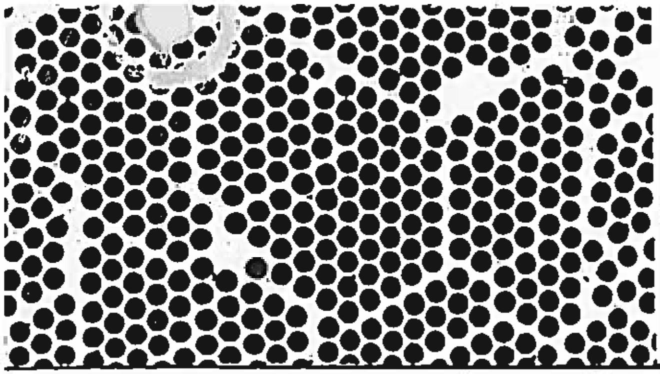

Secretary: D H Napper
School of Chemistry
University of Sydney
NSW 2006
Australia

IPCG

INTERNATIONAL POLYMER COLLOIDS GROUP

NOVEMBER 1992

VOLUME 23 NUMBERS 1/2

NEWSLETTER

INDEX

FROM THE EDITOR'S DESK

THE MISSING NUMBER 1

Many members were concerned that Volume 22 Number 1 did not appear. Unfortunately, the response of contributors was marginal so far as justifying the production of a Newsletter. The contributions submitted then have been held over to this issue.

MEMBERSHIP

Changes of Address

Please note that Dave Bassett has transfered from South Charleston, W Va to UCar Emulsions in Cary, NC. His new postal address is : 410 Gregson Drive, Cary, NC 27511, USA (Ph: (919) 469–6751). Also note that David Blackley's revised address is : School of Polymer Technology, University of North London, 166–220 Holloway Rd, London N7 8DB, UK. Their new FAX numbers are included in the lists in this Newsletter. Klaus Tauer's new address is : Max Planck Institut für Kolloid und Grezflachenforshung, Kantstrasse 55, DO 1530 Teltow–Seehof, Germany.

Retirements

Ron Ottewill, one of IPCG's founding fathers, has formally retired from his Chair at the University of Bristol but will keep active at Bristol in colloids with his SERC and LINK funded programs. David Blackley has also formally retired but will continue his association with the University of North London. Professor V Eliseeva has retired from her post as Head of the Laboratory of the Institute of Physical Chemistry of the Russian Academy of Sciences. Members of the IPCG will unite in wishing all of these esteemed colleagues a long, fruitful and happy retirement.

Book

Sandy Dunn has brought to my attention Jaro Barton's new book *Radical Polymerization in Disperse Systems*, 700 pp ISBN 013752 353X Ellis Horwood (coauthored with I Capek) which was due out at the end of October. Cost £55. Incidentally, Sandy's correct FAX number is also given later in this Newsletter.

Update of Membership List

This will be done in the next Newsletter.

CONFERENCE SCHEDULE

Please note that information about various relevant conferences are included in this newsletter. Especially note the details of the Polymeric Surfactants symposium at the Denver, ACS meeting in March/April 1993 with Irja Piirma as one of the coorganizers. A preliminary program is also included of the 68th Colloid & Surface Science Symposium to be held at Stanford in 1994, chaired by Alice Gast.

ACTIVITY RESPONSE SHEET

An Activity Response Sheet is included in this mailing for return to the Editor by the end of February 1993.

NEXT NEWSLETTER

Copy for the next Newsletter should reach me by 30 April, 1993.

DHN

CONFERENCES

1993

CONFERENCE	LOCATION	DATE/CONTACT
205TH ACS National Meeting	Denver	28 March – 2 April
Surfactant Behaviour	Strasbourg	14 – 17 April
ACS	Toronto	20 – 22 June (van de Ven)
Short Course on Emulsion Polymerization	Lehigh	27 June – 2 July (El–Aasser)
9th Gordon Research Conference	Tilton	27 June – 2 July (Bassett)
206th ACS National Meeting	Chicago	22 – 27 August
Polymers at Interfaces	Bristol	8 – 10 September
Physical Aspects of Polymer Science	Reading	15 – 17 September

1994

207th ACS National Meeting	San Diego	13 – 18 March
Copolymerization in Dispersed Media	Lyon	18 – 22 April (Pichot)
68th Colloid & Surface Science Symposium	Stanford	19 – 22 June (Gast)
35th IUPAC Macromolecules Symposium	Akron	11 – 15 July
208th ACS National Meeting	Washington	21 – 26 August

Newsletter Contribution

Announcement - A Symposium has been scheduled on POLYMERIC SURFACTANTS: 1. at interfaces 2. in heterophase polymerizations, 3. as compatibilizers

for the American Chemical Society Meeting in Denver, Colorado March 28 - April 2, 1993
The Symposium organizers for the ACS Division of Industrial and Engineering Chemistry are I. Piirma and H. M. Cheung of the University of Akron.

Speakers and Topics include:

1. Jaan Noolandi, Xerox Corp. Canada, "Multiblock Copolymers as Polymeric Surfactants: Are "pancakes" better than "dumbbells"?
2. R. Ibbett, S. Reveley, E. A. W. Dunk, Courtaulds Coatings "Carbon 13 NMR Studies of the Surfactant Behavior of a PEO/PPO/PEO Triblock Copolymer in Water and in Emulsions of Water and Methyl Methacrylate"
3. David Hunkeler, Jose Hernadez-Barajas, Vanderbilt University, "The Chemical and Physical Roles of Surfactants in Heterophase Water-in-Oil Polymerizations"
4. C. Pichot, M. T. Charreyre, J. Revilla, Th. Delair, P. Boullanger, B. Gallot, CNRS, Biomerieux "Synthesis of Surface Active (Macro)monomers and the Preparation of Bioreactive Latex Particles"
5. D. Cochin, R. Zana, F. Candau, CNRS, Institut Charles Sadron, "Polymerization of Micelle-forming Monomers"
6. R. Varoqui, CNRS, Institut Charles Sadron "Structural and Kinetic Properties of Water Soluble Polymers at Solid/Liquid Interfaces"
7. C. Yeung, A. C. Balazs, D. Jasnow, University of Pittsburgh, "Lateral Instabilities in a Grafted Layer in a Poor Solvent".
8. M. B. Urquiola, V. Dimonnnie, E. D. Sudol, M. S. El-Aasser Lehigh University, "The Role of the Interface in the Emulsion Copolymerization of Vinyl Acetate With the Polymerizable Surfactant Sodium Dodecyl Allyl Sulfosuccinate"
9. M. D. Foster, M Sikka, N. Singh, F. S. Bates, S. Satija, C. F. Majikzak, The University of Akron "Polyolefin Block Copolymers Near Interfaces"
10. X. Wu, R. H. Pelton, A.E. Hamielec, W. McPhee, D. R. Woods, McMaster University, "The Kinetics of Poly(N-Isopropylacrylamide) Microgel Latex Formation"
11. A. H. Talhi, F. J. Bonner, Univ. of Massachusetts "Effect of Stabilizer and Stirring Speed in Suspension Polymerization"
12. S. Datta, D. J. Lohse, Exxon Chemical Co., "Graft Copolymer Compatibilizers for Blends of Isotactic Polypropylene and Ethene-Propene Copolymers"

Pure and Applied Aspects of Surfactant Behaviour

1st CIRCULAR

14-17th April 1993
Centre Cultural St Thomas
Strasbourg

A meeting is being organised jointly by the Colloid and Interface Science Group (CISG) and the Fast Reactions in Solution Group (FRIS) on the broad topic of surfactants. The aim is to bring together researchers in university together with industrial scientists to discuss topics of mutual interest.

Accommodation will be arranged in the Cultural Centre and the provisional programme is as indicated below. The expected attendance is 100-120 participants.

Wednesday April 14	Arrival, Registration, Reception in Evening	
Thursday April 15	*AM*	Properties of Surfactants I
	PM	Dynamic Aspects
	Poster Session	
	Conference Dinner	
Friday April 16	*AM*	Industrial Aspects
	PM	Properties of Surfactants II
	16.00	Close of Meeting

The programme will be made up in part by invited speakers but a number of slots will be available in response to a call for papers (see below). The registration fee for CISG/FRIS members is expected to be ~£35 (non-members £45). The costs for accommodation (2 nights) and meals (including Conference Dinner) will be ~£75. The local organiser is Professor Raoul Zana.

If you would like to contribute a paper and/or receive the 2nd circular please complete the tear-off form below and return to Professor B.H. Robinson. Please return by mid-July.

	Yes	No
I would like to receive the 2nd circular	☐	☐
I expect to attend the meeting	☐	☐
I would like to present a 20 minute paper*	☐	☐
I would like to present a poster	☐	☐

*If yes, please provide title and half page abstract

Name: ....

Address: ....

Tel: .... Fax: ....

Please return to:

Professor B H Robinson
School of Chemical Sciences
University of East Anglia
NORWICH
NR4 7TJ
UK
Telephone: 0603 592007 Fax: 0603 259396

Bristol September 8-10 1993
Polymers at Interfaces

UNDER THE AUSPICES OF THE MACRO GROUP OF THE SOCIETY OF CHEMICAL INDUSTRY UK AND IN ASSOCIATION WITH THE ROYAL SOCIETY OF CHEMISTRY AND IACIS

An International meeting on all aspects of the Interfacial Behaviour of Polymers.

The meeting is the third in a series which began with the meeting in London in 1981 on the Effect of 'Polymers on Colloid Stability' . The second in this series was held a Veldhoven in The Netherlands in 1987 on 'Polymers in Colloid Systems: Adsorption Stability and Flow'. The third meeting will be held in Bristol in the new Conference Centre in Wills Hall. The format of the meeting will be rather similar to the last and will comprise of a 20 minute presentation followed by a 40 minute discussion. In the discussion period there will be an opportunity for making short contributions of approximately 5 mins. The major papers will be pre-printed but all papers will appear in a special issue of Colloids and Surfaces. The meeting will be broken down into the following sessions. 1] Structure of the Interfacial Region. 2] Dynamic Effects in Polymer Adsorption 3] New Methods and Techniques for Studying Polymer Adsorption. 4] The Structure of an Adsorbed Polymer layer under Constraint. 5] Polymers and Dispersion Stability.

