol, BS8 1TS, England..

31. Dr C. Pichot, C.N.R.S. Laboratoire des Materiaux Organiques, B.P. 24,
69390 Vernaison, France.

32. Dr D.G.Rance, I.C.I. plc, Petrochemicals and Plastics Division, P.O. Box 6,
Welwyn Garden City, Hertfordshire, AL7 1HD, England.

33. Dr P.J.Stenius, The Swedish Institute for Surface Chemistry,
Drottning Kristinas väg 45, S-114 28, Stockholm, Sweden.

34. Dr J. Ugelstad, Institutt for Industriell Kjemi, Norges Tekniske Høgskole,
7034 Trondheim-NTH, Norway.

35. Dr A. Vrij, Rijksuniversieit Utrecht, van't Hoff Laboratorium, Padualaan 8, *Postbus 80.051*
*3508 TB* Utrecht ~~2506~~, Holland.

36. Dr A. Watillon, Universite Libre de Bruxelles, Service de Chemie Analytique
et Minerale, 50 av F.D.Roosevelt, Bruxelles 5, Belgium.

37. Dr V.I.Yeliseyeva, Institute of Physical
Chemistry, Academy of Sciences of the
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117312 Moscow, U.S.S.R.

117312, МОСКВА,
Ленинский пр.; 31, Институт физическо
химии АН СССР,
проф. ЕЛИСЕЕВОЙ В. И.
СССР

# POLYMER COLLOID GROUP

## Rules

The Polymer Colloid Group was founded at a meeting at Lehigh University on 27 September 1931 at which Bob Fitch (Connecticut), Irv Krieger (Case), 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) were present. They decided to invite a further six academics to join the Group. The Group's first Microsymposium was held at Lehigh in June 1972 when 9 members accompanied by 9 of their research students attended. A second Microsymposium at which 17 papers were presented was held at Lehigh in June 1973: industrial scientists interested in the field were invited to this meeting and 4 attended with 8 Group members and 10 students. A third Microsymposium was held at Bristol in 1974. Most subsequent meetings have been held in conjunction with larger Symposia arranged in accordance with the procedures of a sponsoring body which was able to provide some finance for the meeting. Thus the Group met during the first N.A.T.O. Advanced Study Institute on 'Polymer Colloids' at Trondheim in 1975, in 1977 at the first Gordon Research Conference on 'Polymer Colloids' at Holderness School. Polymer Colloid Gordon Conferences have subsequently been held biennially in 1979 and 1931 with a fourth planned for 1933, all at Tilton School, New Hampshire. The 1978 meeting was in conjunction with the 'Polymer Colloids II' Symposium held by the A.C.S. Division of Colloid and Surface Chemistry 'Polymer Colloids II' Symposium held during the Fall National Meeting at Miami Beach, the 1980 meeting preceeded the 54th A.C.S. Colloid and Surface Science Symposium held at Lehigh, and the 1932 meeting in Bristol was during the second N.A.T.O. 'Polymer Colloids' A.S.I. The Group now has 37 members, 18 in U.S.A., 3 in Canada, 4 in England, 7 in the rest of Europe (including 1 in the U.S.S.R.), 2 in Australia, and 2 in Japan.

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

Members keep in touch by attending the Annual Meeting whenever possible and through the Newsletter which is circulated twice a year in May and October. 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 contribute to the Newsletter whenever possible. Newsletter contributions should be typed single-spaced on A4 (21 x 30 cm) paper suitable 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 should circulate the Newsletter within their own research group and may reproduce copies to facilitate this if need be. Items appearing in the Newsletter which have not subsequently been published 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 which they have published during the preceeding 6 months in their Newsletter contributions, and circulate preprints or reprints when they have sufficient copies available.

Special Symposium on "Polymer Colloids"

76th AIChE Meeting, Houston, Texas

March 27-31, 1983

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Program Coordinator:  Mohamed S. El-Aasser (Lehigh University)

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1st Session:  "Kinetics Aspects and Reactor Engineering"

Session Chairman:  Dr. Gary W. Poehlein (Georgia Tech.)

1.  "Kinetics of Seeded Emulsion Polymerization of Styrene Under Batch and Continuous Monomer Addition Conditions"

    Che-I-Kao, The Dow Chemical Co., Midland, Michigan

2.  "Performance of a Tubular Pre-Reactor in Continuous Emulsion Polymerization of Styrene"

    Mamoru Nomura, Nguyen-Dinh-Binh, and Kajumi Fujita, Fukui University, Fukui, Japan and Makota Harada, Atomic Energy Institute, Kyoto University, Uji, Japan

3.  "Reaction Kinetics Within Two-Phase Emulsion Particles"

    Daniel Nelson, Fiber Materials, Inc., Biddeford, ME and Donald C. Sundberg, University of New Hampshire, Durham, NH

4.  "Emulsion Polymerization in a Seed-Fed Continuous Stirred-Tank Reactor"

    Gary W. Poehlein, H. C. Lee and W. Dubner, Georgia Institute of Tech., Atlanta, GA

5.  "Kinetics and Mechanism of Emulsion Copolymerization of Styrene and Methyl Methacrylate"

    Mamoru Nomura, Ichiro Horie, Masayuki Kubo and Kazumi, Fukui University, Fukui, Japan and Makoto Harada, Atomic Energy Institute, Kyota University, Uji, Japan

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2nd Session:  "Interfacial Aspects of Polymer Colloids"

Session Chairman:  Dr. Pranab Bagchi

1.  "Characterization of Acrylamide Modified Ethyl Acrylate Latexes by $^{13}C$ NMR Spectroscopy"

    Dr. C. J. McDonald, Dow Chemical Co., Midland, MI

## 2nd Session: (Continued)

2. "Colloidal Systems for Biomedical Research"

   A. Rembaum, California Institute of Technology, Pasadena, CA

3. "Effect of Pressure on the Steric Stabilization of Nonaqueous Dispersions"

   M. D. Croucher, Xerox Research Centre of Canada, Canada

4. "Interfacial Aspects of Polymer Colloids"

   R. M. Fitch, University of Connecticut, Storres, CT

5. "Neutron Scattering from Interfacially Polymerized Core-Shell Latexes"

   L. W. Fisher, S. M. Melpolder, J. M. O'Reilly, G. D. Wignall, Eastman Kodak Company, Rochester, NY

6. "Interfacial Aspects of Mini-Emulsions and Mini-Emulsion Polymers"

   T. I. Min, M. S. El-Aasser, W. L. Grimm, Y. T. Choi, C. Lack, J. W. Vanderhoff, Lehigh University, Bethlehem, PA

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## 3rd Session: "Colloid Aspects"

Session Chairman: Dr. Mohamed S. El-Aasser

1. "Effects of Agitation, and the Nature of Protective Colloid on Particle Size during Suspension Polymerization"

   S. M. Ahmed, Hercules, Inc., Wilmington, DE

2. "Rheology and Particle Interaction of Thickened Latexes"

   J. T. Lin, M. S. El-Aasser, C. A. Silebi, and J. W. Vanderhoff, Lehigh University, Bethlehem, PA

3. "Control of Surface and Structural Properties in (MMA-Acrylate) Emulsion Terpolymers"

   B. Emelie, C. Pichot, J. Guillot, CNRS, Laboratoire, Vernaison, France

4. "The Influence of Colloid Stability Critical Pigment Volume Concentration "CPVC""

   A. I. Ranka, M. S. El-Aasser, and J. W. Vanderhoff, Lehigh University, Bethlehem, PA

5. "Continuous Emulsion Polymerization - Design and Operation of a Production systems for Poly(vinyl acetate) and Poly(styrene-butadiene) latexes

   A. E. Hamielec, T. W. Hoffman and J. F. MacGregor, McMaster University, Hamilton, Ontario, CANADA

4th Session: "Process vs. Properties"

Session Chairman: Dr. Gordon P. Beirwagen

1. "Preparation and Application of Monodisperse Polymer Particles"

   John Ugelstad, Elias Soleimany, University of Trondheim, Trondheim, Norway and Turid Ellingsen, Arvid Berge, SINTEF, Trondheim, Norway

2. "Core-Shell Emulsion Copolymerization of Styrene Acrylonitrile on Polystyrene Seed Particles"

   Victoria Dimonie, M. S. El-Aasser, A. Klein and J. W. Vanderhoff, Lehigh University, Bethlehem, PA

3. "Reactive Microgels by Emulsion Polymerization of Unsaturated Polyesters and Styrene"

   Dr. W. Funke, University of Stuttgart, Stuttgart, Germany

4. "Grafting of Styrene onto Poly(butadiene) Latices in Batch and Semi-Continuous Reactors"

   Donald C. Sundberg, University of New Hampshire, Durham, NH, Ming-Ya Tang, University of Tennessee, Knoxville, TN and Joseph Arndt, Crown-Zellerbach, Vancuver, WA

5. "Influence of Hydrocolloids on Particle Size Distribution in Suspension Polymerization"

   J. E. Glass, North Dakota State University, Fargo, ND and J. W. Field, Georgia Pacific Company

6. "Properties vs. Process in the Synthesis and Use of Pigmented Suspension Polymer Particles"

   T. K. Rehfeldt, G. P. Bierwagen, M. I. Karickhoff, B. K. Kerr, The Sherwin-Williams Company, Chicago, IL

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5th Session: "Polymer Colloids - Process Development"

Session Chairman: Dr. John W. Vanderhoff

1. "Preparation of Large-particle-size latex in Space: Polymerization Kinetics and Process Development"

   J. W. Vanderhoff, M. S. El-Aasser, F. J. Micale, E. David Sudol, C. M. Tseng, A. Silwanowicz, Lehigh University, Bethlehem, PA and F. A. Vicente, General Electric Space Science Laboratory, Valley Forge, PA and D. M. Kornfeld, MSFC, Alabama

2. "Nucleation in Vinyl Acetate Polymerization"

   Igor Aksman and Kirk Abbey, SCM Corporation, Strongsville, Ohio

## 5th Session (Continued)

3.  "Structure Properties relationships in Acrylonitrile/Acrylate Emulsion Copolymers"

    B. Rocchetti, J. Guillot and A. Guyot, CNRS Laboratoire, Vernaison, France

4.  "Seeded Semi-Continuous Emulsion Co-polymerization of 80:20 Vinyl Acetate-Butylacrylate"

    T. Makgawinata, M. S. El-Aasser, A. Klein and J. W. Vanderhoff, Lehigh University, Bethlehem, PA

5.  "Inverse Emulsion Polymerization: Polymerization Kinetics, Emulsion Stability, and Process Development"

    F. DiStefano, R. O'Leary, D. Visioli, M. S. El-Aasser and J. W. Vanderhoff, Lehigh University, Bethlehem, PA

Registration information from:

A.I.Ch.E. Meetings Dept., 345 E. 47th St., New York, N.Y. 10017.

Telephone (212) 705 7320

# BEHAVIOUR OF POLYVINYLMETHYL ETHER IN POLYMER LATICES

D. C. Blackley, London School of Polymer Technology, The Polytechnic of North London, Holloway, London N7 3DB.

Polyvinylmethyl ether has been used for a number of years as a heat-sensitiser for natural rubber latex. Natural rubber latex which contains small amounts of this substance is colloidally stable at room temperature, although the viscosity of the latex tends to increase gradually during storage. However, on raising the temperature of the latex, it rapidly sets to a firm gel if the conditions of pH and zinc-ion concentration have been adjusted appropriately. Although the details of the mechanism whereby polyvinylmethyl ether heat-sensitises natural rubber latex are not known, it is generally assumed that the mechanism is in some way associated with the unusual solubility behaviour of polyvinylmethyl ether in water; although readily soluble in cold water, this substance is insoluble at temperatures above ca. $33^{\circ}C$, and so aqueous solutions show a cloud-point phenomenon when the temperature is raised. Modified polyvinylmethyl ethers have also been used to a limited extent as chemical agglomerants for synthetic rubber latices, but it is doubtful whether they are being used for this purpose at present.

Because of industrial interest in the heat-sensitisation of latices by polyvinylmethyl ether, we have recently completed a detailed investigation of its behaviour in natural and synthetic latices. Certain aspects of this investigation have confirmed in greater detail what was already known. Thus, for instance, we have confirmed that the heat-sensitivity of natural rubber latex containing polyvinylmethyl ether increases sharply as the pH of the latex is reduced from ca. 10 down towards neutrality, and that the pH at which the latex becomes strongly heat-sensitive depends upon whether or not the latex compound contains a sparingly-soluble zinc compound such as zinc oxide – the transition occurs at higher pH if zinc oxide is present than if it is absent. However, in addition to confirming facts already known, we have also obtained much information which is new. This new information pertains to the effects of variables such as

a) time of maturation of the latex compound
b) level of zinc oxide
c) level of polyvinylmethyl ether
d) volume fraction of rubber in the latex
e) addition of inorganic electrolytes
f) addition of soaps and surfactants
g) molecular weight of polyvinylmethyl ether.

All the observations we have made are broadly consistent with a heat-sensitising mechanism in which the polyvinylmethyl ether becomes adsorbed at any vacant site on the surface of the rubber particles, functions as a steric stabiliser at normal temperatures, but becomes ineffective when the temperature is raised. The mechanism by which the gelation itself occurs may well be through inter-particle bridging of the rubber particles by the adsorbed polyvinylmethyl ether molecules, these adsorbed molecules being no longer able to function as steric stabilisers. This is certainly consistent with the observation that very strong gels can be formed from latices which contain very small amounts of the heat-sensitiser. Reduction of the pH and the presence of zinc ions both encourage heat-sensitivity because they partially remove adsorbed soap anions and therefore make additional sites available for the adsorption of the polyvinylmethyl ether. We have established that the heat-sensitivity at a given pH increases with the amount of zinc oxide present in the latex, until the solubility limit of zinc oxide in the latex is reached. Further additions of zinc oxide have little effect upon heat-sensitivity. A particularly interesting and significant observation is that, whereas the molecular weight of the polyvinylmethyl ether has little effect upon the cloud-point temperature of the polymer in aqueous solution, it has a marked effect upon heat-

sensitivity: the higher the molecular weight of the polyvinylmethyl ether, the more effective it is as a heat-sensitiser under any given conditions. These observations seem to be inconsistent with the older view of the mechanism of heat-sensitisation by polyvinylmethyl ether, namely, that gelation of the rubber occurs because the rubber particles become mechanically entrapped in a precipitate of polyvinylmethyl ether which forms in the aqueous phase of the latex.

We have also made some investigation of the behaviour of polyvinylmethyl ether in synthetic latices. It appears that, in general, synthetic rubber latices are not susceptible to heat-sensitisation by polyvinylmethyl ether in the same way that natural rubber latex is. However, we have observed that polystyrene latices made by conventional emulsion polymerisation do undergo marked increases in viscosity at ambient temperatures when polyvinylmethyl ether is added to them. Presumably this effect is of similar origin to that of the heat-sensitising effect in natural rubber latex. We have investigated the effects of some of the variables listed above upon the ability of polyvinylmethyl ether to increase the viscosity of polystyrene latex. We have also been able to investigate to a limited extent the effect of two other variables, namely, soap coverage of the particles and particle size.

<u>Dr A. S. Dunn - Chemistry Department</u>

Rusli bin Abdul Ghani (i.e. Rusli son of Abd. Ghani) of the University of
Malaysia who has been working here for the last three years has just
finished writing his Ph.D thesis which is concerned with the further
characterisation of polyvinyl alcohol in respect to its application
in the emulsion polymerisation of vinyl acetate. His summary is
reproduced below. The thesis should be available for inter-library loan
from the UMIST Library from March 1933 or thereby. A Xerox copy could be
supplied to anyone willing to pay the cost of reproduction and postage
which will be about £10 but it would be helpful if anyone who wants a
copy would order it by mid-November.

"Variability in the results of the application of commercial grade
poly(vinyl alcohol acetate), PV-OH-OAc, as an emulsifier of poly(vinyl acetate),
PVOAc, latex has persisted for more than 30 years. The variability
concerning the viscosity of the latexes produced from two comparable
specimens, GH-17 (sample of 'Gohsenol' from Nippon Synthetic Chemical
Co., Japan) and Sample B which has recently been disclosed as Chang
Chun CP 17 H (manufactured in Taiwan), which fall into the same grade,
has been studied previously. Previous structural studies indicated that
they are the same in most respects except the extent of short-chain
branching, SCB, which might have caused the difference in the viscosity
of latexes obtained using them. It has been claimed that characterisation
based on acetyl content, -OAc, (specified to be within a range of 2 mole
per cent) and molecular weight, $MW$, (as indicated by the viscosity of 4% w/v
aqueous solution specified within a range of 2 and 10 cP) is not adequate to
define the properties of PV-OH-OAc. In the present work characterisation
using the iodine complex, IC, which is simple was tried on these samples and
with the help of further structural studies on these samples the possibility
of using this method as a further criterion for the specification of PV-OH-OAc
has been clarified. The behaviour of these samples at the solid liquid
interface (adsorption isotherms) has also been examined which may help to
explain the difference in latex viscosities using them as emulsifiers.
To elucidate the effect of $MW$ on latex viscosity a series of samples of
'Gohsenol' from Nippon Synthetic Chemical Co., Japan, which were assumed to
have the same structure except $MW$ were used as emulsifiers in latex
preparation by batch emulsion polymerisation using $H_2O_2$-tartaric acid as the
initiation system and latex viscosities were measured using the Brookfield
viscometer. Particle diameters $D_s$, $D_w$, and $D_s D_w$ (an indication of particle
size distribution) of these latexes were determined by a light scattering
method to see if $D_s$, $D_w$, and $D_s/D_w$ were affected by $MW$ and hence affected
the viscosity. Hydrodynamic thicknesses of GH-17's and Sample B's layers
on the latex particles were calculated using the values of their $D_w$ and
their hydrodynamic diameters determined by Nicholson, to see if this can
explain the difference in latex viscosities. The IC method can be used
as a criterion in addition to the already practised criteria in predicting
the latex viscosity produced from a particular emulsifier, but with the
restriction that the structure of the sample has been studied extensively
and must be the same in regard of $MW$, stereoregularity, blockiness, and
1:2-glycol. This is a major restriction for the method.

"GH-17's molecules are more adsorbed on the latex particles because they have more anchor segments (adsorbable segments) from SCB, but this still needs clarification from experiments using samples which vary only in SCB. Our effort in this respect was not successful because the preparation of the comonomer for introducing SCB was unsuccessful. A further attempt might form the subject of a future investigation.

"The MW of the emulsifier affected the viscosity of the latex markedly. Even though the MW of most samples is close to the grade average, a slight difference of MW between batches (for example, GH-17 batch 6960, 26.4 cP, and GH-17 batch 6070, 30 cP) will cause some variability in latex viscosity.

"$D_s$, $D$, $D_s/D$ and the hydrodynamic thickness cannot explain the difference in latex viscosities found using emulsifiers with different structures (GH-17 and Sample B) and with different MW (GL-05, GL-03, GM-14L, GM-14, GH-17, and GH-20) in this investigation. Therefore the difference in interaction of the PV-OH-OAc in aqueous solution with vinyl acetate, VOAc, as suggested by Shiraishi, or the difference in associative tendencies of the thickener (emulsifier) due to the difference in their structure (SCB and MW most probably in this investigation, blockiness and -OAc content in Shiraishi's) might be the explanation."

## Sheng-haing Tsaur:  MODEL COLLOIDS

We have synthesized a series of monodisperse polystyrene colloids of the same particle size but different surface charge density.  The surface ionic groups are either all alkyl sulfonate or alkyl quaternary ammonium bromide. The initiator introduces no ionic groups.  These latexes are made by a seeded polymerization during which a surface-active comonomer, for example, sodium sulfo-decyl styryl ether (SSDSE), is incorporated into the particle surface. This ionogenic comonomer is synthesized from bromodecyl styryl ether, which in turn comes from the Williamson ether synthesis involving hydroxystyrene (vinyl phenol) and $\alpha,\omega$-dibromodecane.  The cationic monomer is made from the bromodecyl monomer by reaction with a tertiary amine.  Our results with SSDSE are described below.

### Surface Adsorption Isotherms

Using a Wilhelmy apparatus a Gibbs plot of surface tension vs. SSDSE concentration was obtained (Fig. 1).  Subsequently the adsorption isotherm on a polystyrene latex could be found by measuring air/water surface tensions
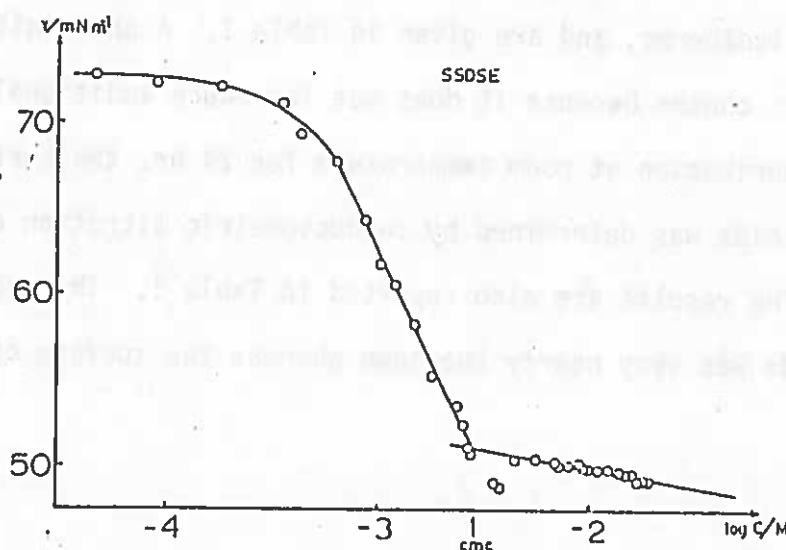
Fig. 1

of the latex containing various amounts of SSDSE.  The results are shown in Fig. 2.  The areas per molecule derived from these measurements are 70 and 14 $\overset{o}{A}{}^2$/molecule for air and polystyrene, respectively.



Fig. 2
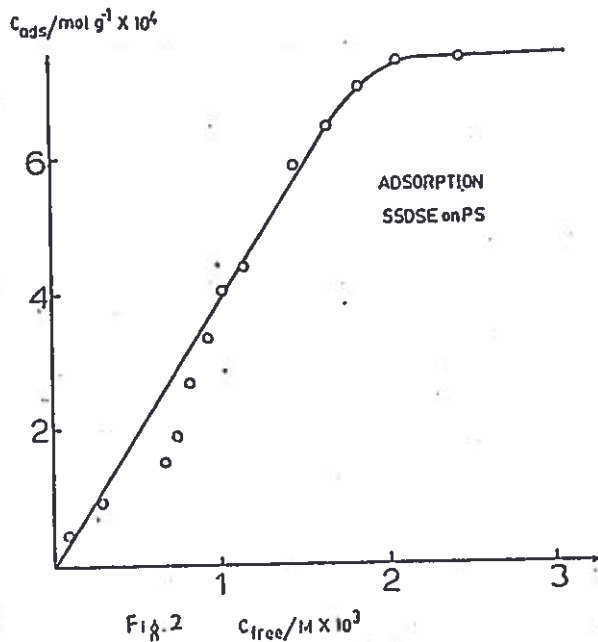
## Synthesis of Polymer Colloids

A monodisperse polystyrene seed latex of 461 $\overset{o}{A}$ diameter was swollen with styrene monomer (about 30 wt % of latex solids).  To this was added various amounts of SSDSE.  The theoretical surface charges were calculated from the adsorption isotherms, and are given in Table I.  A photoinitiator, biacetyl (0.01M), was chosen because it does not introduce additional charged groups. After polymerization at room temperature for 24 hr. the surface charge density of the colloids was determined by conductometric titration of the ion-exchanged latexes.  The results are also reported in Table I.  The particle size of all the colloids was very nearly the same whereas the surface charge varied from

4.1 to 20.9 $\mu$C/cm$^2$. The surface yield of the comonomer, i.e. that found at the polystyrene/aqueous interface was essentially quantitative under favorable experimental conditions.

Table I

Properties of Polystyrene Colloids made with SSDSE

|  | Latex 31 | Latex 33 | Latex 31b | Latex 32b |
|---|---|---|---|---|
| SSDSE added (moles) | $4.24 \times 10^{-5}$ | $1.69 \times 10^{-4}$ | $5.13 \times 10^{-5}$ | $1.08 \times 10^{-4}$ |
| SSDSE adsorbed (moles) | $2.14 \times 10^{-5}$ | $9.92 \times 10^{-4}$ | $2.69 \times 10^{-5}$ | $6.28 \times 10^{-5}$ |
| Theoretical surface charge density ($\mu$C/cm$^2$) | 4.53 | 20.92 | 6.29 | 13.24 |
| Experimental surface charge density ($\mu$C/cm$^2$) | 4.42 | 20.89 | 4.11 | 11.93 |
| % yield of Surface charge | 97.6 | 99.9 | 65.3 | 90.1 |
| Theoretical surface (radius Å) | 501 | 501 | 501 | 501 |
| Experimental size (radius Å) | 463 | 475 | 485 | 462 |

<u>Shu-jan Liang</u>:    Dynamic Behavior of Amphiphilic Polymers at Liquid/Air
and Liquid/Liquid Interfaces

Dynamic behavior of amphiphilic polymers at liquid/air and liquid/liquid
interfaces has been investigated by means of measurements of the interfacial
tension, using a Langmuir trough film balance.  Three hydrophobically
modified water-soluble polymers, polyacrylic acid-cetyl eicosyl acrylate
(PAA-CEA), hydrophobically modified hydroxyethyl cellulose (HM-HEC), and poly-
styrene-Poly(ethylene oxide) diblock copolymer were studied.  Polymer mono-
layers were subjected to hysteresis experiments (repeated compression and expan-
sion cycles) and stress-jump experiments (compression followed by relaxation).
The properties of the monolayers were obtained from the results of surface
pressure vs. surface area relationships and surface pressure vs. time curves.
The compressibility of the polymer monolayers, the rate of adsorption and desorp-
tion of chain segments within the monolayer and of entire molecules between
interface and bulk phase, the rate of conformational change within the mono-
layer and the degree of irreversible adsorption of water-soluble polymers
have been considered.  A simple kinetic model to account for this complex behavior
has been developed.

## Tien-Teh Chen: Thiosulfate-Initiated Polymer Colloids

Sodium thiosulfate with some metal ions as catalyst has been found to be an efficient initiator for the emulsion polymerization of various monomers. The relative catalytic efficiencies of metal ions, judged by the % conversion, are $Cu^{+2} > Fe^{+3} > Ag^{+}$. In fact, the % conversion catalyzed by $Cu^{+2}$ ion in the presence of anionic emulsifier was almost quantitative. Even without emulsifier polystyrene latexes prepared by this initiator system are found to be very monodispersed and very stable. By means of conductometric titration, only strong acid groups were observed. These are hydrolyzed under prolonged heating.

Thiosulfate free radical ion, $\cdot S_2O_3^{-1}$, is considered to be the most probable initiating species; the proposed mechanism is:

$$M^{+n} + S_2O_3^{-2} \longrightarrow M^{+(n-1)} + \cdot S_2O_3^{-1}$$

$$\cdot S_2O_3^{-1} + M \longrightarrow \cdot M-S_2O_3^{-1},$$
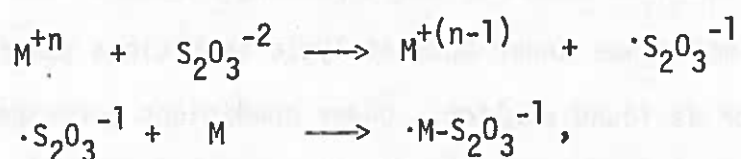
where $M^{+n}$ is the metal ion and M is the monomer. The polymer thus formed would carry thiosulfate end-groups. In order to determine the identity of these groups, the water-soluble monomer hydroxyethylmethacrylate (HEMA) was chosen. The ideal is to prepare a low molecular-weight oligomer to increase the concentration of end groups. By means of Infrared Spectroscopy, our result shows that poly(HEMA) prepared by the $Cu^{+2}/\cdot S_2O_3^{-2}$ system has a weak absorption in the region of 600-650 $cm^{-1}$, which is characteristic of Bunte Salts ($R-S_2O_3^{-} Na^{+}$). Poly(HEMA) prepared by means of $K_2S_2O_8$ initiation didn't show this absorption. The thiosulfate-terminated poly(HEMA) was treated with potassium cyanide (KCN) in order to convert the end groups to the corresponding thiocyanate. The IR spectrum of the resulting polymer shows sharp

absorptions at 2163 and 2137 $cm^{-1}$, corresponding to the -C≡N stretching vibration of organic thiocyanate compounds. The absorptions in the region of 600-650 $cm^{-1}$ are greatly reduced after the reaction. These two facts strongly suggest the presence of thiosulfate end-groups.

Kevin Scholsky:  <u>Controlled Release of Drugs</u>

Acrylate polymer colloids containing surface strong acid groups have been shown to undergo autocatalyzed hydrolysis with zero order kinetics over long periods of time (Fitch, Gajria & Tarcha, JCIS <u>71</u>, 107 (1979)). We have now synthesized two acrylate esters of drug molecules, salicylic acid and chloroamphenicol, and have made the corresponding latexes. The release kinetics of the drug molecules under autocatalytic conditions generally follow the same behavior as found earlier. Under conditions corresponding to blood serum and body temperature, the kinetics are altered and appear to be linear with the square root of time. However, the mechanism cannot be diffusion-control because of (1) the very slow rates, (2) the high energies of activation ($\sim$50 kJ $mol^{-1}$), and (3) the fact that the rate of release corresponds to the rate of hydrolysis determined by titration of the polyacrylic acid (PAA) formed. Release rates are in the therapeutic range and can be varied by means of several experimental parameters, e.g. surface charge density and copolymer ratios. Residual PAA, if low enough in molecular weight, is known to be non-toxic, and is reported to have anti-tumor activity in its own right.

(1)     **Factors Influencing Polymer and Latex Rheology and The**     27 SEP Recd
        **Criteria for Association  -  Ed Glass, NDSU**

Dr. Glass discussed the broad area of interaction or association between latex particles and other coating materials. He discussed the need for different viscosities at different shear rates. These included storage, brush pick-up, application and flow. The important parameter for flow is the Complex Modulus or the Elastic Characteristic of the coating. He pointed out that high molecular weight thickeners suffer from (1) more foaming due to high interfacial tension, (2) low high shear viscosity and (3) higher extensional viscosity (more spattering).

He also discussed Non-Newtonian Pseudoplastic Flow (Shear Thinning) from the standpoint of molecular entanglements and deformation. Moreover, he related the separate work of Debye-Bueche, Graessley and Williams to these same concepts.

He pointed out the work of Krieger which showed that smaller particle size latices give more pseudoplastic characteristics. Thus, the good coalescence and film integrity properties of these latexes are offset by their lower high shear viscosity (less film build) and higher low shear viscosity. This viscosity profile is the opposite of what is really desired.

As references for previous work in these areas, Dr. Glass listed the following:

F. L. Saunders, J. Colloid Interfacial Sci., 23, 230 (1967)

C. F. Goodever, Trans. Faraday Soc., 35, 342 (1939)

T. Gillespie, J. Colloid Sci., 15, 218, 313 (1960)

R. W. Kreider, Off. Dig., 36, 1244 (1964)
         J. Poly. Sci., C-27, 275 (1969)

F. L. Saunders, J. Coll. Interf. Sci., 28, 475 (1968)

R. K. Khanna, Paint Techn., 33, 23 (1969)

Dr. Glass concluded with a more detailed discussion of Complex Modulus and the requirements for true association. (R. L. Kleinlein)

(2)     **Associative Thickeners for Coatings . . . The Nightmares of an**
        **Innovative Supplier  -  James Miller, Dow Chemical**

Mr. Miller started by saying that $30 - 50 million dollars are spent each year on thickeners for Trade Sales paints. While Associative Thickeners have been projected to take a large percentage of this market for a number of years, they still only represent approximately 10%.

Jim also discussed the requirements of a thickener from three different perspectives: painter, paint manufacturing and thickener manufacturer. These criteria are:

Painter:

- Easy to apply (variety of methods)
- One coat coverage - foolproof
- No spatter or sag
- Good flow and leveling
- Uniform color development
- Good durability (during cleaning and scrubbing)

Paint Manufacturer:

- Low cost
- Good film build
- Good flow and leveling
- Minimum spattering
- No adverse impact on adhesion or color development
- Biological resistance
- Wide formulation range

Thickener Manufacturer:

- Necessary rheology
- No adverse effect on film properties
- Low raw material cost
- Low capital equipment cost
- Good environmental properties
- Broad application

Jim went on to describe the early Dow thickeners and many of the current ones as a water-soluble polymer backbone with hydrophobic sidechains attached at various intervals. Factors which caused the greatest problems for the Dow materials were (1) lifting tendencies, (2) poor water resistance and (3) a formulation's specific nature. While they originally placed the most emphasis on the lifting problem, they retrospectively view the latter two areas as being more important.

Factors which led them get out of commercial production of their associative thickener were (1) lower than projected production and usage levels and(2) higher than anticipated capital equipment costs. In summary, they are still looking at these type thickeners in the laboratory but are not currently sampling or producing any for sale. In addition, their work to date would indicate very little possiblity of developing a "universal" associative thickener. (R. L. Harper)

(3)     Structure Property Relationships Reflecting the Rheological
        Characteristics of Synthetic Water-Soluble Polymers -
        William Arney, Union Carbide Corp.

This speaker told of two studies. The first was aimed at
understanding the effect an associative thickener's backbone has on the
rheological properties of an acrylic paint and a vinyl acrylic paint.
100% hydrolyzed polyvinyl acetate, 89% hydrolyzed polyvinyl acetate,
polyethylene oxide and polyvinyl pyrrolidone backbones were studied.
The amount of thickener used and, to a lesser extent, the composition of
the backbone had an effect on the high shear viscosity (14,000 sec$^{-1}$)
of the paints. Molecular weight had no effect. Flow and leveling was
influenced not only by the backbone composition but also by the molecular
weight (low MW gave best results).

The second study involved the case of a styrene/acrylic acid
backbone with polyethylene oxide side chains capped with various hydrophobic
groups. The sequential distribution and polydispersity of the backbone
were varied by running its polymerization in different solvents and under
different conditions. Such changes had relatively little effect on the high
or low viscosities but flow and leveling of paints were greatly influenced.
When used with an acrylic latex, optimum results were achieved with a
low styrene to acrylic acid ratio (under 3 to 10). When used with a vinyl
acrylic latex, the styrene to acrylic acid ratio was not as critical. In
both cases best results were obtained with a low side chain to acrylic acid
ratio and polyethylene oxide lengths of 30-40 units capped with a large
hydrophobe group (e.g., -OC$_9$H$_{19}$). All other combinations gave significantly
inferior results. Attempts to match these performances by copolymerizing
the polyethylene oxide and hydrophobic groups into the backbone or by
mixing the side chain and backbone components without grafting them
together were totally unsuccessful.

To explain these results, researchers at Union Carbide have
developed a theoretical model. They propose that the side chain caps are
adsorbed onto latex and/or pigment particles. These adsorbed particles
are linked together via "hydrophobic clusters" which are entanglement
sites and are composed of the hydrophobic segments of several thickener molecule
backbones, the unadsorbed hydrophobic end groups of some side chains
swollen with paint, cosolvent and surfactants. The only basis for this
model is the circumstantial evidence described above. (W. J. Culhane)


(4)     Formulating Trade Sales Latex Paints with High Efficiency
        Rheology Modifiers  -  Edward Schaller, Rohm & Haas Company

QR-708 is Rohm & Haas' associative thickener. It gives good ICI
high shear viscosity and high KU low shear viscosity. Other benefits
include improved flow and leveling, greater film build and a lack of roller
spatter.

The KU low shear viscosity can be decreased by  dding a surfactant.
While anionic surfactants are very effective at this, they can impart
water sensitivity.

RM-4 and RM-5 have a much lower degree of associative functionality.

Degree of association is affected by surfactants and cosolvents, both of which decrease structure build up. One sees the most change in low shear viscosity, less in high shear viscosity. QR-708 gives near Newtonian rheology so that 110-120 KU is a satisfactory low shear viscosity (like an alkyd). While the variation from 90 to 110 KU is readily measurable in the lab, it is not nearly as observable to the consumer.

He suggested formulating by adding thickener to get the necessary high shear viscosity and then adjusting surfactant and cosolvent levels until a desirable low shear viscosity is reached. An example of surfactants and cosolvents effects in conjunction with QR-708 was given with following table:

QR-708, propylene glycol + $H_2O$ reduced to 10% solids with following:

|  | Brookfield Viscosity | ICI |
|---|---|---|
| $H_2O$ | 1180 | 2.8 |
| Methyl Carbitol | 140 | 1.6 |
| Propylene Glycol | 465 | > 5.0 |
| Ethylene Glycol | Gel | Gel |
| Butyl Carbitol | 130 | 1.6 |
| Carbitol | 190 | 2.2 |
| Dalpad A | 575 | > 5.0 |
| Texanol | N O T   S O L U B L E | |

Problem areas with associative thickener:

A.  Formulation sensitivity
B.  In store tinting
C.  Settling in can, color floating, stability problems
D.  Sagging
E.  Choice of dispersant
F.  Lapping problems
G.  Picking

Formulating is a compromise. Recommends QR-708 be used in conjunction with cellulosic thickeners.

QR-708 acts as a plasticizer which gives superior gloss but poor blocking in interior gloss paints. For exterior paints, it imparts good grain crack resistance, but poorer dirt pick-up and poorer early water blister resistance (even more so for RM-4).

Formulation Hints with QR-708

A.  Enamel Formulations

Order of addition important. In an enamel, QR-708 works best when added last. Recommends 20# butyl carbitol as coalescent.

B.     V/A Formulations

Add before latex. 5# Attagel 50 controls sag.

C.     Semi-Gloss Formulations

QR-708 in grind. May need as much as 30# Attagel 50 in lower quality formula.

D.     Premium Quality Flat Interior

Recommends using Natrosol for sag control.

E.     Exterior Flat

Methyl Carbitol - for wet edge
QR-708 before latex
Butyl Carbitol fine tunes KU's.

To Start Formulating

Strip formula

| | |
|---|---|
| Stormer (low shear) too low | Reduce level of following:<br>propylene glycol<br>surfactants<br>W.S. coalescent<br><br>Add Attagel 50 |
| Stormer (low shear) too high | Add butyl carbitol<br>propylene glycol<br>Triton GR-7M<br>Triton X-405<br>Triton X-100 |

(D. E. Slawikowski)

(5)     Associative Cellulose Ethers   -   L. M. Landoll, Hercules, Inc.

Dr. Landoll discussed work he is doing with low molecular weight nonionic water soluble polymers and low level $C_{10} - C_{25}$ hydrocarbon modification of these polymers.

He stated that with the exception of the earlier Dow thickeners and QR-708, all other associative thickeners are polyelectrolytes. They have 100-150 hydrophobes per polymer chain and have strong intrachain association. The nonionic thickeners, such as QR-708 and his modified cellulose ethers, have strong interchain associations and, consequently, exhibit much higher aqueous solution viscosities. The level of modification he has achieved with these cellulose ether polymers ranges from a low of one hydrophobe per polymer chain with very large hydrophobes up to

up to approximately 40 hydrophobes per polymer chain with small hydrophobes. Some of his work was published in the <u>J. Polymer Science</u> last February.

Dr. Landoll went on to say that these modified cellulose ethers do not show the same depletion flocculation mechanism that is common with straight cellulosics. He reasoned this as support for true direct absorption of these materials on polymer particles.

In studying these lower molecular weight cellulose ethers which can be modified to produce higher viscosities, they have also observed less tendency for viscosity loss due to enzyme attack. They explain this by the fact that less viscosity is coming from the polymer backbone and any degradation of this backbone consequently causes less drop in viscosity.

Dr. Landoll concluded by saying that all of their current work is still on a laboratory scale. They are not sampling any commercial or laboratory materials. They feel a need to better understand how these thickeners function and how other formulation parameters influence viscosity development and final paint rheology before sampling any of the new thickeners. (R. L. Harper, R. L. Kleinlein)

(6)     Advantages and Disadvantages of Associative Thickeners in Coatings Performance - F. G. Schwab, Coating Research Group, Inc.