The numbers of places at the meeting will be limited so ***BOOK*** **early!**. Please give a FAX number and if possible a BITNET number. You may either mail the form below to me : **Terence Cosgrove, School of Chemistry, University of Bristol, Cantock's Close Bristol BS8 1TS.** or send it by **FAX on 44 272 250612** [UK] or by **EMAIL to COSGROVE@UK.AC.BRISTOL.SIVA**

PLEASE SEND ME MORE INFORMATION ON THE BRISTOL MEETING

NAME:..

AFFILIATION:..

ADDRESS:..

....

FAX NO:................................BITNET:...

PREFERRED PRESENTATION [LONG/SHORT/POSTER YES/NO] AND TITLE

....

68th COLLOID AND SURFACE SCIENCE SYMPOSIUM

Stanford University, June 19-22, 1994

Supported by a grant from the Henkel Corporation with additional support from Stanford University Industrial Affiliates Program.

Preliminary Program

CHAIRPERSON Professor Alice P. Gast, Stanford University

SESSIONS AND CHAIRS

- **Polymers at Interfaces**

Curtis W. Frank	ChE, Stanford University	(415)723-4573	cwf@rio.stanford.edu
Ravi Sharma	Eastman Kodak Company	(716)477-8261	ravi.sharma@kodak.COM

- **Rheology**

Andrea W. Chow	Lockheed	(415)424-2015	
Eric Shaqfeh	ChE, Stanford University	(415)723-3764	eric@ajax.stanford.edu

- **Dynamics, Aggregation and Flocculation**

Robert Pecora	Chemistry, Stanford University	(415)723-0681	
Charles F. Zukoski IV	ChE, University of Illinois	(217)333-7379	

- **Physics of Proteins at Interfaces**

Robert Tilton	ChE, Carnegie Mellon University	(412)268-2230	tilton@andrew.cmu.edu
Abraham Lenhoff	ChE, University of Delaware	(302)831-8989	lenhoff@che.udel.edu

- **Interfacial Fluid Dynamics**

George M. Homsy	ChE, Stanford University	(415) 723-2419	bud@thelimit.stanford.edu
Sandra J. Troian	Exxon	(908)730-2260	stroian@erenj.bitnet

- **Nucleation Symposium**

Joseph L. Katz	ChE, The Johns Hopkins Univ.	(301)516-8484	

- **Thin Films and Self-Assembly**

Clayton J. Radke	ChE, Univ. of California, Berkeley	(510)642-5204	
David Devore	Henkel Corporation	(215)628-1586	

- **Catalysis - Symposium honoring Michel Boudart on his 70th Birthday**

Robert J. Madix	ChE, Stanford University	(415)723-2402	rjm@rio.stanford.edu
Dan Sajkoski	Amoco Oil Comapny	(708)961-7755	

- **Electron Microscopy of Complex Fluids**

Ishi Talmon	The Technion, Haifa	CERITIT@TECHNION.BITNET	
John Minter	Kodak Research Labs	(716)722-3407	minter@kodak.com

- **Microemulsions and Complex Fluids**

John S. Huang	Exxon Research and Engineering	(908)730-2865	JSHUANG@ERENJ.BITNET
Eric Kaler	ChE, Univ. of Delaware	(302)831-3553	kaler@che.udel.edu

- **General papers**

Anastasia Morfesis	PPG Industries	(412)967-2122	
Dennis Prieve	Carnegie Mellon University	(412)268-2247	

International Polymer Colloids group meeting

Irsee, Germany. Sept 16 1992

present: Barton, van de Ven, Ottewill, Nomura, Asua, Okubo, Tauer, Guillot, Candau, Hansen, German (Chair), Fitch, Gilbert, El-Aasser, Joosten.

Membership

It was agreed that the following be invited to join the group:

Jaromir Snuparek, Peter Lovell, Martien Cohen-Stuart, Sunil Jayasuriya, Gregor Ley (with a letter to Kast first of all to ask if this would be acceptable to BASF). These people will be notified by letter from Napper.

Invitation to attend next meeting (New Hampshire) will be issued to Roque Hidaldo.

It was agreed that the membership list will be updated by sending around a Response Form to each present member asking if they wish to continue as members of the Group. Suggestions for new membership would also be sought in this response form.

Alternate Members will be added to the mailing list to receive all information in the same way as normal members.

Future meetings

Gordon Conference June 27-July 2 1993 (Basssett).

ACS Toronto June 20-22 1993 (van de Ven).

National colloids meeting Stanford 1994 (Gast). Napper to send letter to Gast to check on status.

Lyon April 18-22 1994 Copolymerization in Dispersed Media (Guillot).

Gordon Conference 1995 (van de Ven).

In 1996: the preference is the following: (1) NATO 2 weeks Advanced Study Institute; (2) European Gordon Conference; (3) European Science Foundation Meeting. Asua to be Chair. Preference for European Gordon Conference every 4 years. At business meeting on Friday morning (all attendees), Tauer was voted Vice-Chair for next European Gordon Conference meeting (Chair for subsequent meeting, presumably in 2000).

Newsletter

To be continued as before. Gratitude expressed to Napper and Ottewill for their hard and effective work.

IPCG Membership FAX Numbers

JM Asua	34–43–21–2236
J Barton	42–7–37–5923
DR Bassett	1–919–469–6797
DC Blackley	44–71–753–5081
F Candau	33–88–41–4099
JS Dodge	1–216–933–0509
AS Dunn	44–61–236–7677
MS El–Aasser	1–215–758–5880
VI Eliseeva	7–095–230–2332
AP Gast	1–415–725–7294
AL German	31–40–44–2576
RG Gilbert	61–2–692–3329
JW Goodwin	44–272–25–1295
A Hamielec	1–416–528–5114
FK Hansen	47–2–45–5441
H Kast	49–621–609–2505
Do Ik Lee	1–517–638–7510
J Lyklema	31–83–708–3777
S Muroi	81–462–21–7212
DH Napper	61–2–692–3329
M Nomura	81–776–8767
RH Ottewill	44–272–25–1295
R Pelton	1–416–521–1350
C Pichot	33–72–72–8080
I Piirma	1–216–972–5290
GW Poehlein	1–404–894–3120
G Riess	33–89–59–9859
WB Russel	1–609–258–6744
PR Sperry	1–215–592–3377
VT Stannett	1–919–737–3465
PJ Stenius	46–820–8998
DC Sundberg	1–603–862–3564
K Takamura	1–519–332–5933
RE Uschold	1–302–695–3645
A Vrij	31–30–52–1877
TGM van de Ven	1–514–398–7249
JW Vanderhoff	1–215–758–5423
JA Waters	44–753–57–8218
M Winnick	1–416–978–8775

INTERNATIONAL POLYMER COLLOIDS GROUP NEWSLETTER

Contribution from the Grupo de Ingeniería Química, Facultad de Ciencias Químicas, Universidad del País Vasco, Apdo. 1072, 20080 San Sebastián, Spain.

Reporter: José M. Asua

HIGH SOLIDS CONTENT BATCH MINIEMULSION POLYMERIZATION

(Lourdes López de Arbina and José M. Asua)

The feasibility of obtaining high solids content latexes through miniemulsion polymerization was investigated. It was found that, for the batch terpolymerization of styrene, 2 ethyl hexyl acrylate and methacrylic acid, coagulum free 60 wt% solids content latexes can be obtained through the miniemulsion process whereas the maximum coagulum free solids content latex attainable by means of conventional emulsion polymerization was 50 wt%. The effect of the type and amount of surfactant, amount of cosurfactant and sonication time on both the amount of coagulum and particle size was studied. In addition, the chemical, freeze-thaw and mechanical stabilities of the latexes were determined.

SEMICONTINUOUS MINIEMULSION TERPOLYMERIZATION: EFFECT OF THE OPERATION CONDITIONS

(María J. Unzué and José M. Asua)

The effect of solids content, initiator concentration, feed flow rate and amount of cosurfactant on the kinetics of the high solids content semicontinuous miniemulsion terpolymerization of butyl acrylate, methyl methacrylate and vinyl acetate was studied. In addition, the effect of the operation variables on the feasibility of obtaining a 65 wt% solids content latex with low amount of coagulum was investigated. The operation variables studied were: i) Partition of the monomer between the initial charge and the feed, ii) type and concentration of emulsifier, iii) feed flow rate, and iv) sonication.

A COMPARISON BETWEEN MINIEMULSION AND CONVENTIONAL EMULSION TERPOLYMERIZATION OF STYRENE, 2-ETHYLHEXYL ACRYLATE AND METHACRYLIC ACID

(Juan A. Masa, Lourdes López de Arbina and José M. Asua)

The kinetics of the high solids content miniemulsion terpolymerization of styrene, 2-ethyl hexyl acrylate and the methacrylic acid and the final properties of the latexes produced by this method were compared with those resulting from the corresponding conventional emulsion polymerization process. The final latex properties considered were: latex viscosity both prior and after neutralization, mechanical stability, chemical stability, and freeze-thaw stability.

ON-LINE MONITORING OF CONVERSION AND POLYMER COMPOSITION IN EMULSION POLYMERIZATION

(José R. Leiza, J. C. de la Cal, M. Montes and José M. Asua)

A polymerization reactor equipped with an automatic sampling system was developed for on-line monitoring of conversion and polymer composition in emulsion polymerization systems. The sampling device withdraws a sample from the reactor by using vacuum and introduces it into a dilution loop. After homogenization, the diluted sample is automatically injected to a gas chromatograph where the residual monomer is analyzed. This measurement and the monomer material balance in the reactor are combined to calculate the conversion and the polymer composition. The accuracy of the on-line G. C. measurements of conversion and polymer composition was checked by comparison with those obtained by gravimetric and proton nuclear magnetic resonance spectroscopy. The robustness of the instalation was demonstrated by carrying out 10 consecutive semicontinuous emulsion copolymerizations taking about 15-20 on-line samples per reaction without any problem in the sampling, dilution and analysis system. The ability of the equipment to handle high solids content latexes was showed during the 55 wt% solids content seeded semicontinuous emulsion terpolymerization of methyl methacrylate, butyl acrylate and vinyl acetate.