Advantages of Cellulosic Thickeners Effects on Paints:

| Consistency | Color Acceptance | F/T |
| Stability | Open Time | Water Resistance |
| Compatibility | Holdout | Stain Removal |

Associative Thickener Advantages:

| Improved flow + leveling | Paint viscosity latitude |
| Controlled spreading | Resistance to bacterial attack |
| Cost savings (not always true) | Convenient liquid form (some) |
| Less roller spatter | |

Example of Cost Savings:

| Paint | A | B | C |
|---|---|---|---|
| Lbs/TiO$_2$ | 330 | 283 | 218 |
| High Shear | .9 | .85 | 1.6 |
| C/R | | | |
| Drawdown | .985 | .969 | .954 |
| Brushout | .972 | .940 | .969 |
| Spreading Rate Sq ft/gal. | 540 | 570 | 404 |

Major Disadvantages of Associative Thickener:

Sagging
Phase Separation
Picking

Potential Disadvantages of Associative Thickener:

Sensitivity to coalescents, surfactants and colorants

Blocking and softer films
F/T
Color Problems

Less Important Potential Disadvantages of Associative Thickeners:

| | |
|---|---|
| Water resistance | Wet adhesion |
| Alkali resistance | Chalk adhesion |
| Exterior durability | Open time |

## Associative Thickener Formulation Hints:

1. Check data accuracy.
2. Study order of addition.
3. Test brushouts vs. drawdowns

    a. Flow + leveling
    b. Hiding
    c. Gloss

4. Test roller application.
5. Get several opinions on results.
6. Evaluate aged paints.

Associative Thickener: Manufacturer Problems:

1. Resistance to change.
2. Handling

    a. Viscous materials (some)
    b. Pre-mix
    c. Order of addition
    d. Viscosity adjustments
    e. pH sensitivity
    f. Clean-up

Consumer Acceptance: Potential Problems:

1. Appearance in can
2. Excessive brush drag
3. Excessive thinning

(D. E. Slawikowski)

(7)   Summation: Associative Thickeners, Are they here to stay?
      - J. E. Glass, North Dakota State University

After a brief summary of the advantages and disadvantages of latex thickeners, the speaker described how QR-708 (Rohm & Haas) and Polymer 20 (Dow) differ.  (QR-708 has a double edge, not single, hydrophobe and a larger backbone to side chain ratio.)  It was suggested that a study of the effect of controlled modifications of either would lead to a better understanding of why associative thickeners work.  It was pointed out that there is no published systemized study of the mechanisms which cause the rheological behavior of thickeners and that association is an inferred, not proven, event.  It was suggested that an extensive study be carried out where the normal forces, yield stresses and extentional viscosity characteristics of a carefully controlled series of paints are examined.  Emphasis was placed on how latex variations might affect this series.

The talk ended by saying that the future is bright for latex thickeners and that many research opportunities are still available. (W. J. Culhane)

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## DEPARTMENT OF CHEMICAL ENGINEERING

2 8 SEP Recd

COLLOID RESEARCH AT McMASTER UNIVERSITY - RECENT DEVELOPMENTS.

by

Archie Hamielec

## 1. McMaster Institute of Polymer Production Technology

Four 1-gallon s.s. high pressure stirred autoclaves (700 psi) and one 2-gallon s.s. autoclave (700 psi) have been installed in walk-in fume cupboards and reactor startup is now scheduled for late fall. The search for sponsor companies for the Institute is being delayed until the western economies improve. Funds received from the Federal Government of Canada will cover the operation of the Institute for a 3-year period (until Jan. 1985).

## 2. Semi-batch and continuous emulsion polymerization of vinyl acetate

No significant progress to report.

## 3. Semi-batch and continuous emulsion polymerization of styrene/butadiene

A steady-state model for a stirred tank reactor train has been developed. This model predicts conversion, copolymer composition, particle size distribution, $\bar{M}_N$, $\bar{M}_W$ and both tri and tetrafunctional long chain branching down the reactor train. The model employs redox initiation and a chain transfer agent which partitions in monomer droplets, polymer particles and the water phase. A dynamic CSTR model has been formulated and a computer program is being written. This dynamic model should be operational by December, 1982.

## 4. Semi-batch emulsion polymerization of styrene/acrylonitrile

A dynamic model for semi-batch operation is being developed. This model should predict polymerization rate, copolymer composition and molecular weight distribution and permit determination of optimal feed rates of active monomer to give copolymer of uniform composition at highest productivity.

The work reported herein is being done in collaboration with Dr. J.F. MacGregor, McMaster University

# CONTRIBUTION TO POLYMER COLLOID GROUP NEWSLETTER

## Case Western Reserve University

## EMULSION POLYMERIZATION STUDIES (M. Sugie)

Efforts have been made to nucleate emulsion poly-
merization using polyelectrolytes in lieu of surfac-
tants. Copolymers of styrene with styrenesulfonic acid
(SSA) were used in persulfate-initiated emulsion poly-
merization of styrene. When the copolymers contained a
high proportion of SSA, the polymerizations proceeded
at rates comparable to those of the Ottewill-Shaw
emulsifier-free recipes, producing stable latices only
at volume fractions below 10%. When the copolymers
contained enough styrene to make them marginally water-
soluble, rates were comparable to those in emulsifer-
containing recipes, and stable latices could be produced
at volume fractions of 30% and above.

Addition of methanol provided considerable insight
into the process. When methanol was added to the
recipes in sufficient concentration (ca. 40%) to make
the water-soluble polyelectrolytes marginally soluble,
rates and final concentrations again were comparable to
those in emulsifier-containing recipes. The inference
is that the polyelectrolytes micellize when their char-
ges are insufficient to make them highly soluble, and
that the micelles are the loci of polymerization. This
implies further that, in those recipes where ionic como-
nomers replace surfactant [J. Polymer Sci., Chem Ed.
14, 2089 (1976; 19, 3013 (1981)], the reaction may
proceed via the formation of micelles, as growing SSA
oligomers add styrene after the SSA becomes depleted.
Further study is needed to test the micellization hypo-
thesis.

## RHEOLOGY OF STERICALLY-STABILIZED DISPERSIONS (G. Choi)

Sterically stabilized dispersions were prepared by
polymerization of methylmethacrylate in hexane, using
the triblock copolymers (PDMS-PS-PDMS, where PDMS is
polydimethylsiloxane and PS is polystyrene) of Everett
and Stageman as stabilizers. These were then redis-
persed in silicone fluids of various viscosities, by
simply adding the silicone and pumping off the hexane in
a rotary evaporator. Monodisperse nonaqueous latices
were obtained with particle diameters ranging from 0.17
to 0.64 micrometers.

Rheological behavior of these dispersions depends strongly on the molecular weight of the silicone (PDMS) fluid used as dispersing medium. With a low molecular weight siloxane fluid, dispersions behave as noninteracting rigid sphere dispersions, obeying the same principle of corresponding rheological states as do aqueous latices. As the molecular weight of the siloxane fluid increases, dispersions exhibit complex rheological behavior, including time-dependent thixotropy, yielding, and viscoelasticity. Apparently the siloxane molecules of the medium are capable of bridging between polymer particles, either by entangling with the stabilizing siloxane fragments or through exclusion.

I. M. Krieger

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September 17, 1982

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TO:   Dr. A. S. Dunn, Dept. of Chemistry
      Polymer Colloid Group Newsletter

FROM: Mohamed S. El-Aasser, Andrew Klein, F. J. Micale,
      Cesar Silebi, and J. W. Vanderhoff
      Emulsion Polymers Institute, Lehigh University,
      Bethlehem, Pennsylvania

1. We have currently 28 active projects in the area of polymer
   colloids. The titles for these projects are enclosed together
   with the cover page of our latest Graduate Report Issue No. 18,
   July 1982. A few copies are available on a first come - first
   serve basis for the members of the "Polymer Colloids" Group.
   Please write to M. S. El-Aasser, Lehigh University.

2. We have enclosed progress reports on three projects. The first
   two are related to the production of large-particle-size mono-
   disperse latexes in space. The third report is a follow-up on
   core-shell emulsion polymerization showing the aging effect on
   the morphological stability of polybutyl acrylate-polystyrene
   core-shell latex particles. The first part of this work was
   given in the previous newsletter.

3. Four of our Graduate Students completed their M.S. Thesis; and
   their abstracts are enclosed.

4. The special symposium on "Polymer Colloids" which is part of
   the 76th AIChE Meeting in Houston, Texas on March 29-31, 1983
   is shaping-up. There are now five sessions with a total of
   27 papers. Enclosed is the tentative list of authors and titles
   for the five sessions.

MSEA/kd
enclosure

# INDEX

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Index (Contd.)

Toward the Production of Large-Particle-Size Monodisperse Latexes
(E.D. Sudol, C.M. Tseng, M.S. El-Aasser, F.J. Micale, J.W. Vanderhoff)

Objectives:

    1. To obtain kinetic data on the polymerization of monodisperse latexes in microgravity.

    2. To use this information in the development of a process for the production of large-particle-size monodisperse latexes, 2 - 40μm.

Progress:

STS - 3 Flight Experiments - Results

    On March 22 the Space Shuttle Columbia carried into orbit a set of four reactors containing monomer swollen latexes to be polymerized in microgravity. The experiment was begun on the second day of the mission by flipping a switch into the "process" mode. The reaction time, temperature, and agitation conditions for each reactor, along with the data acquisition system were controlled automatically.

    The polymerizations in the piston/cylinder type dilatometers were conducted for approximately 10.5 hrs. at 70°C with an hour at 90°C. Mixing was achieved using the redesigned stainless steel MLR blade [GRPR No. 16, p. 10] in the oscillatory stir mode at about 13 rpm. The piston position (LVDT voltage) and the fluid, cylinder, base, and piston temperatures were recorded at 65 second intervals throughout the experiment.

    Three of the four reactors contained recipes designed to produce three different large-particle-size monodisperse latexes, while the fourth was to act as a control. The seed for the three experiments was a monodisperse polystyrene latex having a 2.52μm diameter. The monomer/polymer (styrene/polystyrene) swelling ratios were by design, 2:1, 4:1, and 10:1 with a 30% final solids content. An oil soluble initiator, aqueous phase inhibitor, and complex stabilization system completed each recipe. The control recipe consisted of a monodisperse 0.19μm polystyrene seed swollen with twice its weight in styrene monomer. Potassium persulfate served as the initiator, sodium bicarbonate as the buffer, and Aerosol-MA as the stabilizer.

    Two weeks after the initial loading of the reactors, the latexes and data tape were recovered for analysis. A complete ground run, paralleling the flight time-line, was also accomplished shortly afterwards for comparison with the flight results.

Particle size analysis of the product latexes was done by measuring particle diameters from TEM photos. This analysis included the determination of the relative number of over-sized particles with respect to the main distributions. These distributions, along with a representative micrograph of each (excluding the control), are presented in Figures 1-3. The main distributions of both the flight and ground latexes for recipes 1 and 2 have standard deviations of less than 2%. The ground latex from recipe 3 has a standard deviation of about twice that of the flight latex, i.e., 3.5% vs. 1.6%. The ratios of oversized particles to that of the main distributions are given in Table I. These results show that the number of oversized particles increases with increasing particle size (swelling ratio) and that the improvement of the distribution due to polymerization conditions does not occur until larger particle sizes.

### TABLE I

### OVER-SIZED PARTICLES

| Run | Monomer/Polymer | Number Relative to Main Distribution |
|---|---|---|
| Flight #1 | 2:1 | 1/264 |
| Ground #1 | 2:1 | 1/339 |
| Flight #2 | 4:1 | 1/207 |
| Ground #2 | 4:1 | 1/172 |
| Flight #3 | 10:1 | 1/99 |
| Ground #3 | 10:1 | 1/65 |

The polymerization kinetics, both flight and ground, for the large-particle-size latexes are presented in Figures 4-6, where represents the grams of polystyrene produced, , the polymerization rate, +, the fluid temperature, and X, the cylinder temperature. The 90°C portion of the data is not included. Any small amount of noise in the conversion data is magnified in the rate determination as can be seen by the scatter in the rate data. A comparison of the flight and ground data reveals a number of interesting points. The first and most important is that there does not appear to be any significant difference in the polymerization rates in microgravity versus on the ground. This is not unexpected in light of the similarity of the latexes produced. Secondly, none of the data is complete in terms of the rate passing through a maximum and slowing due to the gel effect. The curves in Figure 4 (Recipe #1) do show an abrupt cessation of polymerization but this is believed to be caused by nitrogen bubble formation resulting from the decomposition of the initiator and saturation of the fluid. This problem will be discussed further in the following report. The kinetics for Flight Recipe #2 (Figure 5a) does not show this difficulty while the ground run apparently does,
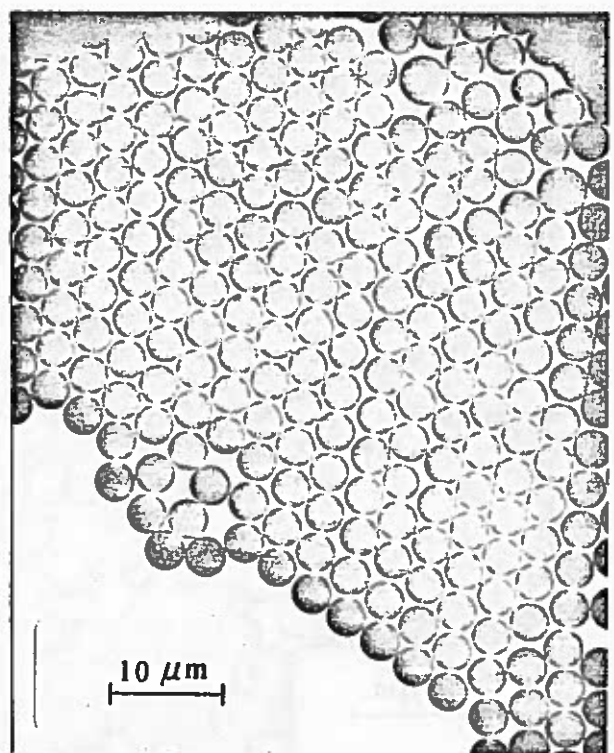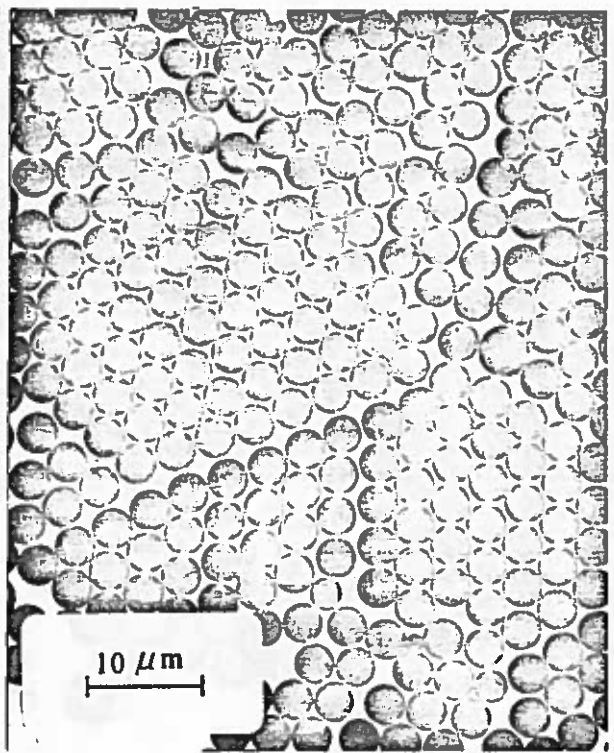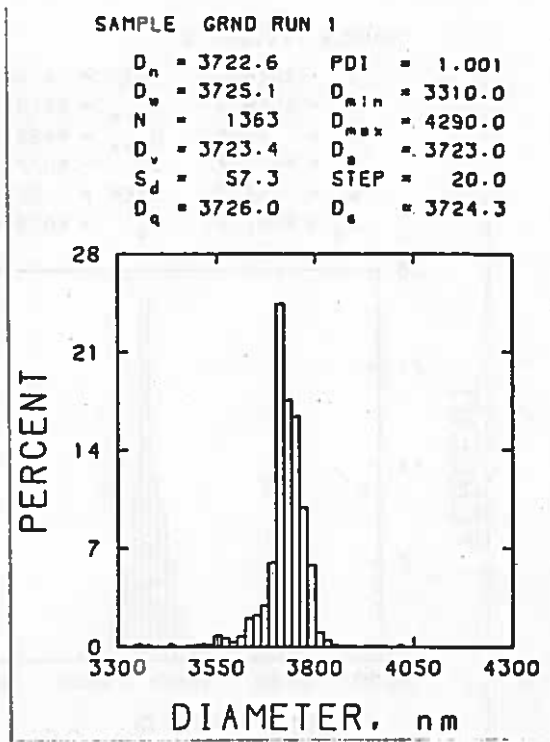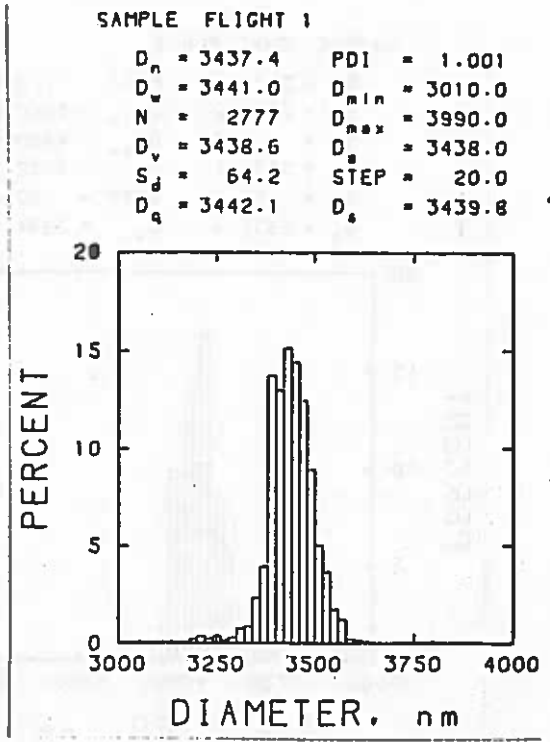
SAMPLE FLIGHT 1

| | | | |
|---|---|---|---|
| $D_n$ = 3437.4 | | PDI | = 1.001 |
| $D_w$ = 3441.0 | | $D_{min}$ | = 3010.0 |
| N = 2777 | | $D_{max}$ | = 3990.0 |
| $D_v$ = 3438.6 | | $D_a$ | = 3438.0 |
| $S_d$ = 64.2 | | STEP | = 20.0 |
| $D_q$ = 3442.1 | | $D_s$ | = 3439.8 |

SAMPLE GRND RUN 1

| | | | |
|---|---|---|---|
| $D_n$ = 3722.6 | | PDI | = 1.001 |
| $D_w$ = 3725.1 | | $D_{min}$ | = 3310.0 |
| N = 1363 | | $D_{max}$ | = 4290.0 |
| $D_v$ = 3723.4 | | $D_a$ | = 3723.0 |
| $S_d$ = 57.3 | | STEP | = 20.0 |
| $D_q$ = 3726.0 | | $D_s$ | = 3724.3 |