INTERNATIONAL POLYMER COLLOIDS GROUP NEWSLETTER

Contribution from the Grupo de Ingeniería Química, Facultad de Ciencias Químicas,
Universidad del País Vasco, Apdo.1072, 20080 San Sebastián, Spain.

Reporter: José M. Asua

ON-LINE COPOLYMER COMPOSITION CONTROL IN THE EMULSION COPOLYMERIZATION OF ETHYL ACRYLATE AND METHYL METHACRYLATE

(José R. Leiza, José C. de la Cal, Gregorio R. Meira and José M. Asua)

A closed-loop strategy for copolymer composition control in emulsion polymerization systems is presented. This strategy is based on a non-linear adaptive plus proportional-integral controller that calculates the flow rate of the more reactive monomer to be added into the reactor to produce a copolymer of a given composition. The non-linear adaptive part of the controller is based on a simplified mathematical model of the process that includes an on-line adjustable parameter. A conventional proportional-integral feedback controller is also incorporated to eliminate the offset produced by the non-linear part. The controller was checked by computer simulation and also experimentally verified during the emulsion copolymerization of ethyl acrylate and methyl methacrylate carried out in a computer controlled experimental setup using both purified and technical grade monomers.

INTERNATIONAL POLYMER COLLOIDS GROUP NEWSLETTER

Contribution from the Department of Polymerization Reactions, Polymer Institute, Slovak Academy of Sciences, Dúbravská cesta 9, 842 36 Bratislava, Czech and Slovak Federative Republic

Reported by J. Bartoň

Dispersion Copolymerization of Poly(ethylene oxide) Macromonomer and Styrene

Median Riza[1], Mitsuru Akashi[2], Akio Kishida[2], Ignác Capek[3]
1) Department of Polymer Science, Faculty of Science, Hokkaido University, Sapporo 060, Japan; 2) Faculty of Engineering, Department of Applied Chemistry and Chemical Engineering, Kagoshima University, Korimoto, Kagoshima 890, Japan; 3) Polymer Institute, Slovak Academy of Sciences, 842 36 Bratislava, CSFR

The aqueous/ethanol dispersion copolymerization of methacryloyl - terminated poly(ethylene oxide) (PEO-MA) macromonomer and styrene, initiated by an ethanol - soluble radical initiator (VA, 2,2'-azobis(N-methylisobutyramide), was investigated. The rate of polymerization, the size of latex particles, the number of polymer particles were determined as a function of PEO-MA concentration.

In the range of low macromonomer concentrations the rate of polymerization was found to be proportional to the 1st order with respect to the macromonomer concentration ([PEO-MA]). The reaction order was independent of conversion. Somewhat different reaction orders were determined from the relationship the rate of polymerization (R_p) versus the higher macromonomer (PEO-MA) concentration; 3 (at 5 - 30% conversion) and 1.5 (at and above 40% conversion).

The PEO - MA macromonomer acts as comonomer and as emulsifier as well. Besides, the graft copolymer is supposed to act as co- and/or emulsifier agents. Contrary to a conventional stabilizer, the macromonomer and its graft copolymer molecule probably become a constitute of the micelles or polymer particles and do not participate in the dynamic exchanger process between particles themselves and micelles via continuous phase.

The reaction order on [PEO-MA] seems to consist of several contributions; 1)monomer and comonomer, 2) emulsifier and 3) variation in particle concentration.

Generally, the polymerization in particles proceeding under the monomer saturated conditions is independent of monomer concentration but strongly increases by addition of additional emulsifier (due to the increase of the particle concentration). Therefore, the dependence of R_p versus particle concentration is overlapped with that of R_p versus particle concentration.

The rate of polymerization (in the medium conversion range) is proportional to the 0.6th order with respect to the particle concentration (N). This relationship is connected mainly with graft copolymer accumulation and its active role in the particle nucleation or formation.

The order on [PEO-MA] is ca. 3 times as large as that on N (at medium conversion range). Thus, besides the monomer and particle parameters also others influence the polymerization process. They include the formation of surface active graft copolymers and variation of termination (due to variation of viscosity of reaction medium) and initiator efficiency with macromonomer concentration.

The dependence of R_p versus the total monomer concentration differs from that of R_p versus the macromonomer concentration.

The reaction orders on the total monomer concentration were found to be arround 6 (at low conversions) and 4 (at medium and high conversions). This indicates that the dispersion copolymerization of styrene and PEO - MA macromonomer differs from the conventional (solution) copolymerization. The difference can be attributed to the multifunctional role of macromonomer in the surfactant - free dispersion polymerization.

The graft copolymer can be considered as an emulsifier with very high molecular weights and therefore it can become a constitute of the polymer particles and does not participate in the dynamic exchange process between latex articles themselves via the continuous phase. This may favor the stabilization of particles and so the increase of the rate polymerization.

The strong decrease of the reaction order with conversion from the start up to 40% conversion can be ascribed to depressed nucleation of particles (due to the decrease of macromonomer concentration) and the increased adsorption capacity of premature polymer particles. After 40% conversion the reaction order is nearly constant. But it increases with increasing macromonomer fraction in the monomer feed. The reaction orders on [macromonomer] and N indicate that styrene does not act as a inactive component. Styrene takes part in copolymerization with macromonomer leading to formation of amphiphilic macromolecules able to accociate and so to increase the local monomer concentration at reaction loci and the rate of polymerization.

Recent Presentations:

The following were presented at the Gordon Research Conference of Polymer Colloids, Irsee, Germany, September 13 - 18, 1992.

"Kinetics and Mechanism of Inverse Microemulsion Polymerization. New Aspects", a lecture presented by J.Bartoň.

"Preparation of Crosslinked Particles by Inverse Microemulsion Polymerization", a poster presented by J.Bartoň (co-authors: M.Stillhammerová, V.Vašková).

"Experimental study of Desorbed Free Radicals in Emulsion Polymerization", a poster presented by I.Lacík (co-authors: Casey B.S.,Sangster D.F.,Gilbert R.G.,Napper D.H), in cooperation with the School of Chemistry, University of Sydney).

INTERNATIONAL POLYMER COLLOIDS GROUP NEWSLETTER

Contribution from the Department of Polymerization Reactions,
Polymer Institute, Slovak Academy of Sciences, Dúbravska cesta 10,
842 36 Bratislava, Czech and Slovak Federative Republic

Reported by J. Bartoň

The following papers will be presented at 34th IUPAC International Symposium on Macromolecules, Prague 13-18 July 1992 :

ON THE USE OF INHIBITORS FOR THE DETERMINATION OF THE LOCUS OF INITIATION AND THE POLYMER PARTICLE FORMATION AND GROWTH OF FREE - RADICAL POLYMERIZATION IN OIL-IN-WATER AND WATER-IN-OIL DISPERSE SYSTEMS.

J. Bartoň

The basic features of the method of "Partitioned Free-Radical Polymerization" are illustrated on the examples of emulsion polymerization of polar and non-polar vinyl monomers (methyl methacrylate, butyl methacrylate, styrene, 2-ethylhexyl acrylate) and inverse microemulsion polymerization of acrylamide. For initiation of free-radical polymerization a water-soluble and/or oil-soluble initiator (ammonium peroxodisulfate and dibenzoyl peroxide) in combination with oil-soluble and/or water-soluble nitroxide radicals (2,2,6,6,-tetramethyl-4-octadecanoyloxypiperidinyl-1-oxyl and potassium nitrosodisulfonate) were used.

The monomer conversion curves at 60°C and the polymer particle size were determined. Oil-soluble inhibitor has no effect on the course of free-radical polymerization in oil-in-water emulsion if water-soluble initiator was used. No inhibition of emulsion polymerization was found when oil-soluble initiator in combination with water-soluble inhibitor was used. A water-soluble inhibitor does not influence the course of inverse water-in-oil polymerization initiated by oil-soluble initiator. The inverse microemulsion polymerization of acrylamide initiated by water-soluble initiator is not inhibited in the presence of oil-soluble inhibitor.

On the basic of obtained results the applicability of the Partitioned Free-Radical Polymerization method for the determination of loci of initiation of free-radical polymerization and mechanisms of polymer particle formation and growth in investigated disperse systems are discussed.

INVERSE MICROEMULSION POLYMERIZATION OF ACRYLAMIDE IN THE PRESENCE OF BI-UNSATURATED VINYL MONOMER. 1. Divinylbenzene.

V. Vašková, M. Stillhammerová, J. Bartoň

The effect of divinylbenzene (DVB) on the polymerization of acrylamide (AAm) initiated by dibenzoyl peroxide (DBP) in percolating inverse microemulsion Toluene/Water/Sodium salt of bis(2-ethylhexyl) sulfosuccinate (AOT) was studied.

The acrylamide conversion curves at 60°C and the polymer particle size and chemical composition were determined. Contrary to acrylamide polymerization in percolating inverse microemulsion in the absence of DVB the region of "slow" acrylamide polymerization was observed. On increasing the ratio DVB/AAm from zero to 1 and keeping constant water/AAm ratio the time interval of the "slow" polymerization of acrylamide becomes shorter. The rates of "slow" acrylamide polymerization increased slightly but the polymerization rates in the region of "high" acrylamide polymerization rates (between 20-70 % conversion) decreased on increasing the DVB/AAm ratio. The polymer particle size for a given water/AAm ratio increases with increasing DVB/AAm ratio. At overall (AAm + DVB) concentrations around 40% the content of acrylamide structural units in polymer particles slightly decreases (from 88% to 76%) with increasing DVB/AAm ratio (from 0 to 1).

The obtained results were interpreted on the basis of previously proposed mechanism of the initiation step of free-radical polymerization and polymer particle formation and growth in inverse microemulsion.

BATCH EMULSION POLYMERIZATION OF METHYL METHACRYLATE IN THE PRESENCE OF POLY(BUTYL ACRYLATE) SEED PARTICLES

V. Juraničová, J. Bartoň

The effect of the mass ratio of methyl methacrylate/poly(butyl acrylate) particles MMA/PBA on the kinetics of methyl methacrylate batch emulsion polymerization initiated by ammonium peroxodisulfate (APS) and dibenzoyl peroxide (DBP) in the presence and/or absence of potassium nitrosodisulfonate (FS, Fremy's salt) was investigated.