Figure 1: *Comparison of particle size distributions of the main particle populations produced in microgravity (FLIGHT 1) and on the ground (GRND RUN 1) with representative micrographs of each.*
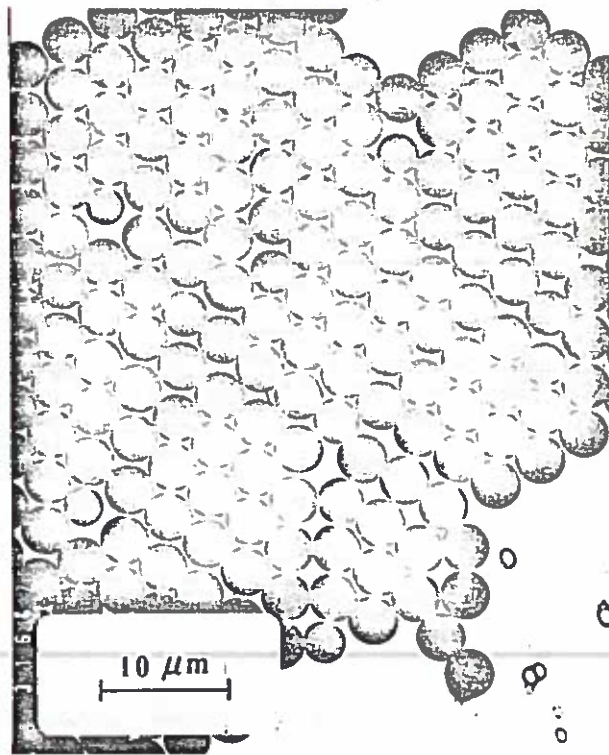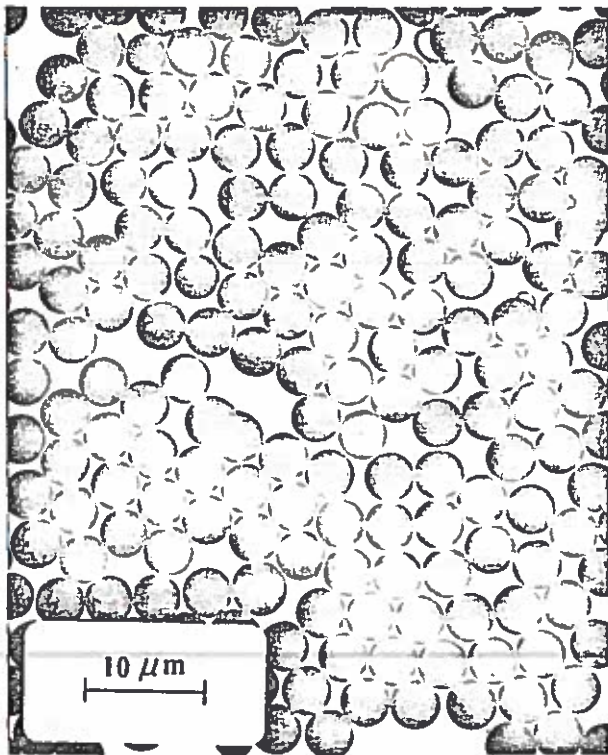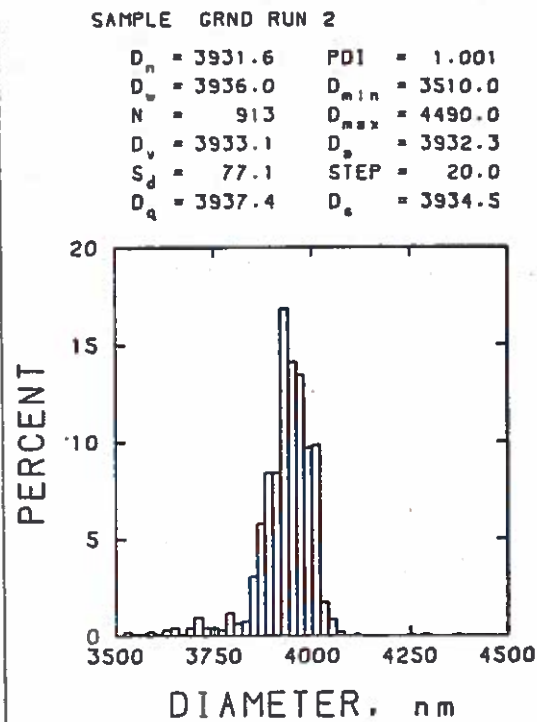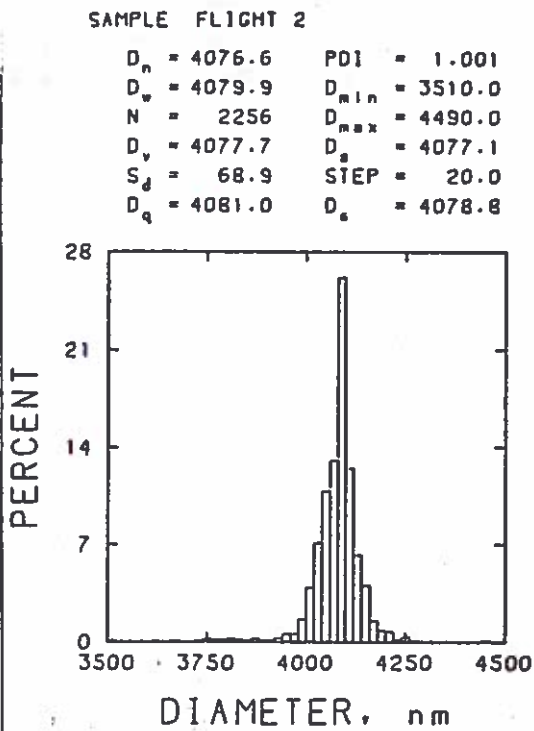
SAMPLE  FLIGHT 2

$D_n$ = 4076.6    PDI  = 1.001
$D_w$ = 4079.9    $D_{min}$ = 3510.0
N   =   2256     $D_{max}$ = 4490.0
$D_v$ = 4077.7    $D_s$ = 4077.1
$S_d$ =    68.9   STEP =   20.0
$D_q$ = 4081.0    $D_e$ = 4078.8

SAMPLE  GRND RUN 2

$D_n$ = 3931.6    PDI  = 1.001
$D_w$ = 3936.0    $D_{min}$ = 3510.0
N   =    913     $D_{max}$ = 4490.0
$D_v$ = 3933.1    $D_s$ = 3932.3
$S_d$ =    77.1   STEP =   20.0
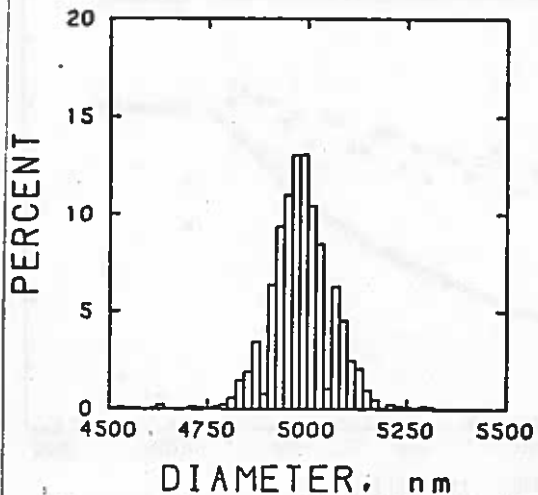$D_q$ = 3937.4    $D_e$ = 3934.5



Figure 2:   Comparison of particle size distribution of the main particle
populations produced in microgravity (FLIGHT 2) and on the ground
(GRND RUN 2) with representative micrographs of each.

SAMPLE FLIGHT 3

| | | | |
|---|---|---|---|
| $D_n$ = 4984.3 | | PDI | = 1.001 |
| $D_w$ = 4988.3 | | $D_{min}$ | = 4510.0 |
| N = 2095 | | $D_{max}$ | = 5490.0 |
| $D_v$ = 4985.6 | | $D_a$ | = 4985.0 |
| $S_d$ = 81.7 | | STEP | = 20.0 |
| $D_q$ = 4989.6 | | $D_e$ | = 4987.0 |

SAMPLE GRND RUN 3

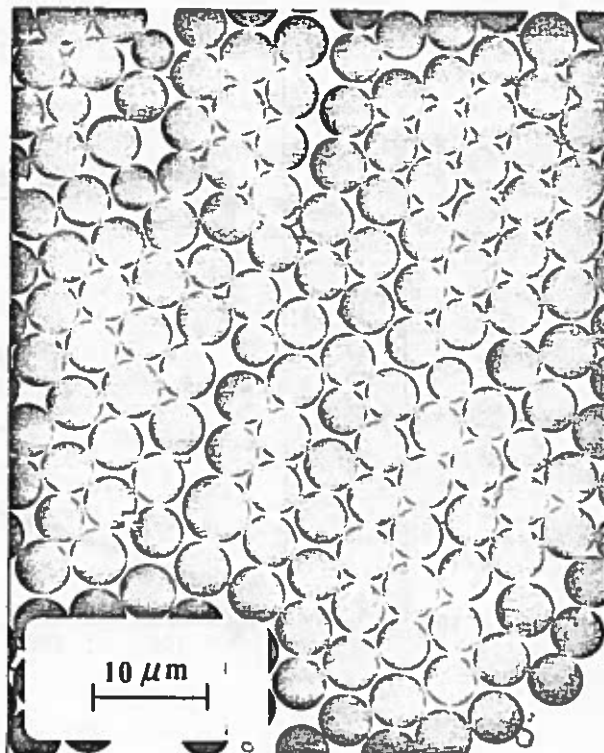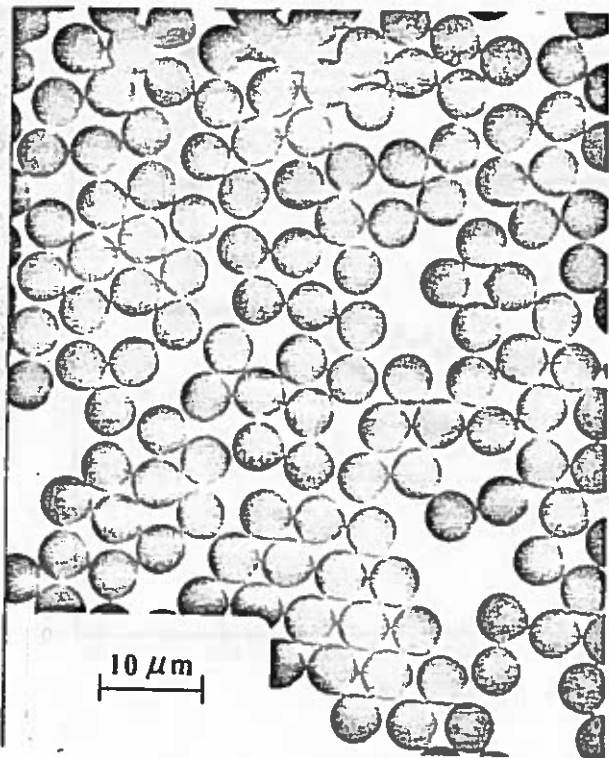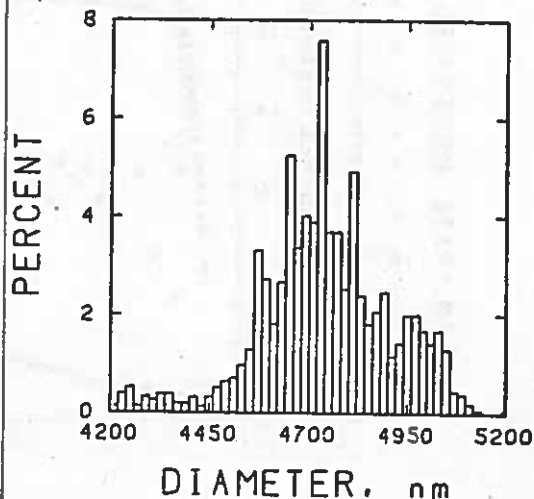| | | | |
|---|---|---|---|
| $D_n$ = 4741.1 | | PDI | = 1.004 |
| $D_w$ = 4758.4 | | $D_{min}$ | = 4210.0 |
| N = 1233 | | $D_{max}$ | = 5210.0 |
| $D_v$ = 4746.9 | | $D_a$ | = 4744.0 |
| $S_d$ = 166.8 | | STEP | = 20.0 |
| $D_q$ = 4764.1 | | $D_e$ | = 4752.7 |



Figure 3: *Comparison of particle size distributions of the main particle populations produced in microgravity (FLIGHT 3) and on the ground (GRND RUN 3) with representative micrographs of each.*
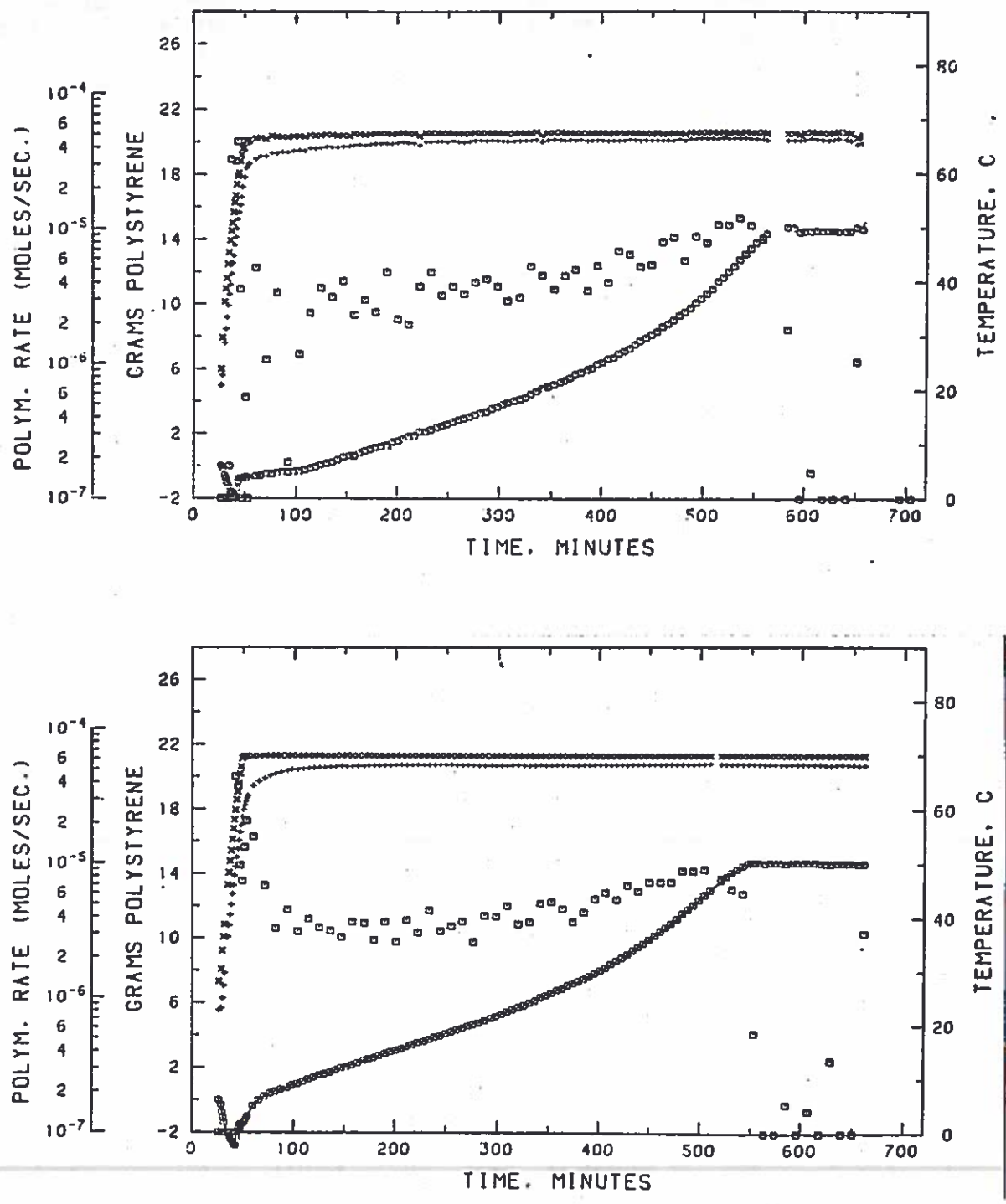
Figure 4: Comparison of the polymerization data obtained in microgravity
(top) and on the ground (bottom) for Recipe #1 corresponding to
a 2:1 monomer/polymer swelling ratio. ○ represents the grams
PS produced, □ , the polymerization rate, + and x, the fluid
and cylinder temperatures, respectively.

Figure 5: Comparison of polymerization data obtained in microgravity (top)
and on the ground (bottom) for Recipe #2 corresponding to a 4:1
monomer/polymer swelling ratio. ⊕ represents the grams PS pro-
duced, ⊡ , the polymerization rate, + and x, the fluid and
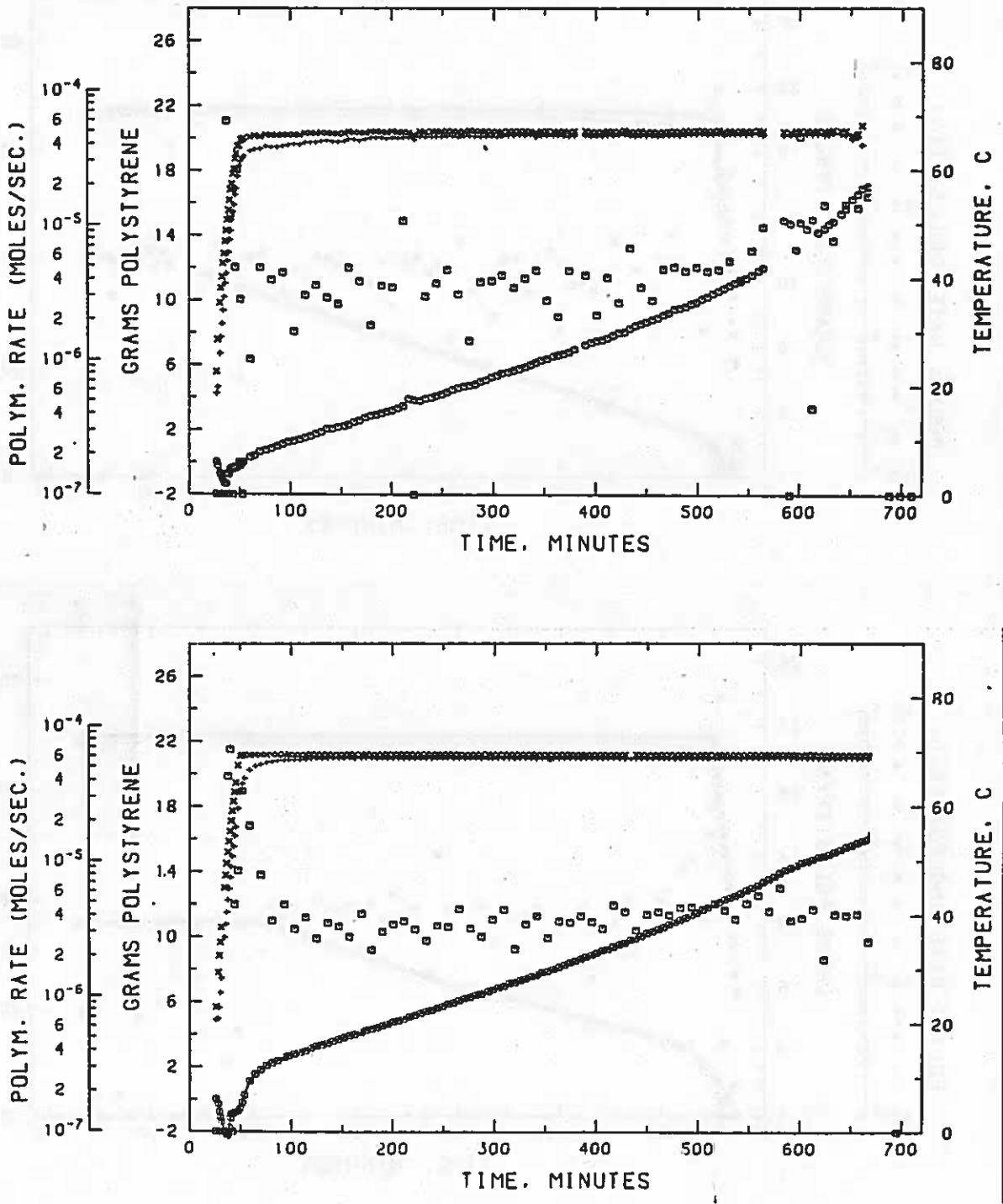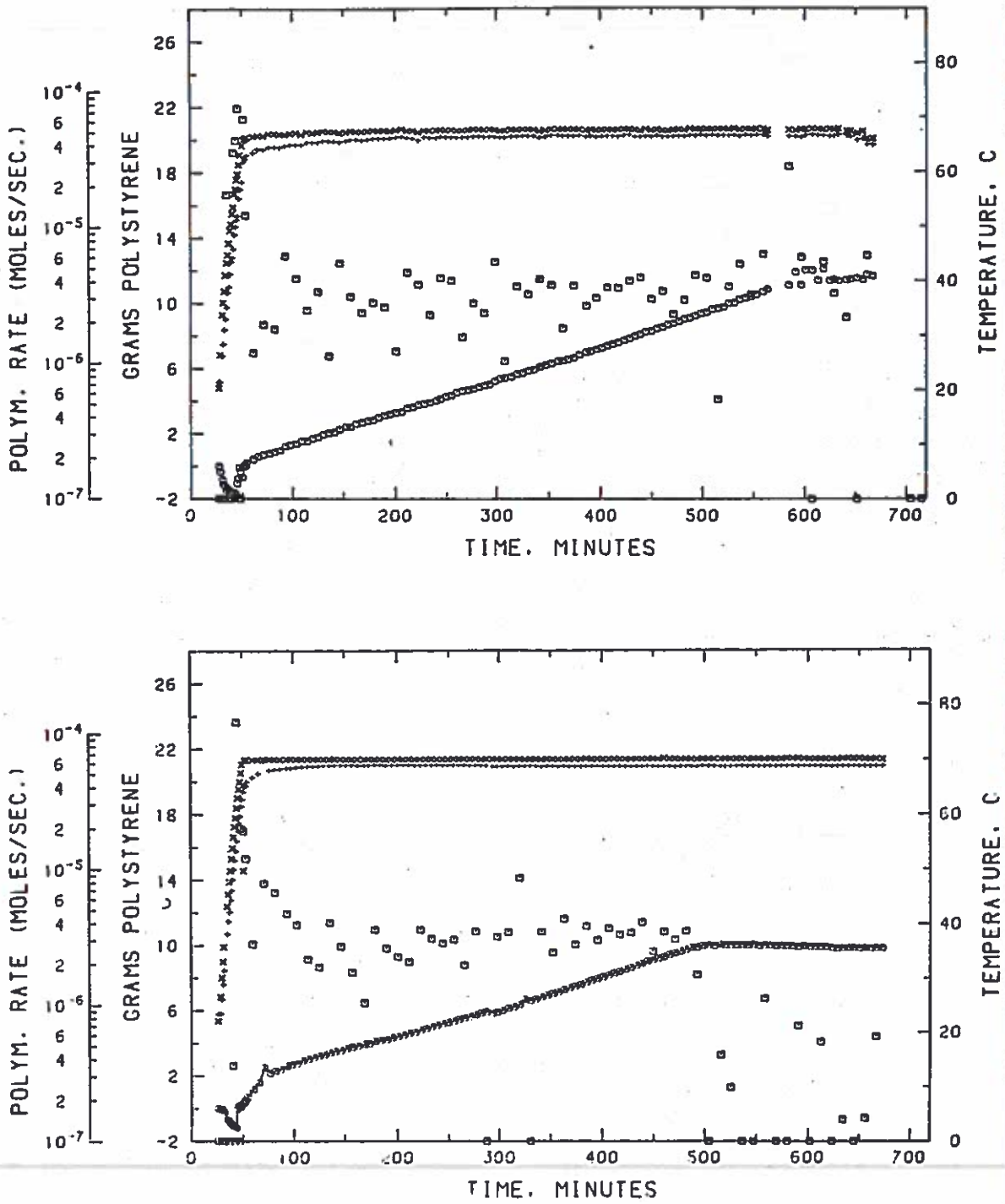cylinder temperatures, respectively.