The conversion curves of MMA at 60°C and the polymer particle size during polymerization were determined. The water soluble inhibitor FS inhibits the polymerization of MMA initiated by APS for "low" value (0.676) as well as for "high" value (3.25) of MMA/PBA ratio. For system with "low" value of the MMA/PBA ratio the polymerization after inhibition period is not retarded with respect to the rate of polymerization in the absence of FS. The retardation of polymerization after inhibition period was, however, observed for system with "high" value of MMA/PBA ratio. No inhibition of MMA polymerization initiated by DBP for "low" value (0.676) as well as for "high" value (3.25) of MMA/PBA ratio was observed. The polymerization of MMA after inhibition period is, however, retarded with respect to the polymerization system without FS. The increase of the final polymer particle size with respect to polymer particle size of PBA seed is 1.1 for system with "low" MMA/PBA ratio and 1.4 for "high" MMA/PBA ratio regardless the nature of initiator and the presence and/or absence of FS.

The results were discussed on the basis of "Partitioned Free-Radical Polymerization" approach for establishing the loci of initiation of MMA emulsion polymerization initiated by water- and/or oil-soluble initiators and mechanism of polymer formation in seeded emulsion polymerization system.

STEADY STATE FLUORESCENCE STUDY OF ACRYLAMIDE POLYMERIZATION IN INVERSE MICROEMULSION

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The steady state fluorescence technique has been used to study the structural properties of polymerized inverse microemulsion (acrylamide in water) / bis(2-ethylhexyl) sulfosuccinate sodium salt / toluene initiated by dibenzoyl peroxide and/or $K_2S_2O_8$ at 50°C for various initial amount of AAM and various composition of initially prepared microemulsion.

The main aim was to investigate the possible impact of the depletion of acrylamide (which evidently acts as a cosurfactant and has the stabilizing effect) on the stability of microemulsion during the polymerization. The indolic fluorescence probes were located into the various places of microemulsion system. Their fluorescence emission, measured in regards of conversion, was quenched by AAM molecules and, in this way, the immediate concentration of AAM at the various loci of microemulsion - water pool, interphase, toluene phase - has been determined.

The smooth increase of fluorescence emission indicates that the sharp change of polymerized system does not occur which, generally, refers to the present picture on the mechanism of polymerization in inverse microemulsion.

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Influence Of Water Solubility And Glass Transition Temperature On Alkali- Soluble Associative Polymer Solution Rheology

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Introduction

Alkali - soluble associative polymers are made by emulsion co-polymerizing an acid-containing monomer, an associative macromonomer (i.e., a surfactant that has been capped with a polymerizable double bond), and a non-associative unsaturated monomer. The polymers are in the form of a latex following polymerization. After adding a base, such as potassium hydroxide, the particles "explode" due to the Coulombic repulsions among the ionized carboxyl groups along the polymer backbone, and the associative polymers go into solution. These polymers thicken both through association, and from the expansion of the high molecular weight polymer backbone at high pH.

The following synthesis parameters control the steady shear viscosity profile, viscoelastic, and extensional properties of alkali- soluble associative polymer solutions:

I) The structure and concentration of the associative macromonomer in the polymer, including: a) the size and structure of the hydrophobe; b) the moles of ethoxylation between hydrophobe and the double bond; c) the chemical nature of the bond between the ethoxylated portion and the reactive double bond (e.g., ester, ether, or urethane linkages); and d) the structure of the double bond itself (acrylic, methacrylic, crotonic, styrenic, etc.);

II) the structure and concentration of acid monomer in the polymer (e.g., acrylic, methacrylic, crotonic, itaconic, etc.);

III) the structure and concentration of the non-associative macromonomer, including monomers that cross-link the polymer during polymerization (e.g., trimethoyl propane triacrylate), and those that leave cross-linkable functionality in the associative polymer without cross-linking during polymerization (e.g., 2-hydroxyethylacrylate);

IV) the molecular weight of the polymer, as controlled by chain transfer agents during polymerization.

Parameters Ia) and Ib) control rheology by regulating the morphology, thermodynamics, and kinetics of the association junctions. Parameter Ic) controls the hydrolytic stability of the bond that connects the surfactant to the polymer backbone. Parameter Id) controls the sequence of incorporation into polymer for the macromonomer. Parameters II and III control the glass transition temperature (i.e., chain stiffness), hydrophobicity, and water solubility of polymer backbone; these factors determine how solution properties depend on temperature, and at what pH the latex particle becomes soluble. In this communication, we describe the influence of polymer glass transition temperature and water solubility on solution rheology.

Results and Discussion

Figure 1 compares the influence of pH on the viscosities of polymers composed of 40% methacrylic acid, 30% ethyl acrylate, 10% associative monomer, and 20% of an "other" monomer by weight, where the "other" monomer is selected from the first five monomers listed in Table 1. Comparison of the curve for methyl methacrylate to the curve for styrene in Figure 1 reveals that decreasing the water solubility of the polymer

Table 1: Glass Transition Temperatures and Water Solubilities of Monomers Used in Alkali - Soluble Associative Polymers.

Monomer	Glass Transition Temperature (°C)	Monomer Solubility in Water (wt%)
butyl acrylate	-54	0.20 - 0.34
ethyl acrylate	-22	1.50 - 1.84
methyl acrylate	8	5.00 - 5.69
methyl methacrylate	105	1.50
styrene	100	0.03

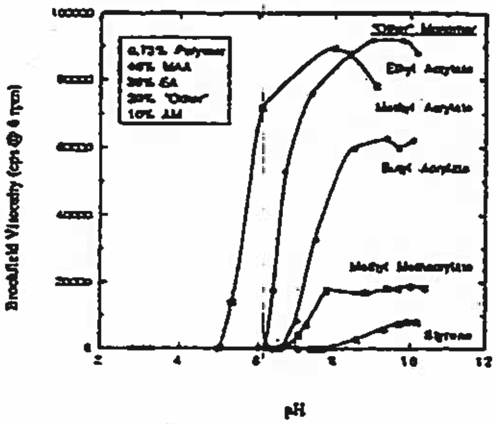

Figure 1: Influence of Monomer Water Solubility and Glass Transition Temperature on the Titration of Alkali - Soluble Associative Polymers with 2-amino - 2-methyl - 1-propanol (AMP-95).

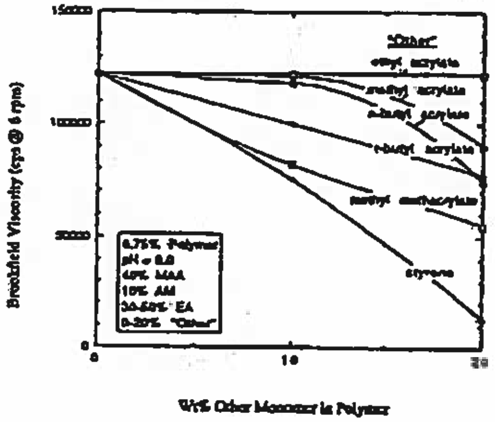

Figure 2:Influence of Monomer Water Solubility and Glass Transition Temperature on Alkaline Solution Viscosity.

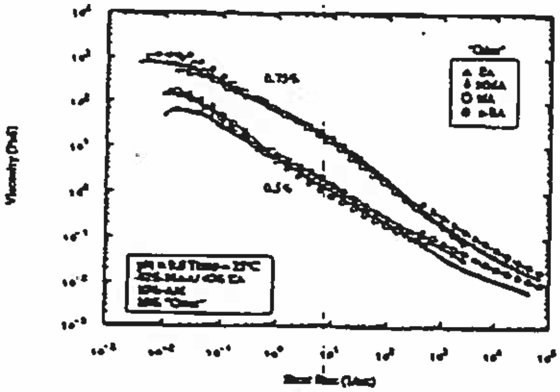

Figure 3: Influence of Glass Transition Temperature and Water Solubility On Steady Shear Viscosity.

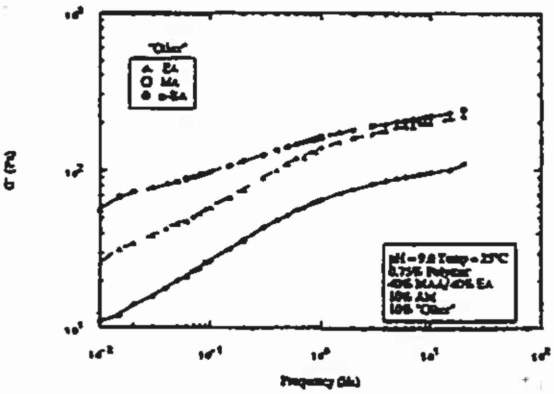

Figure 4: Influence of Glass Transition Temperature and Water Solubility On Dynamic Storage Modulus.

backbone, holding all else (including glass transition temperature) constant, decreases thickener efficiency, and delays solubilization of the latex polymer until a higher pH. As shown in Table 1, ethyl acrylate and methyl methacrylate have approximately the same water solubility, but differ in glass transition temperature (-22°C for ethyl acrylate and 105°C for methyl methacrylate); thus we can vary the glass transition temperature of the polymers by replacing some of the ethyl acrylate with methyl methacrylate. As the glass transition temperature of the polymer increases, and the polymer backbone becomes stiffer, the thickening efficiency decreases. Although glass transition temperature and water solubility influence thickening efficiency, they do not strongly alter the nature of the steady shear solution viscosity profile; the power law indexes of the strongly shear-thinning solution viscosities are nearly independent of glass transition temperature and water solubility (Figure 3).

Sometimes the water solubility of a thickener has a larger influence on solution properties than the thickener's glass transition temperature. For example, even though a polymer made with 20% butyl acrylate has a lower glass transition temperature than that of a polymer containing an equivalent concentration of ethyl acrylate or methyl acrylate instead, it solubilizes at a higher pH, and is less efficient (Figures 1 and 2). In order of increasing water solubility, the monomers rank as methyl acrylate > ethyl acrylate > methyl methacrylate > butyl acrylate > styrene, and in order of increasing glass transition temperature, the monomers rank as methyl methacrylate, styrene > methyl acrylate > ethyl acrylate > butyl acrylate. From the perspective of maximizing thickener efficiency, ethyl acrylate exhibits optimum of water solubility and glass transition temperature. We note, however, that thickener efficiency is only one property among many that must be optimized; the influence of thickener structure on coatings film properties and solution rheology are also important.

In general, the storage modulus and steady shear viscosity profile can increase or decrease in magnitude as the glass transition temperature and solubility of the backbone changes (Figure 4). Replacing some of the ethyl acrylate with methyl methacrylate holds the water solubility constant, but increases glass transition temperature: this lowers the low shear viscosity and the storage modulus. Replacing some of the ethyl acrylate with butyl acrylate decreases the glass transition temperature and water solubility simultaneously. As the fraction of butyl acrylate increases, the low shear viscosity and the viscoelastic response decrease; replacing some ethyl acrylate with methyl acrylate increases the glass transition temperature and water solubility of the polymer backbone, and the low shear viscosity and viscoelastic response increases. These changes in solution rheology correlate more strongly with the water solubility of the monomer than with its glass transition temperature. Because water solubility and glass transition temperature have a larger influence on viscoelasticity, as compared to changes in the steady shear viscosity profile, judicious selection of monomers can optimize the viscoelastic and extensional properties for a given application while holding the steady shear rheology nearly constant.

Conclusion

The glass transition temperature and water solubility of the thickener backbone can be used to manipulate the viscoelastic properties of a solution. In general, the storage modulus and steady shear viscosity profile decrease in magnitude as the glass transition temperature of the backbone decreases, and the storage modulus and steady shear viscosity increase as the water solubility of the backbone increases. By judicious selection of monomers, the steady shear viscosity profile can be held constant while the viscoelastic properties and extensional viscosity can be optimized for a given application.

ZINC DESTABILISATION OF CARBOXYLATE-STABILISED LATICES

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I have recently been reviewing some of the work we have carried out in previous years on the colloidal destabilisation of carboxylate-stabilised latices by sparingly-soluble zinc compounds, in by particular, zinc oxide. Our principal interest has been in ammonia-preserved natural rubber latex, but we have also investigated the behaviour of other latices in this respect. Much of this work is as yet unpublished. The matter of the colloidal destabilisation of carboxylate-stabilised latices by sparingly-soluble zinc compounds is of technological interest for at least three reasons:

i) Ammonia-preserved natural rubber latex can be made heat-sensitive by the addition of compounds such as zinc oxide. A latex is heat-sensitive if there is little apparent effect upon the colloid stability of the latex at normal ambient temperatures, but there is pronounced and rapid colloidal destabilisation, usually taking the form of uniform gelation, once the latex is heated sufficiently for its temperature to exceed some threshold value.

ii) Zinc compounds, notably zinc oxide, are often added to carboxylate-stabilised rubber latices for purposes other than heat-sensitisation, *e.g.*, as an aid to vulcanisation by sulphur. Some colloidal destabilisation occurs at temperatures below those at which rapid gelation occurs, and this is manifest as a gradual thickening and eventual gelation. This phenomenon, which is often troublesome technologically, is known as zinc oxide thickening.

iii) In some technological processes which use carboxylate-stabilised rubber latices, colloidal destabilisation induced by zinc-containing ions is used to supplement colloidal destabilisation by other influences, and to modify the character of the latex gels obtained by colloidal destabilisation.

Thus the chemical reactions by which zinc-containing ions impart heat-sensitivity to carboxylate-stabilised latices also have significance for the technology of latex processes for which heat-sensitivity is not obviously an important feature. These reactions can also be important for the heat-sensitisation of ammonia-preserved natural rubber latex by other substances, because zinc compounds are present in the majority of industrial formulations based upon this type of latex. For all these reasons, the chemistry and technology of the behaviour of zinc ions of various types in carboxylate-stabilised aqueous latices is important, especially for latices which contain ammonia or other nitrogenous compounds capable of forming complex ions with zinc.

The prerequisites for the heat-sensitisation of a rubber latex by zinc ammine ions are as follows:

i) there should be present in the latex a sparingly-soluble source of zinc ions, free ammonia, and ammonium ions; and

ii) the latex should be stabilised with surface-bound anions (usually carboxylate ions) which are capable of forming an insoluble zinc compound either with un-amminated zinc ions or with zinc ammine ions of low degree of ammination.

If these conditions are fulfilled, slow thickening and gelation of the latex occurs at normal ambient temperatures. The gelation rate increases as the temperature is raised, and becomes very marked at temperatures above 50°C. The chemistry of this system is not well understood. In outline, the mechanism of the colloidal destabilisation is commonly believed to be as follows: In the presence of water, zinc oxide behaves as though it were zinc hydroxide. In the absence of ammonia, the zinc ions which are released into the latex aqueous phase are fully hydrated. If ammonia is present in the aqueous phase, some of the water molecules coordinated to the zinc ions are reversibly displaced by ammonia molecules to give zinc ammine ions which contain both coordinated ammonia molecules and coordinated water molecules The number of ammonia molecules which are associated with each zinc ion may vary from one to four. At the concentrations of free ammonia normally present in ammonia-preserved natural rubber latex, the average number of ammonia molecules associated with each zinc ion is virtually four. The zinc tetraammine ion therefore predominates over all the others, including "free" zinc ions. The ability of zinc ammine ions to heat-sensitise ammonia-preserved natural rubber latex is commonly believed to have its origin in the thermal lability of the ions of higher ammonia content, in particular, of the zinc tetraammine ion. According to this view, when the temperature is raised, these ions tend to lose ammonia to give lower zinc ammine ions and, ultimately, "free" zinc ions. Either the resultant "free" zinc ions or the lower zinc ammine ions (or possibly both) are then postulated to interact with the surface-bound carboxylate ions which stabilise the latex. Insoluble zinc derivatives of these stabilisers are formed at the surface, with consequent destabilisation of the latex through loss of surface charge and hydration, and possibly also through the loss of steric stabilisation arising from the presence of proteinaceous stabilisers. In the case of ammonia-preserved natural rubber latex, it is not known whether the heat-sensitisation by zinc ammine ions is primarily a consequence of interaction between zinc ions and the carboxylate ions of the soap stabilisers, or of interaction between zinc ions and the carboxylate ions of the proteinaceous stabilisers, although experimental investigations have provided some indications. If the latter interaction does make a significant contribution, then it may be that loss of steric stabilisation makes is an important factor for the colloidal destabilisation which occurs when the temperature is raised, as well as loss of electrostatic and hydration stabilisation. In any event, two essential features of this theory for the mechanism of heat-sensitisation by zinc ammine ions are that:

i) a much larger concentration of zinc ions of various types capable of forming insoluble carboxylates is liberated by the thermal decomposition of the higher zinc ammine ions than was initially present in equilibrium with the zinc oxide at lower temperatures, and

ii) the initial concentration of zinc ions capable of forming insoluble carboxylates and present at lower temperatures is insufficient to cause rapid colloidal destabilisation of the latex.

An extensive investigation of the colloidal destabilisation of various anionic latices by zinc ammine ions was undertaken some years ago by one of our research students, Dr. B. Nithi-Uthai. His results for the colloidal destabilisation of ammonia-preserved natural rubber latex by zinc ammine ions illustrate clearly the main features of the phenomenon. He demonstrated close qualitative correlation between the effects of various variables, such as concentration of added ammonium salt, upon the heat-sensitivity, the mechanical stability of the latex, and the increase in latex viscosity during storage at 25°C. He also investigated the tendency of three types of synthetic latex, namely, those of polystyrene, polymethyl methacrylate and poly-*n*-butyl acrylate, to be colloidally destabilised by zinc oxide under various circumstances. The latices were prepared by conventional emulsion polymerisation using four types of surfactant as colloid stabiliser, namely, potassium laurate, sodium dodecyl sulphate, sodium dodecylbenzenesulphonate and a non-ionogenic ethoxylate. Colloidal destabilisation was observed visually as gelation. The effect of zinc oxide alone and in combination with (a) ammonia, (b) ammonium ions and (c) ammonia and ammonium ions was investigated. No colloidal destabilisation was observed if ammonia and ammonium ions were present, but zinc oxide was absent. Also, no colloidal destabilisation was observed if zinc oxide alone was present. However, colloidal destabilisation was observed if zinc oxide and ammonia, zinc oxide and ammonium ions, and zinc oxide, ammonia and ammonium ions were present, provided that the latex was stabilised by an anionic surfactant. As regards polymer type, the poly-*n*-butyl acrylate latices were more resistant to colloidal destabilisation by the various combinations than were the polystyrene and polymethyl methacrylate latices. This was attributed to lower Hamaker constant.

The colloidal destabilisation which occurred in the presence of zinc oxide and ammonium ions cannot have been due to the presence of significant concentrations of zinc ammine ions. That colloidal destabilisation occurred in the presence of this combination, but not in the presence of zinc oxide alone, was presumably a consequence of enhanced concentration of zinc ions caused by suppression of the hydroxyl-ion concentration by the ammonium ions. Possible interactions between the stabiliser surfactants and the zinc or zinc ammine ions were investigated by conductometric titration and visual examination for the formation of precipitates. Evidence of reaction with zinc ions and possibly the lower zinc ammine ions was found in the case of potassium laurate only. Sodium dodecyl sulphate and sodium dodecylbenzenesulphonate appeared to form precipitates with zinc tetraammine ions.