*Figure 6:* Comparison of polymerization data obtained in microgravity (top) and on the ground (bottom) for Recipe #3 corresponding to a 10:1 monomer/polymer swelling ratio. ⊙ represents the grams PS produced, ▯ , the polymerization rate, + and x, the fluid and cylinder temperatures, respectively.

in that the rate appears to be reaching its maximum at the end
of the 70°C portion of the process for the flight run while the
ground run does not show an increasing rate as expected.  Both
curves in Figure 6 (Recipe #3) show the same phenomenon but at
slightly different conversions.  It should be noted that there
was no evidence of an incomplete reaction at the time the latexes
were recovered from the reactors.  A third point is that all re-
actions show an "aberration" in the conversion curves as the
latexes are raised to their polymerization temperature.  This is
due to the unpredictability of the piston movement during this
period.  A modification in the O-ring piston seal can greatly
reduce this problem, as has been proven in the prototype reactor
(LUMLR).  Further comparison reveals other minor differences
such as a greater noise in the flight data and slightly lower
steady state temperatures.  The cause of these is not known.
Overall, however, the reactions of the three large-particle-size
latex recipes behaved as expected.

The submicron control latex was found to be unable to survive
the four day delay prior to activation of the experiment without
a substantial amount of polymerization occurring.  When the data
was examined, no piston movement was found to take place after
the latex reached temperature.  This behavior was entirely un-
expected.  A test experiment had previously revealed that little
polymerization would occur at ambient conditions over an eight
day period for the same latex in a glass bottle under a nitrogen
blanket.  Also the left-over, swollen flight latex was brought
back and loaded into the LUMLR on the same day the experiment
took place in orbit.  The expected kinetics were recorded as
shown in Figure 7.  The parallel ground run, however, also showed
a substantial amount of polymerization occurring prior to the
actual experiment.  The reason for this is not well known.  The
differences between the conditions of the tests reveal a number
of possibilities.  The fact that the recipe was degassed, thereby
removing most of the dissolved oxygen, was considered to have
possibly reduced any inhibiting effect of the oxygen.  However,
a later test showed little difference between a recipe that had
been degassed and one that had not.  Other differences include
the presence of a vapor space in a bottle versus none in the re-
actor, glass versus stainless steel containers, and one atmosphere
versus approximately two atmospheres pressure in the reactor.  Any
of these may be responsible for this phenomenon.  Work has begun
to find an inhibitor that can induce an appropriate induction
period without affecting the reaction kinetics.

Preparations for the second set of experiments aboard the
Columbia are well underway.  The reaction time at 70°C has been
increased to approximately 20 hrs. in order to accommodate the
need of complete reaction kinetics during the experiment.  The
preparation of monodisperse latexes greater than 5µm in diameter
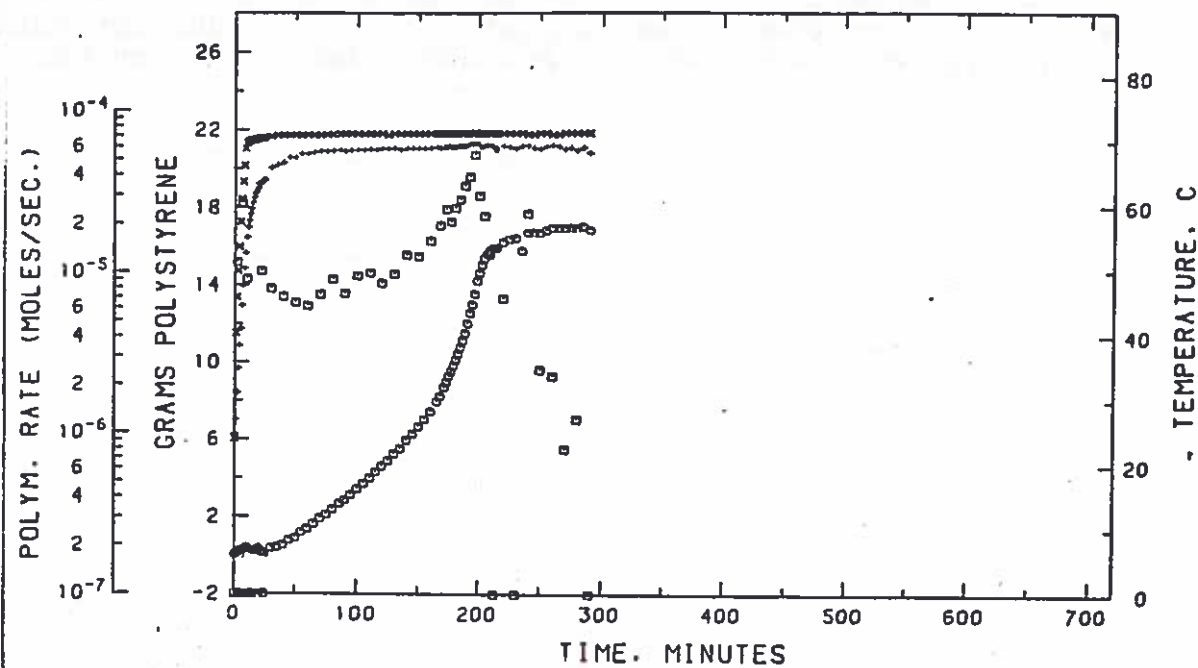will be the goal of these experiments.

*Figure 7: Polymerization data obtained for the control recipe (#4) in the LUMLR. ⊙ represents the grams PS produced, ▥ , the polymerization rate, + and x, the fluid and cylinder temperatures, respectively.*

## Acknowledgements:

## Future Work:

These seeded emulsion polymerization experiments are scheduled to be included in the next three flights of the Columbia, STS 4, 5 and 6. Each requires much in terms of recipe preparation and product analysis. The feasibility of producing successively larger monodisperse particles will be evaluated.

## Toward the Production of Large-Particle-Size Monodisperse Latexes
(E.D. Sudol, A. Silwanowicz, C.M. Tseng, M.S. El-Aasser, F.J. Micale, J.W. Vanderhoff).

### Objectives:

1. To study the kinetics and mechanism of successive seeding of monodisperse latexes.

2. To obtain kinetic information for the development of recipes for polymerization in microgravity.

### Progress:

### Kinetics of Successive Seeding - Oil Phase Initiation

Work has continued on the effect of inhibitors on the kinetics and monodispersity of polystyrene particles produced in a seeding sequence. The previous report [GRPR No. 17, p. 6] described the effects of two ionic inhibitors, $NaNO_2$ and $NH_4SCN$, which have a secondary electrostatic effect causing shrinkage of the double layer, destabilizing the particles. A nonionic, water soluble inhibitor, hydroquinone, was employed next in a sequence. The emulsifier surface coverage (15%) and the initiator concentration (4mM on monomer) were held constant as in the previous experiments. Using the same molar concentration of inhibitor as before (14.5mM on the aqueous phase) the polymerizations were found to again require more time for each successive step. Figure 1 presents the conversion histories for four seeding steps. A fifth step was also attempted but proved to be excessively slow and was terminated at a low conversion. The hydroquinone may inhibit the polymerization initially, as evidenced by an induction period, but more importantly, it is found to retard the polymerization. The conversion (based on the initial monomer) is limited to around 90% when the rate slows and the experiment is concluded. This conversion is 4-5% lower than in previous experiments. The polymerization rate as a function of the overall conversion (Figure 2) decreases with increasing particle size. Even though there may be some buildup of hydroquinone from step-to-step, this is evidently resulting from the decrease in the surface-to-volume ratio of the particles in the sequence. This would, therefore, indicate an interfacial effect in terms of initiator decomposition and/or effectiveness in initiating polymerization. The apparent efficiency of the initiator would also decrease with increasing particle size. It is clear from the interpretation of the results that the efficiency should indeed be low but the scatter is too severe to detect any distinct difference between each of the steps. This may be verified in future through the use of smoothing techniques and/or modeling.
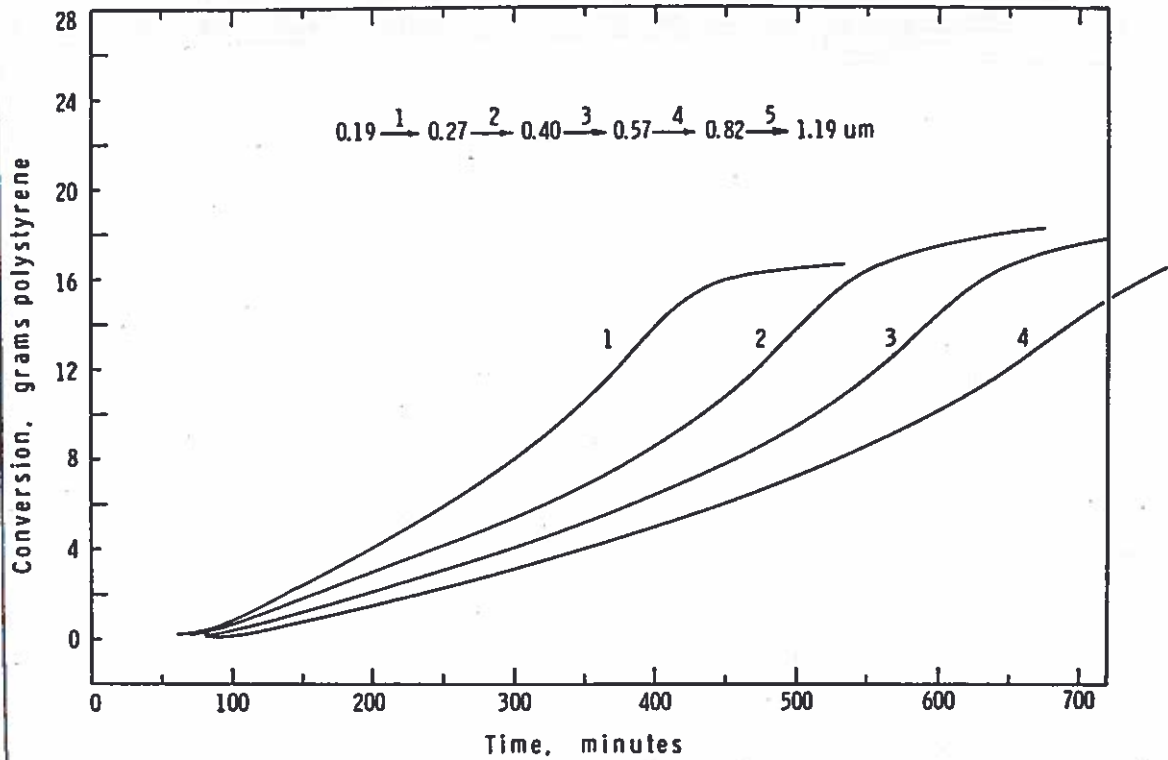
Figure 1: *Conversion histories for emulsion polymerization in a seed sequence (SSMLR 10) using AIBN as initiator and hydroquinone as inhibitor, in a polystyrene/styrene system.*
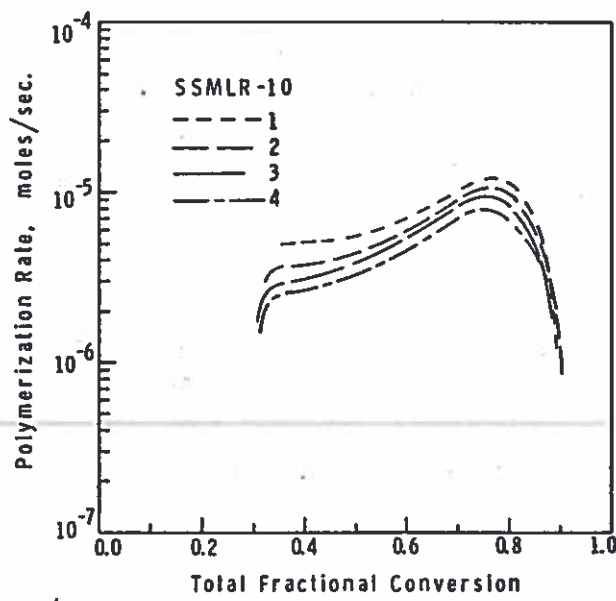


Figure 2: *Polymerization rate as a function of the total fraction of polymer in the particles for the seed sequence (SSMLR 10) given in Figure 1.*

It was suggested from the above and other evidence, including the literature, that the role of the emulsifier at the particle-water interface may be a significant variable in the kinetics of seeded emulsion polymerizations using oil soluble initiators. As a consequence, three polymerizations were carried out with surface coverages of 10, 15, 20% using Aerosol-MA emulsifier (0.19µm polystyrene seed particles, 2/1 - styrene monomer/polymer) using AIBN initiator as in the seed sequences. Figure 3 presents the conversion histories obtained for these experiments. The differences observed here are not great enough to conclude that the change in emulsifier concentration over this range has any significant effect on the polymerization kinetics. A more sensitive test might be better conducted at larger particle sizes (>1µm) where interfacial effects might be more apparent.
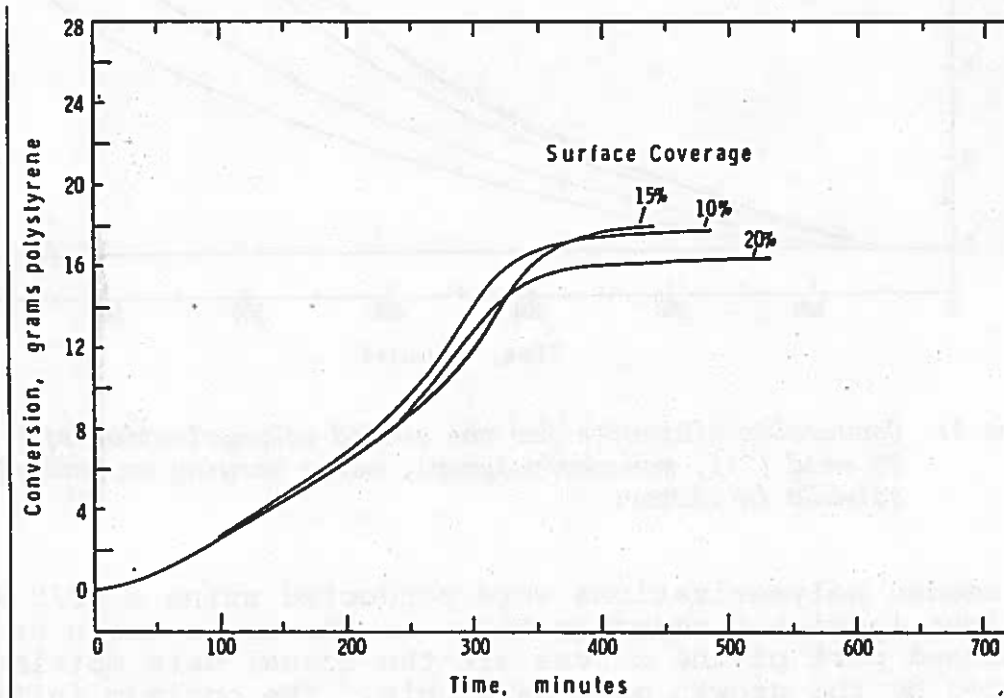


Figure 3: *Conversion histories for a seeded emulsion polymerization using a 0.19µm PS seed, AIBN initiator and varying emulsifier surface coverage (Aerosol - MA).*

## Flight Recipe Development - Initiator Concentration

The amount of initiator that could be used in any MLR (Monodisperse Latex Reactor) flight recipe (see STS-3 Flight Experiments, this report p. 6), was bound by two constraints: 1) the time restriction of the experiment (ca. 10 hrs. at 70°C plus one hr. at 90°C) and 2) the ability of the system to absorb the $N_2$ gas evolved from the decomposition of the initiator. The ideal situa-

tion is obviously one in which high conversion ( 90%) is obtained within the 10 hr. restriction along with the entire conversion history. This situation is illustrated in Figure 4.
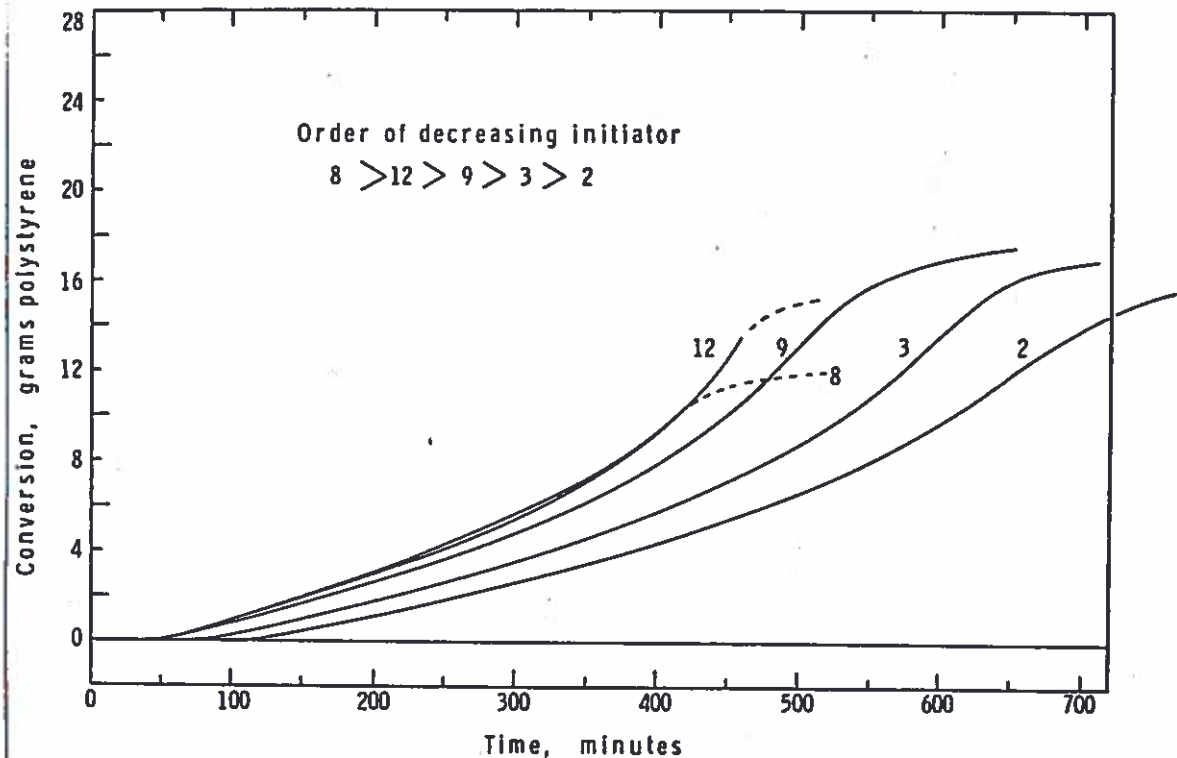


Figure 4: *Conversion histories for the seeded polymerization of a 2.5µm PS seed (2:1, monomer/polymer), using varying amounts of oil soluble initiator.*

Five seeded polymerizations were conducted using a PS/S system with different initiator concentrations in the order shown on the graph. The dashed part of the curves are the actual data obtained, influenced by the growth of a $N_2$ bubble. The optimum initiator level is that used to obtain curve 9, in which a conversion greater than 90% has been reached within the allotted time and with complete kinetics. These data were obtained using a 2.5µm PS seed swollen with twice their weight in styrene monomer. Polymerizations using greater monomer/polymer swelling ratios required a compromise solution to this problem in order to ensure completion of the polymerizations by the end of the 90°C portion. Some loss of kinetic information had to be accepted for these cases. A longer polymerization time should alleviate this problem for future flight preparations.

Future Work:

    1.   Additional kinetic information will be gained for both

successive seedings and flight recipe development.

2. Computer simulations will be run to aid in verification of the proposed kinetic mechanisms.

## Mechanism of Core-Shell Emulsion Polymerization(II)
### (T.I. Min, A. Klein, M.S. El-Aasser, J.W. Vanderhoff)

### Objectives:

1.   To obtain information about the control of morphology in core-shell latex particles.

2.   To investigate thin-layer chromatographic separation of core-shell particle systems according to the difference in chemical composition.

### Progress:

In the previous report [GRPR No. 17, p. 40], the features of the growth of seed latex particles and the sag-value of the PBA-PS core-shell latex particles were described.  During the present period the aging stability of the core-shell latex particles and the characterization of the PBA-PS core-shell latex samples prepared in the absence of emulsifier were investigated.

### (1) Aging Stability of PBA-PS Core-Shell Latex Particles.

For investigation of the features of breakdown in the core-shell latex particles, the migration of core-PBA polymer from the core-shell latex particles during aging in latex state was studied by using TEM.  Figure 1 shows the electron micrographs of the core-shell latex particles as a function of aging time, in dispersion, after the polymerization, for sample #3 produced by the semi-batch process (for condition of polymerization see [GRPR No. 16, p. 43]).  In Figure 1, micrographs #3(a) shows the morphology of the particles shortly after polymerization, #3(b) after 6 months, #3(c) after 10 months, and #3(d) after 12 months.  These observations show clearly the features of breakdown of the core-shell latex particles of sample #3, which was found to be of a low degree of grafting [Org. Coating Appl. Polym. Sci. Pro., 46, 314 (1982)].  However, such a phenomenon was not observed for the core-shell latex particles prepared by the swelling equilibrium process or the batch process, sample #2 and #4, both have a high degree of grafting.  The micrographs shown in Figure 2 were taken 12 months after preparation. These results allow us to conclude undoubtedly that the stability of the core-shell latex particles depends on the amount of graft copolymer formed during the seeded emulsion polymerization.  In other words, the graft copolymer species in the PBA-PS core-shell latex particles may increase the compatibility between the core-PBA and the shell-PS.

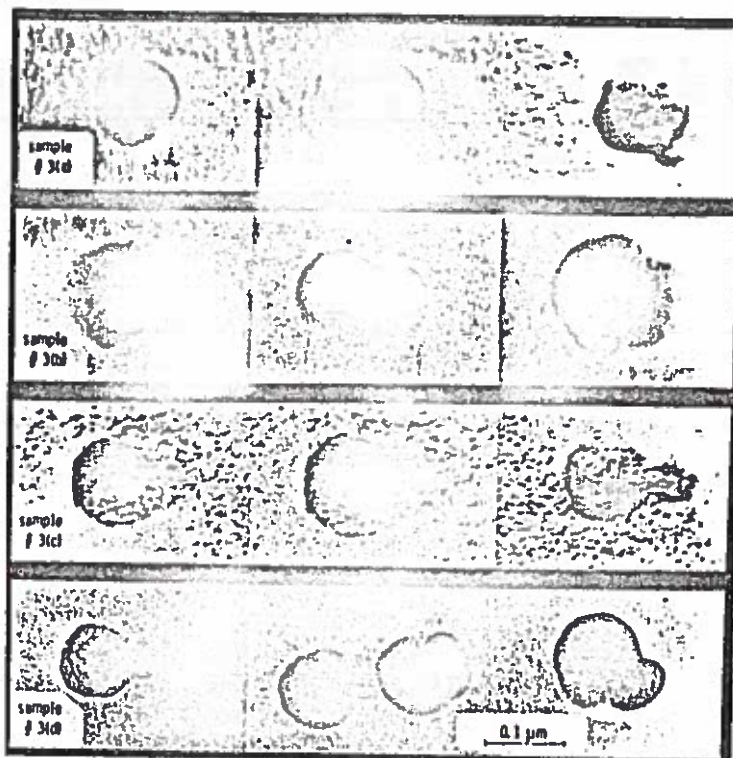### (2) Characterization of the PBA-PS Anomalous Particle Structures.

Figure 1: Electron micrographs of PBA-PS core-shell latex sample #3 as a function of aging time in dispersion, after polymerization; 3(a) taken shortly after polymerization, 3(b) after 6 months, 3(c) after 10 months and 3(d) after 12 months.
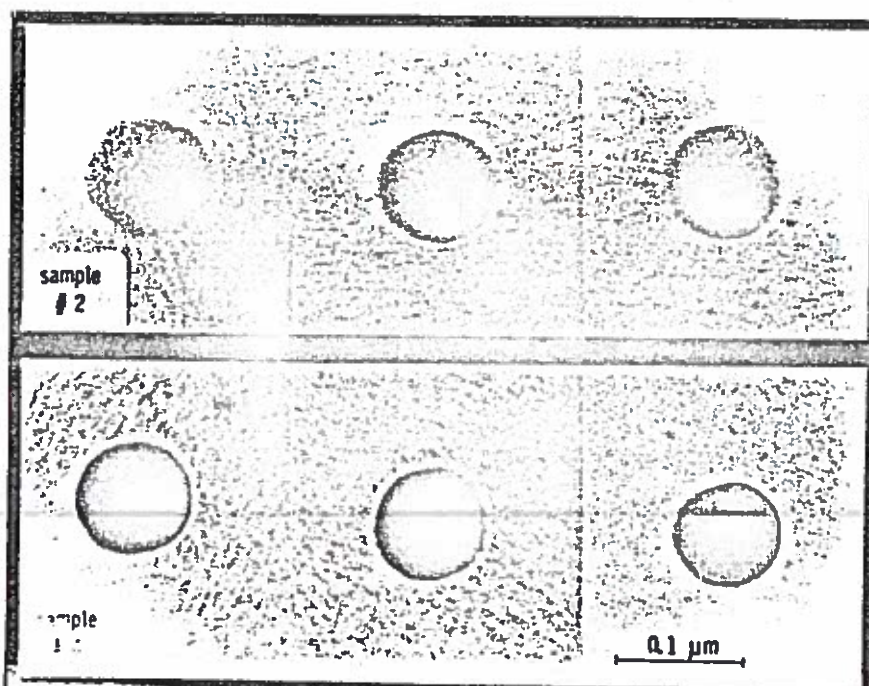


Figure 2: Electron micrographs of PBA-PS core-shell latex samples #2 and #4 taken 12 months after preparation.

The emulsifier-free latex samples prepared according to the previous report [GRPR No. 17, p. 40] were characterized. Figure 3 shows electron micrographs of the core-shell latexes produced by the seeded emulsion polymerization as a function of the concentration of second-stage monomer(styrene). As shown in Figure 3, the particles are not spherical but rather with anomalous shapes. The morphology of the core-shell particles was found to change with increasing second-stage monomer concentration. This might be due to the difference in the formation of shell-particles during the seeded emulsion polymerization.

Figure 4 shows a schematic representation, of a proposed mechanism for the change in the morphology of these core-shell particles. Figure 4(a) shows a model of the core-shell latex particle formed at a low concentration of second-stage monomer. Increasing the second-stage monomer concentration results in the agglomeration of the microphase and its separation into the macro-phase, which might occur due to requirement of a minimization of the interfacial area of the micro-phase as shown in Fig. 4(b) and 4(c). The reason for this transfiguration at the surface layer may be also explained by the difference in hydrophilicity between PBA and PS.



(a)         (b)         (c)
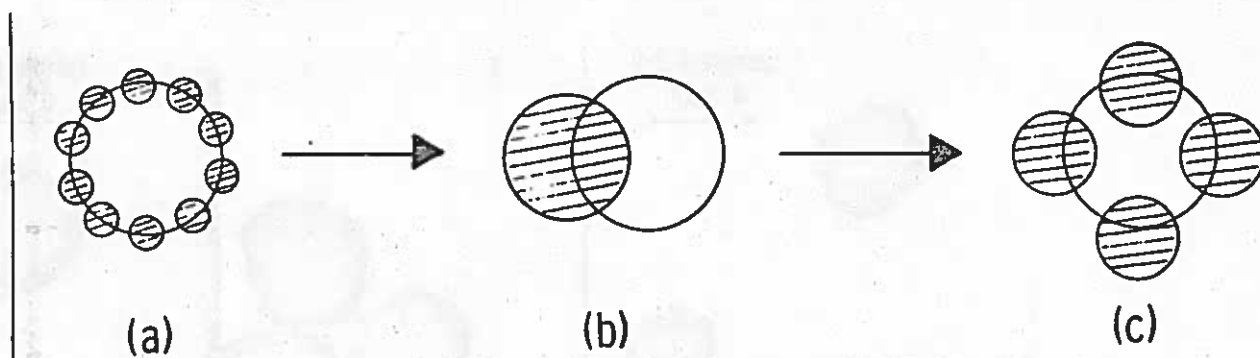
*Figure 4: Schematic representation of polymer morphology in core-shell latex particles.*

Figure 5 shows the electron micrographs of core-shell latex particles prepared with an addition of chain transfer agent, $CCl_4$. Fig. 5(a) shows mushroom-like particles similar to the schematic in Fig. 4(b); and Fig. 5(b) and 5(c) show particles with voids. These results indicate that the formation of voids within particles shown in Fig. 5(b) and 5(c) might be attributed to the high mobility of polymer molecules involved due to the low molecular weight polymer which resulted from the use of chain transfer agent or high concentration of initiator during the polymerization respectively.

Table I shows the particle sizes of the latex samples, which show that the seed particles increased by 20-25 fold. This growth of the seed particle might be due to the agglomeration of the microphase during the seeded emulsion polymerization. Coagulum was observed for all samples in the absence of emulsifier.
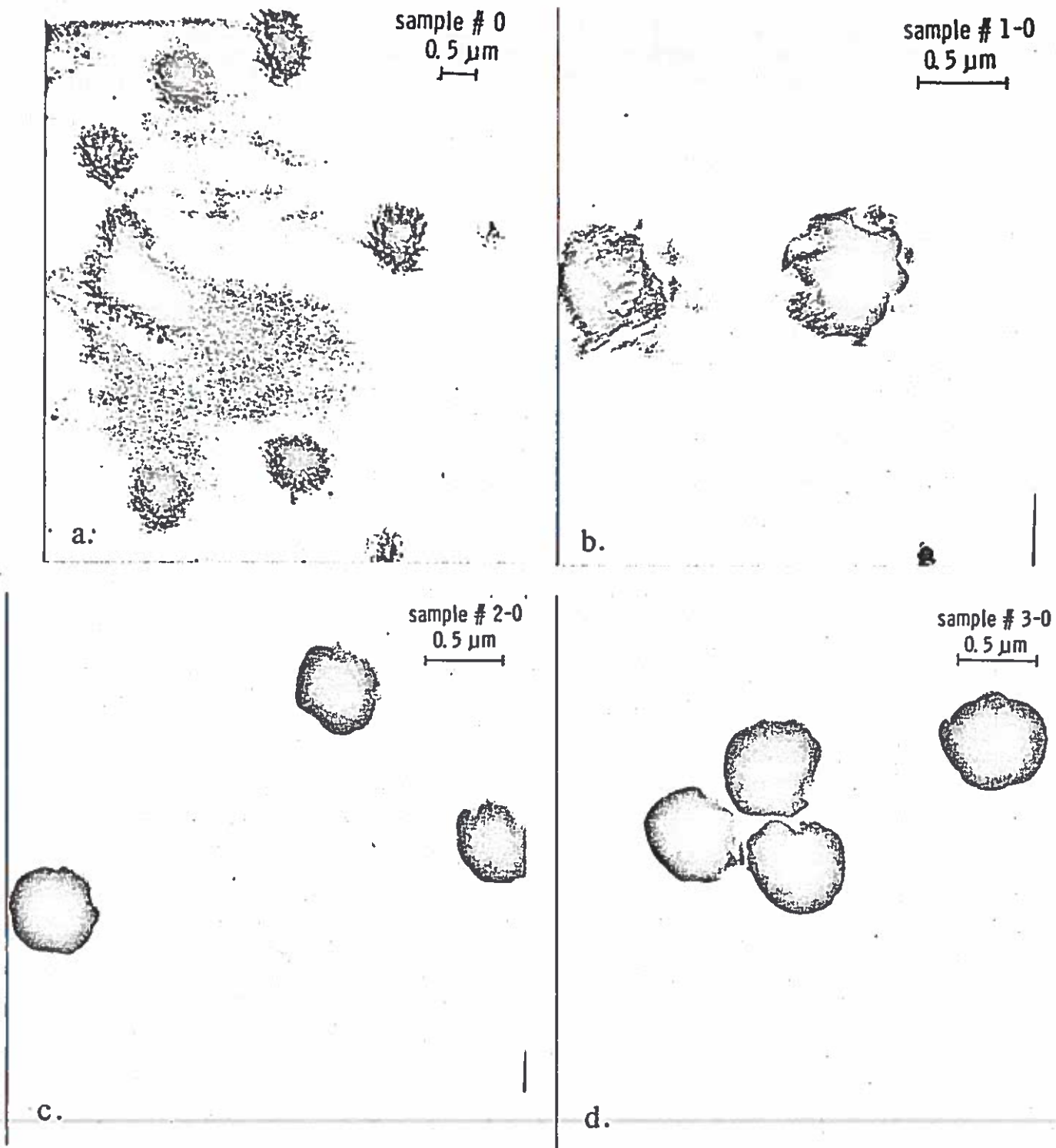
Figure 3: *Electron micrographs of: (a) sample #0, polybutyl acrylate latex particles, (b) sample #1-0, PBA/PS (4.5:1.65 by Wt.) core-shell latex particles, (c) sample #2-0, PBA/PS (4.5:3.3 by Wt.) core-shell latex particles, and (d) sample #3-0, PBA/PS (4.5:4.95 by Wt.) core-shell latex particles all prepared in the absence of emulsifier.*

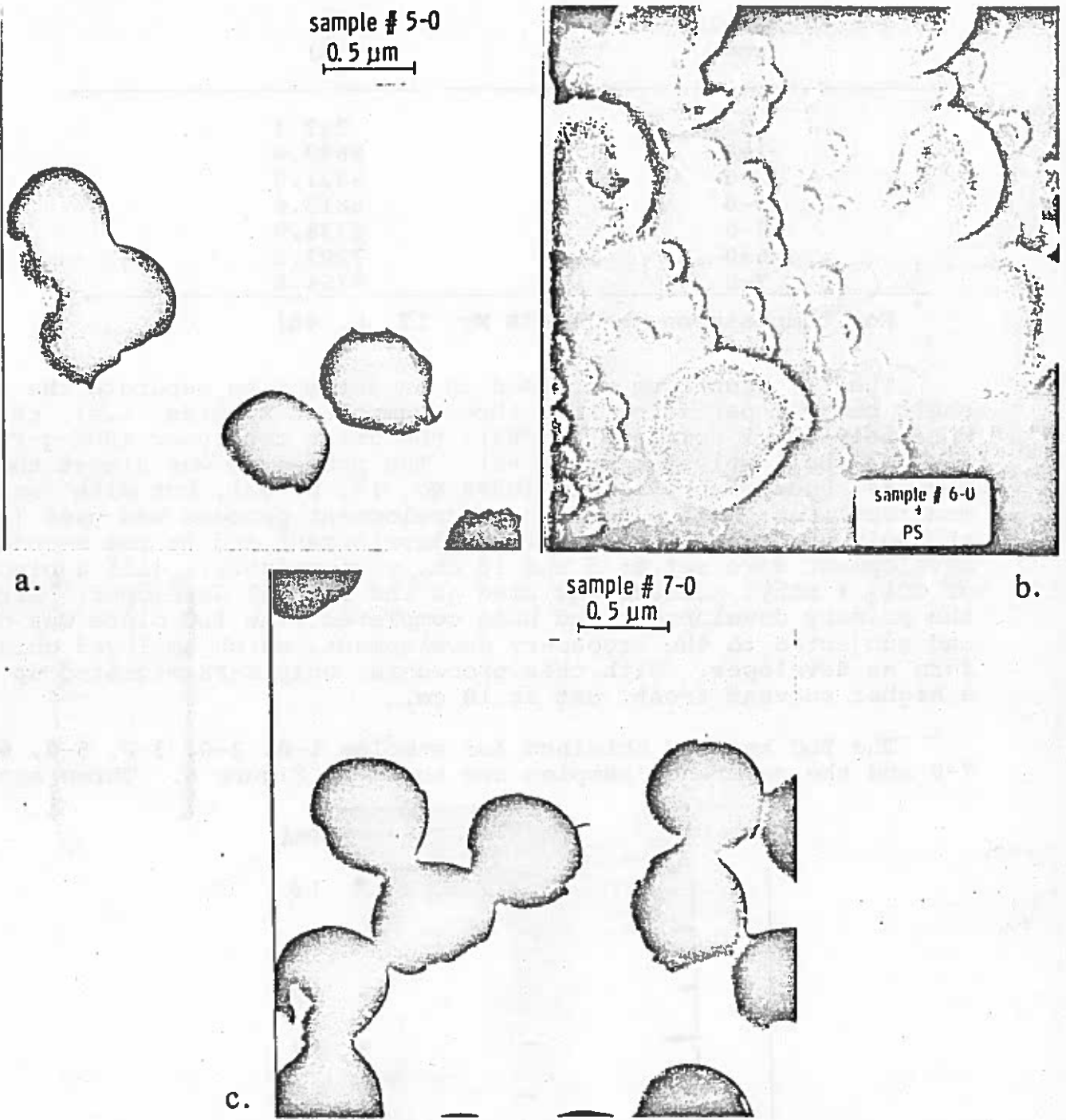*Figure 5:* *Electron micrographs of (a) sample #5-0, PBA/PS (4.5:3.3 by Wt.) core-shell latex particles and in (b) sample #6-0, PBA/ PS (4.5:4.95 by Wt.) core-shell latex particles both prepared in the presence of chain transfer agent (CCl₄) and without emulsifier and (c) sample #7-0, PBA/PS (4.5:?.3 by Wt.) core-shell latex particles prepared with a high concentration of initiator and without emulsifier.*

TABLE I.   RESULTS ON PARTICLE SIZE DETERMINATION BY TEM

| Sample* code | $\overset{D}{\overset{o}{(A)}}$ |
|---|---|
| 0 | 317.1 |
| 1-0 | 8893.6 |
| 2-0 | 6821.3 |
| 3-0 | 6813.6 |
| 5-0 | 6338.9 |
| 6-0 | 7207.3 |
| 7-0 | 6764.5 |

\* For composition see [GRPR No. 17, p. 40]

The TLC technique was used in an attempt to separate the core-shell polymer particles into three component species, i.e., the core-poly-butyl acrylate (C-PBA), the graft copolymer (PBA-g-PS), and the shell-polystyrene (s-PS).  The procedure was almost the same as reported previously [GRPR No. 16, p. 43], but with some modifications:  (i) a two-stage development process was used (e.g., the solvent fronts in the primary development and in the secondary development were set at 5 and 10 cm, respectively); (ii) a binary of $CCl_4$ + Ethyl acetate was used as the initial developer.  After the primary development had been completed, the TLC plate was dried and subjected to the secondary development, which employed chloroform as developer.  With this procedure, only s-PS migrated up to a higher solvent front, set at 10 cm.