Nithi-Uthai also carried out a detailed investigation into the colloidal destabilisation of well-characterised model polystyrene latices by zinc ammine ions. The intention of this aspect of the investigation was to gain deeper understanding of the colloidal destabilisation of ammonia-preserved natural rubber latex, both at normal ambient temperatures as well as at elevated temperatures, by using these polystyrene latices as models for natural rubber latex. The polystyrene latices were prepared by seeded emulsion polymerisation, and were essentially monodisperse with particle diameters ranging from *ca.* 90 nm to *ca.* 830 nm. In most cases, the latices were stabilised by adsorbed laurate anions, the effective surface potential in alkaline medium being *ca.* −19 mV. The results were interpreted using a value of 4.3×10^{-21} J for the effective Hamaker constant for polystyrene particles in water. This value is the average of the results of several determinations under various conditions, the range of values being *ca.* 2.1×10^{-21} J to *ca.* 6.8×10^{-21} J. The zinc ammine ions used to colloidally destabilise the latices were pre-formed in aqueous solution by dissolving precipitated and washed zinc hydroxide in ammonium hydroxide solution. The kinetics of colloidal destabilisation were followed by measurement of turbidity as a function of time. For this purpose, the latices were diluted sufficiently to reduce the optical density to a value in the range 0.3 − 0.8. The volume fraction of polymer contained in the diluted latices was typically *ca.* 1.5×10^{-3}, and the particle concentration typically in the range 10^{10} − 10^{11} particles cm^{-3}. From measurements of the variation of turbidity with time elapsed after the addition of the destabilisative influence, it was possible to calculate values of k_{11}, the second-order rate coefficient for the reduction of particle number by binary encounters between primary particles. The coefficient k_{11} was taken as an inverse measure of the colloid stability as initially reduced by the addition of zinc ammine ions, and thus as a direct measure of the extent to which the latex had been initially colloidally destabilised by the zinc ammine ions. The variables investigated were concentration of zinc ammine ions, concentration of ammonia, concentration of ammonium ions, pH, nature and concentration of colloid stabilisers, particle size of latex, concentration of polymer in latex, and temperature of colloidal destabilisation. Some of the conclusions reached from this very extensive investigation will be summarised in future contributions to the Polymer Colloids Group Newsletter. All that there is space to note this time is that the complexity of the effects of zinc ammine systems upon carboxylate-stabilised anionic latices has been amply confirmed by this investigation, and many issues remain unresolved.

POLYMER COLLOID GROUP NEWSLETTER

Contribution from the Institut Charles Sadron (CRM-EAHP)
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by

Françoise CANDAU

AQUEOUS SOLUTION PROPERTIES OF AMPHOLYTIC COPOLYMERS PREPARED IN MICROEMULSIONS (with J.M. Corpart)

Water-soluble polymers of high molecular weight and more particularly polyelectrolytes are used in a large number of applications including sewage treatment, flocculation, paper manufacture and enhanced oil recovery. The long range repulsive interactions associated with the presence of positive or negative charges along the polymer chains, result in an increase in the hydrodynamic volume, making these materials very effective thickeners. However, a major drawback for some applications is the sharp decrease in polyelectrolyte solution viscosity observed in the presence of brine. Another alternative is to use polyampholytes, which are good candidates for high salinity media. These copolymers contain both positive and negative charges distributed along the chain.

The purpose of the present work was to investigate the properties in aqueous solution of polyampholytes of variable composition with special emphasis given to the effect of the net charge. The experimental results were compared with the recently developed theory of Higgs and Joanny.[1] Therefore a series of high charge density copolymers of sodium 2-acrylamido-2-methylpropanesulfonate (NaAMPS) with methacryloyloxyethyltrimethylammonium chloride (MADQUAT) was synthesized by polymerization in microemulsions. This process was previously developed in our laboratory for various types of other water-soluble monomers (acrylamide and/or sodium acrylate, MADQUAT).

The synthesis and characterization (macrostructure and microstructure) of the series of polyampholytes investigated here have been described in the previous Newsletters. The solution behaviour of polyampholytes is essentially controlled by the competition between repulsive (polyelectrolyte effect) and attractive (polyampholyte effect) electrostatic interactions. These are directly related to the sample composition. The solubility in NaCl aqueous solutions of the series of copolymers has been investigated by turbidimetry experiments (Fig.1). NaAMPS homopolymer exhibits a typical polyelectrolyte behaviour ; it is soluble in pure water and in NaCl solutions within the range investigated. In the case of sample A80/M20 the polyelectrolyte effect also dominates and the chains are soluble in fresh water and for all salt concentrations. However, the optical transmission goes through a minimum at intermediate salt concentrations. Sample A60/M40 sample 3 is soluble in water and has a high viscosity, suggesting that the chains adopt a highly extended polyelectrolyte configuration. The sample precipitates at $C_{NaCl} \simeq 0.05$ M but dissolves again upon further addition of salt ($\simeq 0.8$ M NaCl). Sample A50/M50 with balanced stoichiometry is insoluble in water and becomes only soluble at high salt concentrations ($\simeq 1$ M NaCl).

The effect of added sodium chloride on the zero-shear intrinsic viscosity of the same series of samples is shown in Figure 2. The results show that their behaviour is directly dependent on their charge level. NaAMPS homopolymer and sample A80/M20 display a polyelectrolyte behaviour with a decrease in viscosity upon increasing the ionic strength, the effect being less pronounced for sample A80/M20. Samples A60/M40 and A50/M50 show a completely opposite behavior. The intrinsic viscosity increases at low salt concentrations ($C_{NaCl} < 1$ M) and tends to level off at high salt contents.

These results confirm the turbidimetry experiments and can be qualitatively described by a recent theoretical model of Higgs and Joanny[1] established for low charge density polyampholytes. This theory predicts the following behaviour for the case of a single neutral chain at θ condition.

In absence of salt, the chain collapses into a globule. The structure of the globule is that of close-packed blobs of radius equal to the Debye-Hückel length associated with the polymeric charge. The collapse of the chain is due to the strong electrostatic attractive interactions between unlike ions along the polymer chain. Addition of salt screens the interactions and weakens the attractions. The collapsed state is stabilized by the 3rd virial coefficient which counterbalances the electrostatic attractions.

Our experimental results can be explained from the above considerations. In absence of salt, collapsed chains tend to attract each other. The theory of Higgs and Joanny predicts a phase separation between a high concentrated phase of interpenetrating polymer chains and a dilute solution in which each chain is a collapsed globule. In pure water, phase separation indeed occurs for sample A50/M50 which becomes further soluble upon adding salt. Additional experimental support to the theoretical model is provided by viscosity measurements in dilute solution (Fig.2). The initial increase in intrinsic viscosity can be ascertained to the globule-coil transition. The plateau observed upon further addition of salt is likely due to the screening of the interactions resulting in a gaussian conformation of the chain. The gaussian configuration was also confirmed by the almost zero values of the 2nd virial coefficients measured by light scattering.

In the case of polyampholytes with an excess of charges, the overall chain conformation is the result of the competition between the polyelectrolyte effect which tends to expand the coil and the polyampholyte effect which tends to collapse it. For a dilute solution, Higgs and Joanny predict an effective excluded volume given by

$$v^* = -\frac{\pi l^2 (f+g)^2}{K_0 b^3} + \frac{4\pi l (f-g)^2}{K_0^2 b^3} \qquad (1)$$

The quantities f and g are the fractions of positively and negatively charged monomers of size b, respectively. The parameter l is the Bjerrum length and K_0^{-1} is the screening length due to the concentration of added salt.

The first term of the right-hand side of Eq.(1) is the contribution of the polyampholyte term to the excluded volume and decreases like $1/K_0$. The second term refers to the polyelectrolyte effect and decreases like $1/K_0^2$. For sufficiently high values of (f-g), the polyelectrolyte term is dominant. The chains are stretched in absence of salt. Addition of salt produces a decrease of v* which goes through a minimum. Upon further addition of salt, v* tends to zero. Our experimental results are in accordance with these predictions. For (f-g) ranging from 30 to 60, one observes a minimum of turbidity at given salt concentrations. This minimum can be associated with the formation of partial aggregation of chains resulting from the lowered value of v*.

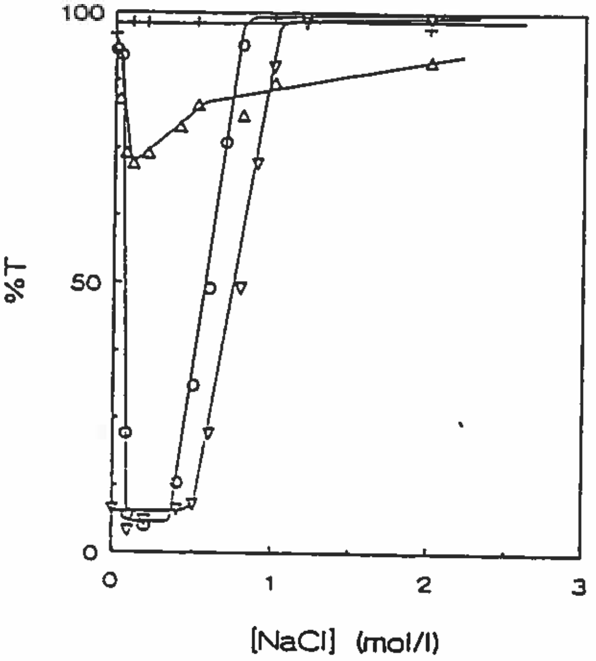

Fig.1 : Optical transmission vs salt concentration. ($C_{pol} = 10^{-2}$ g cm^{-3}). (+) A100 sample ; (Δ) A80/M20 ; (O) A60/M40 ; (∇) A50/M50 (the first number refers to NaAMPS).

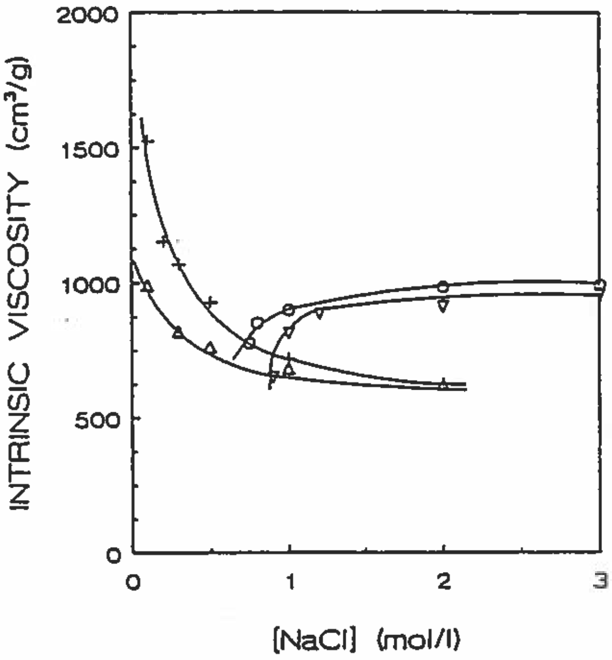

Fig.2 : Zero shear intrinsic viscosity vs salt concentration. (T = 25 °C). (Symbols as in Fig.1).