The TLC results obtained for samples 1-0, 2-0, 3-0, 5-0, 6-0, 7-0 and the reference samples are shown in Figure 6.  Three spots
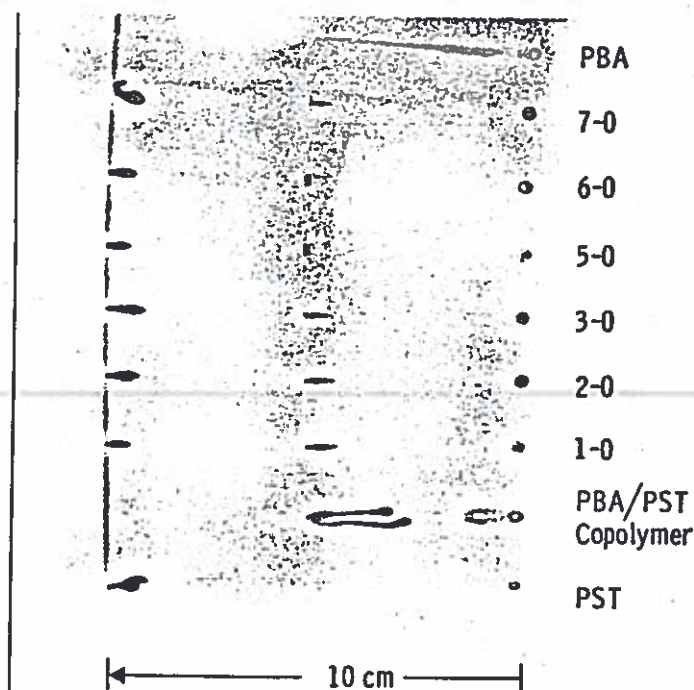


Figure 6:  TLC chromatograms obtained for PBA-PS core-shell composite latex copolymers, #1-0, #2-0, #3-0, #5-0, #6-0, #7-0, and reference samples.

for each core-shell polymer sample appeared on the chromatograms indicating the separation of each sample into three component species, i.e., c-PBA, PBA-g-PS, and s-PS, from right to left in the chromatogram. These results positively indicate that the PBA-PS core-shell particle system prepared in this emulsifier-free emulsion polymerization contains PBA-g-PS graft copolymer chain species.

For quantitative analysis of the chromatograms obtained by the foregoing TLC procedures, the TLC/FID technique as described in the previous report [GRPR No. 16, p. 43] was employed. It was found that the composition of each sample determined by TLC/FID measurement was unexpectedly not in agreement with the values obtained by elementary analysis. Therefore, an attempt was made to estimate the % grafting of PS from the FID-response of the upper part of the chromatogram. The data, summarized in Table II, are difficult to interpret. This might be due to the coagulum of the core-shell latex during the seeded emulsion polymerization.

TABLE II

RESULTS OBTAINED BY TLC/FID FOR PBA-PS CORE-SHELL POLYMERS[1])

| Sample code [3) | PS (wt.fr.)[3) | Upper (mg) | % grafting of PS |
|---|---|---|---|
| 1-0 | 0.3449 | 0.65 | 81.15 |
| 2-0 | 0.5348 | 1.27 | 76.25 |
| 3-0 | 0.5906 | 1.98 | 66.47 |
| 5-0 | 0.5217 | 3.27 | 37.32 |
| 6-0 | 0.6079 | 5.33 | 12.32 |
| 7-0 | 0.4824 | 4.54 | 5.89 |

1) Sample size applied to TLC was 10.0μg.
2) For composition, see [GRPR No. 17, p. 40].
3) Determined by elementary analysis.

Role of Surfactants in Emulsion Copolymerization
(M.P. Merkel, M.S. El-Aasser, J.W. Vanderhoff).

Objective:

To study the effect of surfactant type and concentration on the microstructure of styrene/n-butyl acrylate copolymer latexes.

Progress:

During this period a M.S. thesis was completed by M.P. Merkel, and accepted in fulfillment of the requirement for the M.S. degree. The abstract is as follows:

"The purpose of the present investigation was to study the effect of surfactant type, at a specific concentration, on the microstructure of styrene/n-butyl copolymer latexes.

An emulsifying technique, ultrasonification, at ambient temperature was employed to observe the emulsion stability of a 50/50 wt. percent monomer system of styrene/n-butyl acrylate in a select series of anionic and nonionic surfactants and water at 50% solids.

As the anionic surfactants, a specific class was selected, namely, the Aerosol series of the American Cyanamid Company, being sodium alkyl sulfosuccinates and having a CMC (Critical Micelle Concentration) range of 0.001 to 18.0 wt. percent.

Two series of nonionic surfactants were chosen, namely, the Igepal CO-series of the GAF Corporation, being a homologous series of nonylphenoxypoly(ethylene oxy) ethanols having an HLB (Hydrophile-Lipophile-Balance) range of 4.9 to 17.8, and the Triton X-series of the Rohm and Haas Company, being described as octylphenol ethylene oxide adducts and having an HLB range of 3.6 to 17.9.

The ultrasonification tests revealed emulsion stability (21 hours nonseparation) for the anionic series, in a range of 0.001 to 0.07 wt. percent CMC. For the nonionics, emulsion stability was achieved in the HLB range of 15.3-17.2 (Igepal CO-series) and 13.5 - 17.9 (Triton X-series).

Following the ultrasonification tests and observa-

tions, emulsion polymerizations were conducted by semi-continuous addition method at 30% solids and using potassium persulfate as the free radical initiator. Two very distinct and inversely related physical phenomena were observed. In the Aerosol series, the CMC generally governed the particle size of the resultant emulsion polymer. At a CMC of 18 wt. percent, a particle size of $\bar{D}_W$ 340.5 nm was obtained decreasing to a particle size of $\bar{D}_W$ 61.9 nm at a CMC of 0.05 wt. percent. The molecular weight increased from $\bar{M}_W$ 74,200 at a CMC of 18 wt. percent to $\bar{M}_W$ 751,000 at a CMC of 0.05 wt. percent which is in accordance with the accepted Smith-Ewart polymerization theories.

Similar trends, based on the HLB, were observed for the nonionic Igepal CO-series and the Triton X-series. At low HLB (3.6 and 4.6) large particle size emulsion polymers with low molecular weights were obtained as compared to small particle size emulsion polymers with high molecular weights at higher HLB's (17.8 and 17.9).

Particle size determinations by TEM (transmission electron microscopy) could not be obtained conventionally; polymer particles required high energy irradiation to induce internal crosslinking beyond the deformation temperatures encountered in TEM.

Two other particle size determination methods were used. The first was light scattering, using the dissymmetry method for the smaller size particles and the forward angle ratio method for larger size particles. Results correlate with those of TEM quite well. The third method of particle size determination was by Hydrodynamic Chromatography; again, results are comparable to TEM.

Laboratory surface tension measurements were conducted which conform to published data by manufacturers.

Limited experiments were carried out to characterize the copolymer composition by use of Thin Layer-FID Chromatography".

## Formation and Stabilization of Miniemulsion and Latexes
(W.L. Grimm, Y.T. Choi, T.I. Min, M.S. El-Aasser, J.W. Vanderhoff).

Objectives:

1.  To provide a fundamental understanding of the role of the mixed emulsifier combinations in the formation and stabilization of miniemulsions and latexes.

2.  To investigate the kinetics of styrene mini-emulsion polymerization in the mixed emulsifier systems.

Progress:

During this period an M.S. thesis was completed by W. L. Grimm, for submission to the Department of Chemistry at Lehigh University and the work is being continued by Y. T. Choi. The abstract of the M.S. thesis is as follows:

"Examination of mixed-emulsifier systems of ionic emulsifier with fatty alcohol by means of following the emulsification process by conductometric titration showed a relation between the shape of the conductance curve and the stability of the resulting emulsion. The characteristic shape for a stable emulsion showed, with increasing oil concentration, an initial sharp decrease in conductance followed by an increase and a levelling-off. Emulsions of greatest stability were obtained with a molar ratio of surfactant to alcohol between 1:1 and 1:3, for similar chain lengths of surfactant and alcohol, and for the more insoluble oil phases. A pre-emulsification period of mixing for the surfactant and alcohol in water at a temperature above the melting point of the alcohol of 1.5 hours was found to be necessary.

Polymerization of the emulsion formed at various stages along the conductance curve was carried out for the sodium lauryl sulfate/lauryl alcohol mixed-emulsifier system. Continuously increasing numbers of particles and constant surface for the latex particles were observed.

Measurements of interfacial tension between styrene and aqueous mixed-emulsifier systems by the spinning-drop technique showed unexpectedly large tensions and a maximum value for the molar

ratio forming the most stable emulsions.  The
presence of a tough skin on the oil droplet sur-
face was indicated.

Surface viscosity and elasticity measure-
ments were also made on the aqueous mixed-emulsi-
fier system.  A greater contribution from the
surface viscosity than from the surface elasticity
to the viscoelastic properties of the surface was
observed."

Hydrodynamic Chromatography:  Several Factors Influencing Determination of Particle Size Distribution. (B.M. Secchi, C.A. Silebi).

## Objectives:

1.  To study the recovery of latex particles from HDC columns.

2.  To write a new algorithm for fairly monodisperse samples to be added to the existing computor program for evaluating PSD's from HDC chromatograms.

## Progress:

During this period an M.S. research report was completed, submitted to, and accepted by the Department of Chemical Engineering at Lehigh University.  The report abstract is as follows:

The investigation of the effect of ionic strength, superficial velocity and particle diameter on mass recovery is carried out for the HDC system.

The mass recovery is measured by comparison of the areas of the chromatograms of a sample injected through an HDC column and through a bypass.

The concentration of surfactant is varied in the range 1 mM SLS (sodium lauryl sulfate) up to 0.01 M SLS.

The superficial velocity is in the range between 0.7 cm/m and 2.1 cm/m.  The particle diameter varies between 38 nm and 450 nm.

It has been seen that for particles bigger than 250 nm it is convenient to inject the latex four or five times in a row, due to increased recovery of big particles.

Interception is believed to be the prevailing mechanism for particle capture, instead of Brownian diffusion.

It is also illustrated an alternate algorithm for fairly monodisperse latices introduced in the program for PSD determination.

Coating by Electrodeposition
(A. Hadley, A. Humayun, M.S. El-Aasser, J.W. Vanderhoff).

Objectives:

1. To study and establish the mechanism of film formation in the cathodic electrodeposition of latex systems.

2. To determine the kinetics of film growth during the cathodic electrodeposition process.

3. To develop a latex system which may be applied via the cathodic electrodeposition process to yield a high quality corrosion resistant coating.

Progress:

During this six month period Mr. Arif Humayun completed his M.S. Thesis, which was submitted to, and accepted by the Department of Chemical Engineering. The Thesis Abstract is as follows:

"Most of the fundamental studies of electrodeposition have been carried out with polymer resins that are solubilized with acids or bases, rather than with discrete particles such as latexes. Solubilized polymer resins, when electrodeposited, coalesce easily to form a coherent film which is resistant to the passage of electricity. In contrast, the process of film formation by electrodeposition from a dispersion is more complex, and may be the result of an entirely different mechanism. While the mechanism of film growth from solubilized systems electrodeposited anodically has been fairly well studied, information on the kinetics of cathodic electrodeposition of polymer latexes is practically non-existent.

In the present studies, the kinetics and mechanism of film growth during the cathodic electrodeposition process at constant voltage of an epoxy latex was investigated. Experimental data showed that film growth at the beginning was fast and strongly dependent upon the applied voltage. The film was conducting at this stage. This was followed by a more gradual growth rate at longer deposition times suggestive of consolidation and compaction of the deposited film. During this second stage of film growth, the rate

of growth was independent of the applied voltage
and the film became more insulating. The cur-
rent density - field strength relationship was
non-ohmic in nature. The film mass (or thick-
ness) increased linearly with deposition times
for both stages. A qualitative explanation of
the experimental observations in terms of a
"concentration - accumulation" mechanism was
attempted.

Investigation of the kinetics of film
growth from epoxy resin - curing agent latex
mixtures was also carried out. In contrast to
the epoxy latex system, the film mass for the
two component system was directly proportional
to the deposition time. However, the overall
behavior of the two component system was not
as straight forward as the single component
system. The kinetics of deposition could
perhaps be complicated by the concurrent
heterogeneous flocculation of the mixed latex
particles and the chemical reaction of the
epoxide and amide groups.

An attempt was made to explain the mech-
anism of film formation from this system also
by the "concentration - accumulation" mechan-
ism. This mechanism involves the formation
of a fixed layer of coalesced polymer par-
ticles next to the cathode, and a fluid layer
of uncoalesced particles which could be re-
dispersed. The initiation of coalescence be-
tween the particles in the fixed layer is the
result of the "electrical pressure" associated
with the fluid layer. Weights of the film
deposited at the cathode were found to de-
crease to a limiting value when the films
were left in the bath with the current turned
off (following deposition). This indicates
the redispersion of the particles from the
fluid layer back into the deposition bath.
A mass balance of emulsifier concentration in
the coating bath before and after deposition
also supported the above mechanism.

Preliminary studies on the morphology of
the deposited films indicated that tempera-
ture build up within the film during deposi-
tion affects the coalescence of the polymer
particles."

# POLYMER COLLOIDS AT SYDNEY UNIVERSITY

Reporter:  D. H. Napper

## 1.  ESR of Emulsion Polymerizations

We have recently found that under suitable experimental conditions,
it is possible to detect by ESR the free radicals in styrene and
other emulsion polymerization systems.  By suitable calibration
of the spectrometer it is possible to estimate, albeit with not
very good precision, values for $\bar{n}$ in such systems.  These ESR
values can then be compared with those obtained by kinetic
measurements.  The results obtained thus far show encouraging
agreement between the two techniques.

## 2.  'Inert Diluents' in Seeded Styrene Polymerizations

Azad and coworkers have claimed (ACS 165, 357 (1980)) that inert
diluents (e.g., ethylbenzene) can significantly reduce the rate
of polymerization of styrene in seeded systems when $\bar{n} = 0.5$.
This result, if correct, would be surprising since $\bar{n} = \rho/(2\rho+k)$
in the steady state ($\rho$, $k$ are the entry and exit rate coefficients
respectively).  If $\bar{n} = \frac{1}{2}$, it follows that $\rho \gg k$.  If $\bar{n}$ were reduced
significantly below one-half then $k$ must have been increased
dramatically by the presence of the ethylbenzene.  We have measured
$k$ directly by relaxation methods and can find no evidence for a
dramatic increase in $k$ in the presence of ethylbenzene.  Furthermore
seeded experiments with $\bar{n} \sim \frac{1}{2}$ for styrene fail to display the
reductions in rate reported by Azad et al.  We can, however, observe
the published rate reductions in systems where $\bar{n}$ is significantly
less than 0.5, which is in accord with theoretical expectations.

Polymer Colloid Group Newsletter
Contribution from Fukui University
Fukui, Japan

By M. Nomura

"The 2nd Polymer Microsphere Symposium, Japan" is held in Fukui this fall.
The program is included in this newsletter for reference. Preprints will
be provided in case sombody is interested, though written in Japanese,
please write to Nomura.

## PROGRAM

## 2nd POLYMER MICRSPHERES SYMPOSIUM, JAPAN

### NOVEMBER 11-13

Cosponsored by

The Society of Polymer Science, Japan.
Division of Colloid & Surface Chemistry of
the Chemical Society, Japan.
and four other Societies.

### November 11. Morning Session

| | | |
|---|---|---|
| 9:30 | A-00 | Introductory Remark by Seizo Okamura |
| 9:50 | A-01 | On the Prediction of the Average Number of Radicals per Particle in Emulsion Copolymerization. M. Nomura, K. Fujita . |
| | A-02 | Effect of Methanol on Emulsion Polymerization of Styrene. M. Sugie, I.M.Krieger. |
| 10:40 | A-03 | Emulsion Polymerization of Styrene by High Dose Rate Electron Beams. K. Hayashi, T. Kijima, S. Okamura. |
| | A-04 | Experimental and Simulative Study of Semi-Continuous Emulsion Polymerization. S. Omi et al. |
| 11:40 | A-05 | A Laser Light Scattering Study of Nucleation in Emulsion Polymerization of Methyl Methacrylate. T. Aoyagi, R.M. Fitch. |
| | A-06 | A Kinetic Modelling of the Emulsion Copolymerization of Styrene and Methyl Methacrylate. M. Nomura, et al. |

### November 11 Afternoon Session

| | | |
|---|---|---|
| 1:30 | | Invited Lecture: "Preparation and Properties of Nonaqueous Dispersion Colloids" Ayao Kitahara |
| 2:30 | A-07 | Electrokinetic Studies on the Deposition of Polymer Latices onto Fibers. H. Tamai, T. Suzawa. |
| | A-08 | Stabilization of Latices by Polyelectrolytes. A. Takahashi, et al. |
| 3:20 | A-09 | Introducing High Anionic Character into Styrene Latices Containing Amide Units and Adsorption Flocculation of Their Latices by Polycations. T. Arai, Y. Ootake, M. Akahane. |
| | A-10 | Flocculation of Anionic Latices by Ionene and Ionene Block Copolymer. M. Kawaguchi, Y. Sato, A. Takahashi. |
| 4:20 | A-11 | Flocculation Mechanism of Colloidal Latex Particles by Cationic Polymers. G. Hosokawa, K. Higashitani. |
| | A-12 | Donnan Membrane Equilibrium in Concentrated Latex System. K. Furusawa, S. Yamashita. |
| 5:10 | A-13 | "Two-State" Structure in Polymer Latex Solution. N. Ise, T. Ookubo, K. Ito, M. Sugimura, H.J. Nolte. |
| | A-14 | Reversible Agglomeration with Ordered Structure of Polymer Colloids by Polyelectrolytes. Y. Kobayashi, S. Hachisu. |

## November 12, Morning Session

9:00    A-15   Surface Adsorbability of Homo-and Copolymer Latices. T. Suzawa, H. Shirahama,

         A-16   Preliminary Report on Cationic Charge of Soap Free Cationic Polymer Emulsion. Y. Doi, T. Ikai.

9:50    A-17   Cure Response of Strong Acid Containing Latex. K. Makuuchi, et al.

         A-18   Effect of Crosslinks Distribution in Particle on Mechanical Properties of Latex Film. K. Makuuchi, T. Serizawa, M. Hagiwara.

10:50   A-19   Water-Resistance of PVAc Emulsion Films. T. Sato, T. Okaya.

         A-20   Mechanical Properties of Films from Thermosetting Non-Aqueous Polymer Dispersion. Y. Sasaki, M. Yabuta.

11:40   Invited Lecture: "Application of Latices in Adhesives" Soichi Muroi.

## November 12, Afternoon Session

1:30    Invited Lecture: "Preparation and Application of Monodisperse Particles" John Ugelstad

2:40    A-21   Preparation of Polymer Microsphers Including Hetero-Particles. K. Furusawa, Y. Kimura.

         A-22   Emulsifier-Free Emulsion Polymerization of Styrene and Butyl Acrylate with Poly(methyl Methacrylate)Micro Emulsion as Seed. M. Ookubo, H. Tachika, Y. Itkaku, T. Matsumoto.

3:30    A-23   The Properties of Latex Particles Prepared by Emulsion Polymerization of Tetrafluoroethylene Using Reactive Surfactant. T. Shimizu, et al.

         A-24   Internal Structure of Latex Particles Produced by a Stage Feed Polymerization. H. Hashimoto, S. Muroi.

4:25    A-25   Emulsion Copolymerization of Ethyl Acrylate and Metyl Methacrylate with Alkali Salts of Spiculisporic Acid by Fungi of Penicillium Spiculisporium. S. Yamazaki, Y. Ishigami, Y. Ura.

         A-26   Emulsion Polymerization with High Conversion of Vinyl Acetate in the Presence of Poly(Vinyl Alcohol). S. Hayashi, et al.

6:00    Welcoming Party

## November 13, Morning Session

9:00    B-01   Preparation of Core-Shell Composite Polymer Emulsion Having Temperature-Sensitive Property. M. Ookubo, M. Ando, T. Matsumoto.

         B-02   Localization of Carboxyl Group at Surface Layer of Carboxylated Polymer Particles by Post-Treatment(III). M. Ookubo, M. Miyanaga, Y. Nakamura, T. Matsumoto.

         B-03   Interionic Reactions Catalyzed by Polymer Latices. M. Sugimura, T. Ookubo, N. Ise.

10:10   B-04   Polymer Latices Containing Catalytic Groups of Hydrosis. H. Kitano, Z.-H. Sun, N. Ise.

         B-05   Enzyme Immobilized Polymer Latices. H. Kitano, K. Nakamura, N. Ise.

11:00   B-06   Effect of Chemical Structure of Particle Surface on Interaction between Latices and Proteins, Especially Enzymes. H. Kawaguchi, et al.

         B-07   Immobilization of Enzyme on Polymer-Gel Particles Having Functional Groups on Their Surface. Y. Oostuka, H. Kawaguchi, T. Yamamoto.

12:00   B-08   Adsorption of Enzyme Molecules onto Polymer Microspheres and its Activity (I). M. Ookubo, S. Kamei, K. Mori, T. Matsumoto

         B-09   Adsorption of Enzyme Molecules onto Polymer Microspheres and its Activity(II). M. Ookubo, K. Mori, S. Kamei, T. Matsumoto

November 13, Afternoon Session

1:30 Invited Lecture: "Collidal Systems for Immunological Research and
      Applications" Alan Rembaum.

2:40 B-10 Synthesis and Immunological Applications of Immunolatex Particles.
          T. Suzuta, N. Sibakusa, E. Amano
     B-11 Application of Soap Free Latex to Diagnostics. T. Kuge, et al.
3:35 B-12 Preparation of Microspheres of Poly(glycidyl methacrylate)
          Derivatives and Immobilization of Immunochemicals on Them. S. Hosaka,
          Y. Murao, T. Uchida.
     B-13 A New Photometric Immunoassay of Latex Agglutination Reaction with
          Near Infrared Turbidimetry. S. Tsutsui, et al.
4:40 Closing Remarks by Togoro Matsuo


Current Research Work on Polymer Colloids at Fukui University is:

(1) Kinetic studies on emulsion copolymerization in seeded and
    unseeded systems.

    Study on Styrene-Methyl Methacrylate system was almost over
    and the work on seeded emulsion copolymerization was already
    published in J. Appl. Polym. Sci., 27, 2483 (1982). The work
    on seeded emulsion copolymerization of styrene and methyl
    methacrylate will be presented in AIChE Houston meeting.

(2) Optimal reactors and operation in continuous emulsion
    polymerization

    The validity of the idea presented at Las Vagas meeting
    is experimentally demonstrated.

A REVIEW OF MAIN PROJECTS
IN POLYMER COLLOID RESEARCH
AT THE "LABORATOIRE DES MATERIAUX ORGANIQUES"
( CNRS- VERNAISON - FRANCE)

The group involved in this field is mostly concerned by emulsion copo-
lymers, trying to understand how the introduction of monomer and other
reactives can control the properties of the final materials. For this
purpose, the following areas are systematically investigated :

         ✗ Kinetic and mechanistic studies in emulsion copolymerization
         ✗ Surface and colloidal properties of latexes
         ✗ Influence of the emulsion process on the particle morphology,
           structure and properties of polymer materials.

Different projects are being developped :

1) Thermodynamic approach for emulsion copolymerization

Based on the equality of the chemical potencials of each species in the
different phases, this thermodynamic approach, was found to be an appro-
priate way for predicting the evolution of monomer mixture and of the
resulting copolymer as polymerization proceeds. A simulation model was
achieved and applied to several systems (acrylonitrile-styrene; vinyl-
acetate-butylacrylate). Work is actually directed in view of modifying this
model in order to predict the morphology of polymer particles as function
of many parameters.

2) Control of polymerization process:

With the objective of preparing copolymers of a constant composition, two
main processes are currently carried out, based on the knowledge of the
factors controlling the process : corrected batch process and several
semi-continuous methods of monomer addition.
Correlations are being investigated between the copolymer composition and
microstructure and different polymer film properties (mostly thermal and
mechanical).

3) <u>Control of particle size and surface properties</u>   in copolymer latexes

As a part of a program to develop a study on the molecular and colloidal
properties of copolymer latexes in relation with their surface properties
the preparation of (styrene-butyl acrylate) is being done , using a
copolymers
surfactant -free process : the first objective is to examine the effect
of copolymer composition on the kinetics and nucleation process during
the polymerization as well on the colloidal characteristics  of the latexes.

Another project is related  to the introduction of functional comonomers in
acrylate copolymer latexes in order to control and optimize the surface
properties. A simulation program able to modelize the polymerization of
these comonomers is in progress.

4) <u>Inverse  emulsion copolymerization</u>

A research program has been started in this area and copolymerizations
of acrylamide with some ionic comonomers are being studied. Specific
problems of this process are particularly examined in order to control
the structure of the polymer latexes (molecular and compositional homo-
geneity of the polymer chains-colloidal properties of the latex).

5) <u>Oligomeric emulsifiers</u>

Using a  radical oligomerization process of hydrophilic monomers in the
presence of long hydrocarbon chain mercaptans, the synthesis of amphiphilic
molecules has been developped. Control of the process based on a simula-
tion model of the transfer reactions, results in a better homogeneity of
the products. Physicochemical and micellar properties  of acrylic acid
(and acrylamide) oligomers have been otained. Applications of these well-
characterized surfactants in the field of  emulsion polymerization are
being investigated.

Contribution from The University of Akron

by I. Piirma

## Polymerization of Acrylamide in Water-in-Oil Microemulsion
Mu-Yen Wu

The kinetics of polymerization of acrylamide using AIBN as initiator was found to follow the kinetics typical of bulk polymerization. The rate was found to be proportional to the square-root of the initiator concentration, and 1.8 power of the monomer concentration.

The chain transfer constants of the two "cosurfactants" used were found to be $5.2 \times 10^{-5}$ for hexanol and $3.0 \times 10^{-5}$ for octanol.

The molecular weights of the polyacrylamides were found to be dependent on the microemulsion particle size, the molecular weight decreasing with decreasing particle size. The intrinsic viscosities were determined in 1N NaNO$_3$ aqueous solutions and the equation

$$[\eta]^{30°C}_{1N\ NaNO_3} = 3.73 \times 10^{-4}\ M_w^{0.66}$$

was used for the molecular weight calculations. With hexanol as cosurfactant the molecular weights varied from $0.28 \times 10^6$ to $1.15 \times 10^6$.

The polymerization of acrylamide with ACVAK [4.4'-azo bis(4-cyanovaleric acid) potassium salt] as water soluble initiator was also studied in this microemulsion system. The kinetics of the polymerization was again found to follow the bulk kinetics under comparable conditions. The polymerization with ACVAK as water soluble initiator showed higher rates of polymerization than those of polymerizations with AIBN as oil-soluble initiator.

## Emulsion Polymerization of Styrene
Sam Kincaid

a) Dependence of Molecular Weight on Particle Size

In the enclosed Figure 1, the plot of the degree of polymerization versus particle diameter shows that the molecular weight decreases as the particle size becomes larger, i.e. as the number of particles decrease

The measurements of particle size, molecular weight, and polymerization rate were used to calculate values for the kinetic parameters which determine the dependence of molecular weight on particle size. The domina parameter is the time between entry of radicals into a particle and its dependence on the number of particles. However, the results also showed that the average number of radicals per particle contributed to the change in molecular weight with particle size. For polymerizations with final particle diameter larger than 170nm, the average number of radicals per particle was larger than one-half and increased with particle size.

At 60°C the propagation rate constant was found to be 415 $\pm$ 20$\ell$/mol-sec, and the constant of chain transfer to monomer was determined to be $1.3 \times 10^{-5}$. For an initiator concentration of 0.0137M, the results showed that the overall rate of radical absorption ($\rho_A$ is equal to $1.22 \times 10^{-7}$ mol/$\ell$H$_2$O-sec and is independent of particle size and number. Thus, $\rho_A$ is equal to the rate of production of radicals in the aqueous phase, and does not affect the dependence of molecular weight on particle size.

b) Number of Particles

In the previous Newsletter a plot was presented of N vs percent conversion for 1.0, 1.67 and 3.0% surfactant solutions. At these concentrations of mixed emulsifier, the number of particles passed through a maximum at low conversions and then became constant to yield highly monodisperse latexes. In polymerizations with higher concentrations of the mixed emulsifier (ranging in our studies from 4.5 to 10.0%) the number of particles increased throughout the polymerization to yield broad particle size distributions.
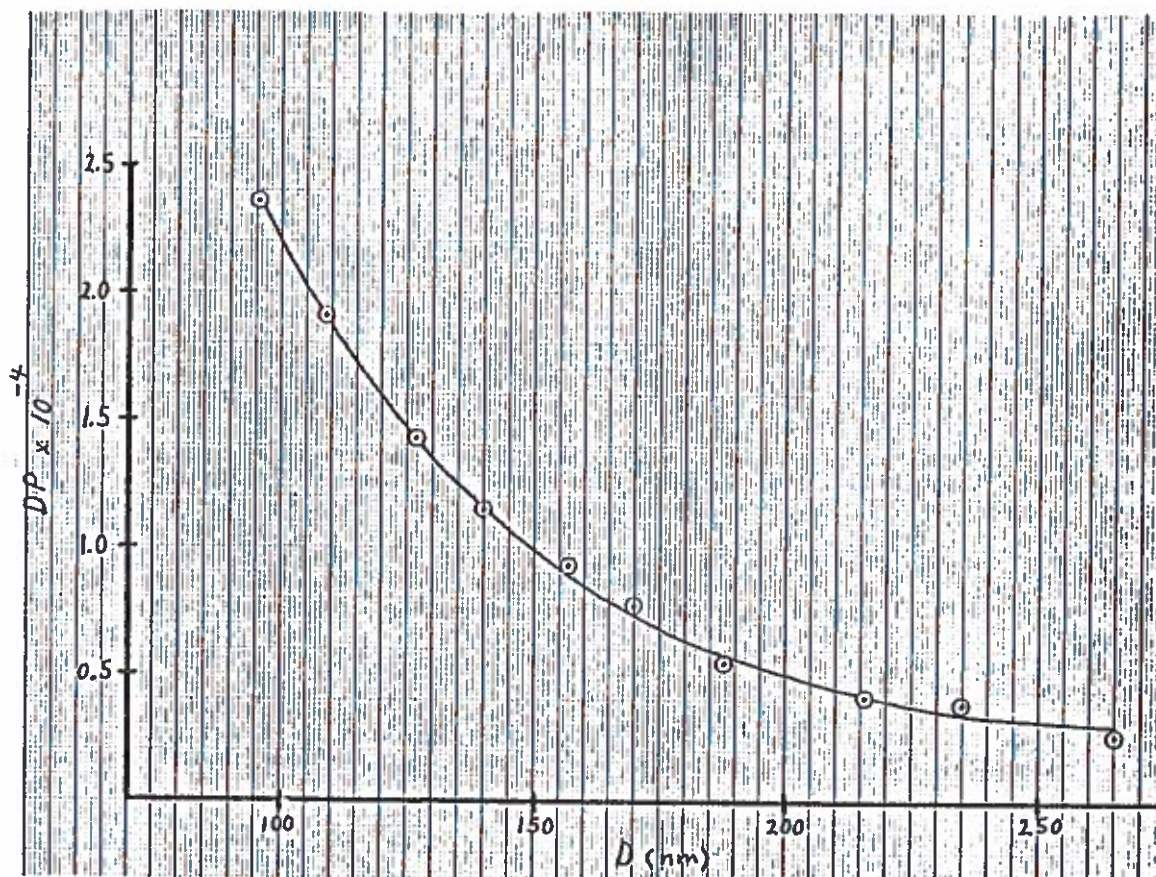


Figure 1. Degree of Polymerization vs. Particle Size

## Emulsion Polymerizations with Nonionic Surfactants
a) Tien-Chieh Chao

The studies of styrene polymerization with the nonionic surfactant Emulphogene BC-840 showed bimodal particle size and molecular weight distributions. It is therefore the aim of this study to systematically investigate a large number of chemically different nonionic emulsifiers in the polymerization of styrene, to establish what causes this unusual kinetic behavior. There are several parameters which can be utilized for the selection of nonionic surfactants, e.g. HLB values, PIT method, etc. We found that the HLB values of nonionic surfactants are the most convenient and well developed parameter in this regard. Therefore, in our study all the kinetic data, i.e. the polymerization rate, emulsion stability, etc., will be compared with the change of HLB values.

The reaction conditions in our study will be at 50°C with the HLB range of the nonionic surfactants being employed from 8 to 18. Initiator used is potassium persulfate and water to monomer ratio varies from 2.2

to 9. The polymerization rates will be investigated and the particle sizes and molecular weights will be checked. Different kinetics is expected because of their solubility in water and stability mechanism are all quite different from that of the ionic surfactants.

b) Tai Shih Maw

The other phase of the same study has been the evaluation of monomers other than styrene in their polymerization behavior in the presence of Emulphogene BC-840. It was found previously that bimodal particle size distributions always showed two constant rate regions in the percent conversion vs. time plots. Thus, the preliminary screening of the monomers was done with the rate studies. Of the three para-substituted styrenes i.e. butyl, methyl and chloro, only p-chlorostyrene showed two constant rate regions (Figure 2).

The temperature in styrene polymerization with BC-840 shows clearly how the solubility of the surfactant affects the different rate regions (Figure 3). As the reaction temperature is lowered from 60°C to 40°C, there is a gradual disappearance of the bimodal behavior, which is also reflected by the rate ratio of the two regions (Figure 4).
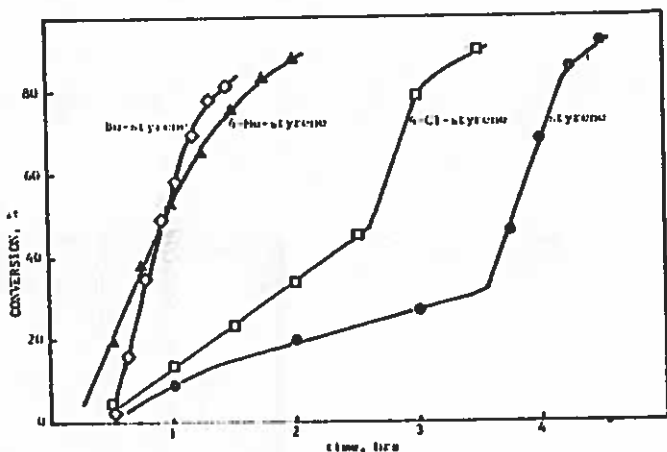


Figure 2.--Conversion-time curves of emulsion polymerization of styrene derivatives at 50 degrees. Emulphogene BC-840,3.0 g, water,55.0 g, $K_2S_2O_8$,0.188 g and monomer, 0.192 mole.
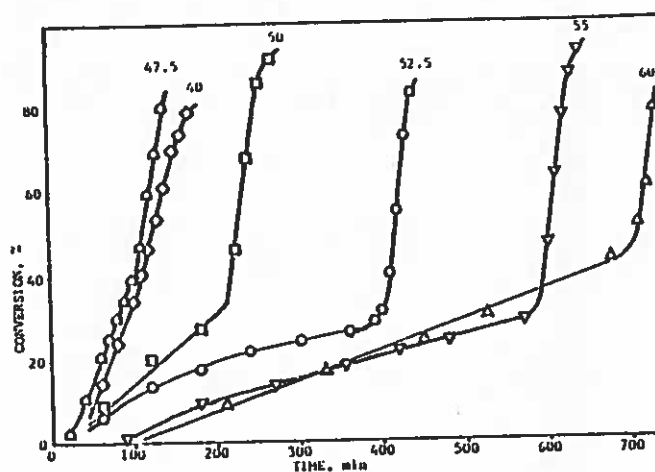


Figure 3.--Kinetics of the emulsion polymerization of styrene at different temperatures. Emulphogene BC-840,3.0 g, water,55.0 g, potassium persulfate 0.188 g and styrene,25.0 g. Temperature(°C),○, 40.0; △, 47.5; □, 50.0; ○, 52.5; ▽, 55.0 and △, 60.0.
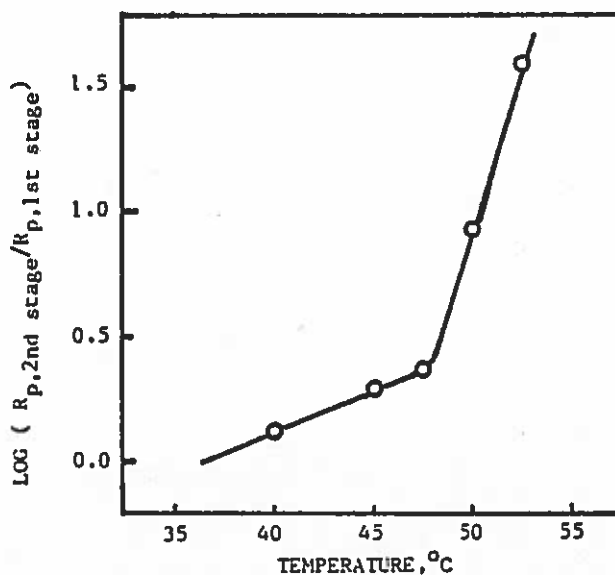


Figure 4.--Polymerization rate of styrene at different temperatures. Emulphogene BC-840,3.0 g, water,55.0 g, $K_2S_2O_8$,0.188 g and styrene,20.0 g.

# NUMERICAL ANALYSIS OF VINYL CHLORIDE EMULSION
# POLYMERIZATION IN A STEADY-STATE SEEDED CSTR

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A theoretical model from previous work [G. W. Poehlein, et al., Brit. Polym. J., In press (1982)] has been developed to predict the particle size distribution (PSD) of the latex product from a steady-state polydisperse-seeded continuous reactor. Simulations were carried out by adapting the reaction conditions of vinyl chloride emulsion polymerization reported by Berens [J. Appl. Polym. Sci., 18, 2379 (1974)]. Fig. 1 shows the normalized experimental PSD's of the seed and steady-state latex product in a single continuous reactor.

Our new model was applied to fit the effluent PSD data published by Berens. In the computer simulations, the termination parameter in the aqueous phase, $Y_c$, was assumed to be zero and other required parameters were computed from Berens' reaction conditions. The fitting procedure involved the variation of only one parameter, $\gamma$, which accounts for the radical desorption from polymer phase. Figures 2 and 3 show some

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of the simulation results of this fitting procedure. The "deviation" shown in the figures represents the area between the simulated and experimental PSD's. The jagged simulation curve is due to our calculation procedure, which involves the division of the seed PSD into twelve monodisperse slices.

One possible reason for the deviation could be that the model conditions were not satisfied by experiment. The experimental PSD data shown in Fig. 1 indicates the product PSD has a particle concentration at the small-size region of the distribution higher than that of the feed seed. The data shown suggest that new particles might be nucleated in the reactor. Another possible reason for the deviation could be the incorrect model components. In our original model, the radical absorption was derived based on continuum diffusion theory. However, Gardon [J. Polym. Sci., A-1, 6, 623 (1968)] and some other resarchers suggested that the rate of radical diffusion flux should be constant. This alternate model was examined by using the same kinetic parameters shown in Fig. 3 and the results are presented in Fig. 4. Apparently, the fit is not as good as shown in Fig. 3. In fact, the shape of the PSD is skewed more toward the large particles and is deviated further from the experimental data. Thus, the continuum diffusion model would seem to be more appropriate than the constant-flux model.