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POLYMER COLLOID GROUP NEWLETTER

Contribution from the Institut Charles Sadron (CRM-EAHP)
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by

Françoise CANDAU

COPOLYMERIZATION OF ACRYLAMIDE AND A HYDROPHOBIC MONOMER IN AN AQUEOUS MICELLAR MEDIUM : EFFECT OF THE SURFACTANT ON THE COPOLYMER MICROSTRUCTURE (S. Biggs, A. Hill, J. Selb and F. Candau)

Water soluble polymers modified with relatively low amounts of a hydrophobic comonomer (1-5 mol %) have recently become the subject of extensive research. In particular, the use of copolymers of polyacrylamide with various hydrophobic functionalities has proved to be of great interest. Many uses for polymers of this type have been suggested, including microencapsulation and catalysis, although the main area of interest remain their use as aqueous viscosity modifiers in tertiary oil recovery and latex paints systems.[1-2]

We have investigated the effects of surfactant (sodium dodecylsulfate) on the radical copolymerization of acrylamide with small amounts of a hydrophobic comonomer, N-4-ethylphenylacrylamide, in an aqueous micellar medium. At all the surfactant and hydrophobe concentrations used here, monomers conversion-time data can be fitted by a theoretical curve calculated for the homopolymerization of acrylamide in pure water solution. Classical light scattering measurements have led to copolymer molecular weights, as a function of monomer conversion, which are in the range 1.5×10^6 to 3×10^6. The molecular weight is seen to depend both on the surfactant and the hydrophobe concentration. The copolymers composition, also as a function of conversion, have been determined by UV spectrophotometry. Comparison with a copolymerization performed in a homogeneous water/formamide mixture has shown clearly that the presence of micelles in the reaction medium increases the initial rate of hydrophobic monomer incorporation into the copolymers. As a result, the average hydrophobe incorporation in the copolymers was seen to decrease towards the feed composition as a function of conversion, the larger the decrease the higher the hydrophobe to surfactant ratio. Analysis of all the above data has led to the proposal of a mechanism of copolymerization in an aqueous micellar medium.

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EFFECT OF SURFACTANT ON THE SOLUTION PROPERTIES OF HYDROPHOBICALLY MODIFIED POLYACRYLAMIDE (S. Biggs, J. Selb and F. Candau)

Abstract :

The interactions in aqueous solution, of sodium dodecylsulfate (SDS) with copolymers of acrylamide (AM) and N-4-(ethylphenyl)acrylamide (eφAM; [eφAM]/([AM] + [eφAM)] between 1 and 1.3 mol %) have been examined in the semidilute concentration range by rheology, fluorescence, and conductometry. Data are discussed with regard to changes in the hydrophobe content, the molecular weight, and the microstructure of copolymers. The hydrophobic groups of such copolymer chains, in pure water solution, are associated by either inter- or intrachain liaisons. The presence of interchain liaisons leads to apparent viscosities much greater than those seen for corresponding polyacrylamides. Addition of SDS to these aqueous copolymer solutions was seen to cause dramatic increases in the viscosity at concentrations below that of the critical micelle concentration (cmc) (Figure).

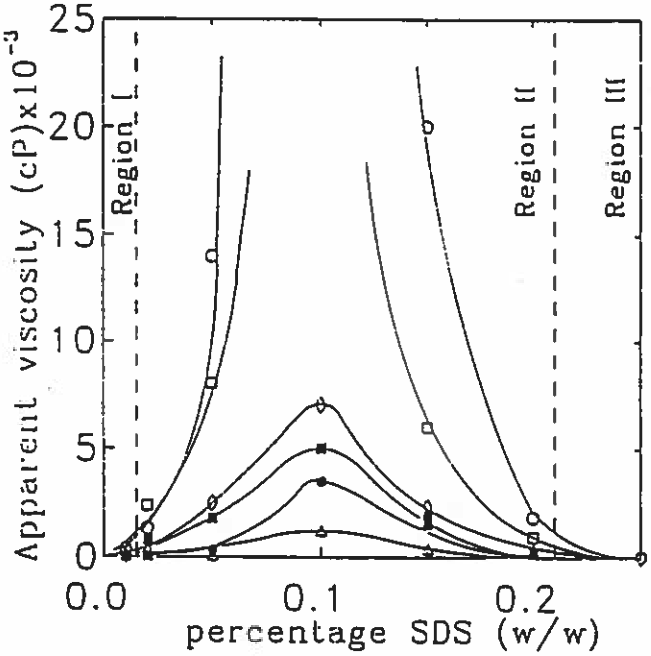

Figure : Apparent viscosities as a function of the SDS concentration (wt %) for copolymers of differing molar hydrophobe contents (mol % = [hydrophobe]/[acrylamide] + [hydrophobe]) : 1.30 (O) ; 1.25 (□) ; 1.12 (◇) ; 1.09 (■) ; 1.03 (●) ; 1.03 (Δ) (concentration of copolymers = 0.5% (w/w) ; shear rate γ = 0.5 s^{-1}).

Examination of the viscosity both as a function of shear rate and as a function of time (fixed shear rate) showed these solutions to have shear thickening, rheopexic, and thixotropic behavior. This complex behavior is explained in terms of the balance between inter- and intrachain liaisons and their effects on chain dimensions. Fluorescence and conductometric data have shown that the SDS associates with the hydrophobic regions of the copolymers in a noncooperative continuous binding process.

Contribution to the International Polymer Colloids Group Newsletter

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The titles of our current research projects are given in the **Contents** of our *Graduate Research Progress Reports*, No. 37, January 1992, which can be found at the end of this report. Summaries of progress in several research areas are presented here.

1. Phase Behavior of Lamellar Surfactants (J. Fred Hessel)

Gel phase surfactant systems composed of sodium dodecyl sulfate (SDS) and long chain alcohols (dodecanol, $C_{12}OH$, to hexadecanol, $C_{16}OH$) have been used to prepare submicron diameter emulsion droplets of monomers for emulsion polymerization (J. Ugelstad, M.S. El-Aasser, and J.W. Vanderhoff, *J. Polym. Sci., Poly. Lett.*, **111**, 503 (1973)) and pseudo-latexes by emulsification of polymers (M.S. El-Aasser, S.C. Misra, J.W. Vanderhoff, and J.A. Manson, *J. Coatings Technol.*, 49(635), 71 (1977)). The polymerization of these "miniemulsions" results in 50 - 500 nm diameter latex particles due to nucleation in the monomer droplets. The mixed surfactant compositions used as emulsifiers are primarily dilute dispersions of multi-lamellar vesicles with rigid, beta-phase bilayers. A property of these gel phase systems that may contribute to their emulsification behavior is a chain melting, gel to liquid crystalline transition.

The phase diagrams of the SDS/dodecanol(ethylene glycol)$_n$ether (where n = 0, 1, or 2) systems were constructed and the phase behavior was found to be governed by the average headgroup area (A_h) as predicted by the geometric packing constraint model (D.J. Mitchell and B.W. Ninham, *J. Chem. Soc. Faraday Trans. 2*, 77, 601 (1981)). At $A_h < 0.48$ nm^2, a lamellar phase was observed with all three systems. For example, the phase diagram of the SDS/$C_{12}OH$ system is given in Figure 1.

The morphology of the lamellar phase aggregates was studied by SANS, optical and electron microscopy and a diverse collection of morphologies was observed (vesicles, continuous lamellae, and tubules). The morphology was composition and method of preparation dependent (metastable), but compositions typically used in preparing miniemulsions are < 1000 nm diameter vesicles (see Figure 2). A minimum in vesicle diameter was observed at SDS/$C_{12}OH$ = 1/3 (mole ratio). SANS experiments found that the bilayer thickness was 3 - 4 nm and the water layers had a distribution of thicknesses between 20 and 40 nm.

The thermotropic phase behavior of these systems is also controlled by the bilayer packing. A maximum in the gel to liquid crystalline phase transition was observed at a 10/1 $C_{12}OH$/SDS mole ratio ($A_h = 0.25$ nm^2). This composition is roughly where the areas of the headgroup and alkyl chains are matched and maximum packing would be expected. The effect of van der Waals, hydrogen-bonding, hydration, and electrostatic forces on the melt transition was studied by systematic variations in surfactant and cosurfactant structure, and electrolyte and solvent composition. The dominant effect is due to bilayer packing and the resulting van der Waals attractive forces, and the hydration, hydrogen-bonding, and electrostatic forces have a minor effect.

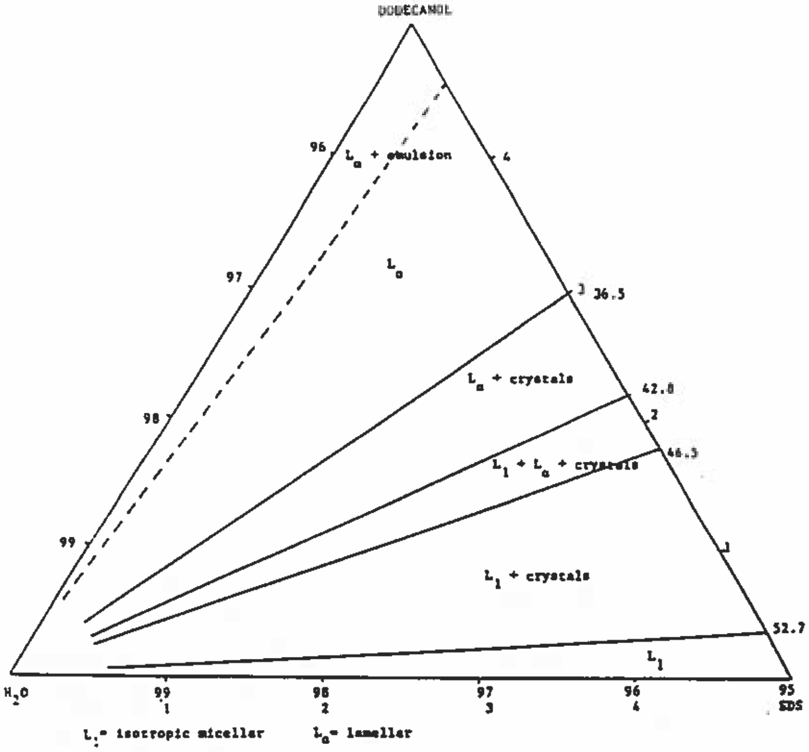

Figure 1: *Ternary phase diagram of the SDS/C_{12}OH system. Concentrations are in weight percent and the numbers at the phase boundaries along the SDS/C_{12}OH axis are the calculated average headgroup areas ($nm^2 \times 10^2$).*

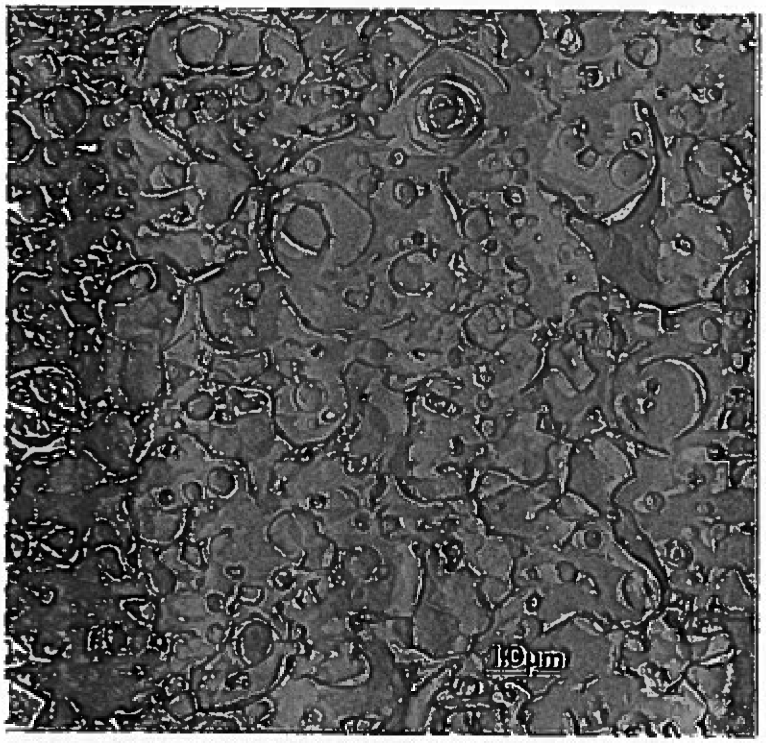

Figure 2: *Freeze fracture TEM of SDS/C_{12}OH 1/3 mole ratio, 41 mM SDS.*

2. Miniemulsion Polymerization of Divinylbenzene-HP: A Facile Route to Highly Crosslinked Particles (Samiuddin Mohammed)

Multifunctional monomers are usually used as crosslinkers in order to obtain network polymers resulting from the formation of intermolecular crosslinks. When the multifunctional monomers are used in excess, or homopolymerized, intramolecular crosslinking is favored, leading to the formation of intramolecularly crosslinked macromolecules (ICMs). These ICMs then undergo intermolecular reactions to form macroscopic networks. In order to avoid the formation of the macroscopic networks, crosslinking has to be limited to microscopic dimensions. This can be achieved by carrying out the polymerization in highly dilute solutions. A more efficient method is via emulsion polymerization, in which the crosslinking is restricted to the volume of the submicroscopic colloidal particles. Conventional emulsion polymerization, however, places a severe constraint on the size of the latex particles obtained. The size of the crosslinked particles prepared using this technique ranges between 5 and 50 nm. The main reason for the limitation on the particle size is the crosslinking which occurs early in the polymerization.

The constraint on the size of the crosslinked particles can be overcome by using the technique of miniemulsion polymerization. The miniemulsion polymerization of the crosslinking monomer, divinylbenzene-HP (DVB-HP, 80% DVB, The Dow Chemical Company) was studied in detail. DVB-HP consists of a mixture of the isomers of divinylbenzene (DVB) and ethylvinylbenzene (EVB). A mechanism is proposed for the growth of the latex particles during the course of the polymerization. The co-surfactant used in these systems, hexadecane, has been identified to be the main component responsible for the growth of the polymer particles to significant sizes. Hexadecane provides a monomer-rich environment near the surface of the growing particles, which has been proposed to be the principal locus of polymerization during the particle growth stage. At high initiator concentrations, the polymerization process was found to involve both homogeneous nucleation and nucleation in the homogenized monomer droplets. However, only the particles nucleated by initiation in the monomer droplets could grow to large sizes. As indicated by the individual conversion histories given in Figure 3 (determined by gas chromatography), the different components of DVB-HP were found to be incorporated into the polymer in the order p-DVB > m-DVB > m-EVB > p-EVB.

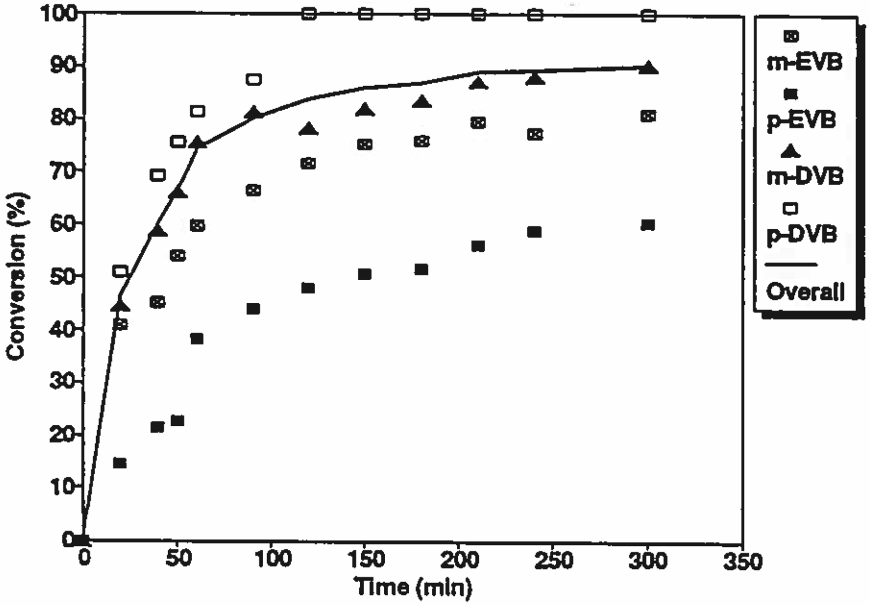

Figure 3. *Conversion-time curves for the different components of DVB-HP during miniemulsion polymerization; 70°C.*

The kinetics of the miniemulsion polymerization of divinylbenzene were followed using reaction calorimetry and dilatometry. The effect of different parameters on the polymerization kinetics was studied. High initiator concentrations and polymerization temperatures were found to give high polymerization rates and smaller particles. However, polymerizations run at low temperatures (e.g., 50°C) exhibited limited conversions due to the glass effect. The miniemulsions were prepared using three different homogenization devices: the sonifier, the Microfluidizer, and the Omni Mixer. Only the sonifier and the Microfuidizer were found to result in stable latexes following polymerization without any coagulum. Homogenization using the Microfluidizer and subsequent polymerization resulted in the formation of latexes with small particle sizes and narrow size distributions, while the latexes prepared using the sonifier resulted in highly polydisperse systems with relatively large particle sizes. The polymerization rate of miniemulsions prepared by the former technique was found to be more than twice that obtained when the sonifier was used.

3. Grafting Reactions in the Emulsion Polymerization of Vinyl Acetate using Poly(vinyl alcohol) as Emulsifier (Guadalupe Magallanes)

The emulsion polymerization of vinyl acetate (VAc) using fully hydrolyzed poly(vinyl alcohol) (PVA) as emulsifier and the grafting reactions of VAc with PVA in emulsion and in solution have been studied.

In emulsion polymerization, the VAc monomer reacts with the water-soluble PVA chains by grafting reactions. When the PVA molecule possesses a certain degree of grafting it becomes water insoluble and precipitates out producing particles by homogeneous nucleation.

The grafting copolymerization was studied in systems where the VAc was above and below of its limit of solubility in water, and the overall conversion of the reaction was determined gravimetrically and by Gas Chromatography (GC). Grafting was monitored during the reactions by measuring the percent hydrolysis of the water soluble PVA as determined by Fourier Transform Infrared Analysis. In the case of the latex samples, the particles were separated from the serum by ultracentrifugation in order to analyze the PVA in the serum (FTIR and solids). One set of results is reported in Figure 4 for an emulsion polymerization with added chain tranfer agent. The corresponding conversion history is given in Figure 5 along with two other results. It can be seen that the percent hydrolysis of the PVA decreases at the beginning of the reaction, while the solids content of the serum increases. These results are explained by the grafting taking place during the polymerization; increased grafting leads initially to a lower degree of hydrolysis and higher solids. This continues until further grafting leads to the precipitation of chains which exceed their water solubility resulting in polymer particles. Grafting continues resulting in further nucleation of particles and growth of the existing ones.

When the VAc monomer concentration is below its limit of water solubility, the precipitation and particle formation take longer depending on the temperature and initiator concentration. However, the hydrolysis level reached before particles appear is independent of the temperature and initiator level used in the recipe. The change in the molecular weight of original PVA due to the grafting reactions was also followed by Gel Permeation Chromatography (GPC); the results indicate that the VAc does not react homogeneously with all the PVA chains.

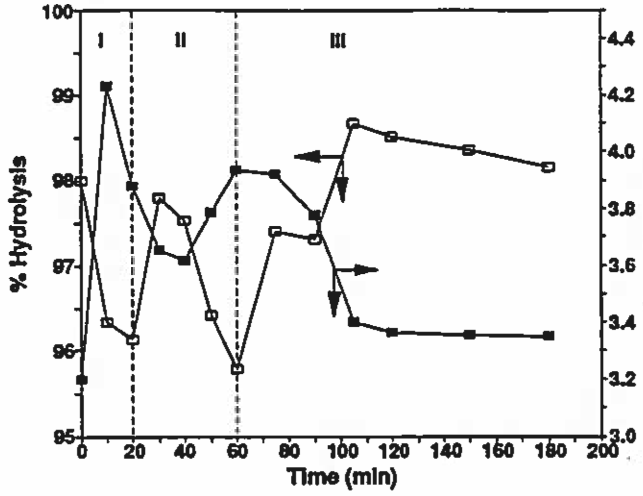

Figure 4. *Percent hydrolysis of the PVA dissolved in the serum and its solids content as a function of time in the emulsion polymerization of vinyl acetate prepared with fully hydrolyzed PVA; CTA/VAc = 0.0021 weight ratio.*

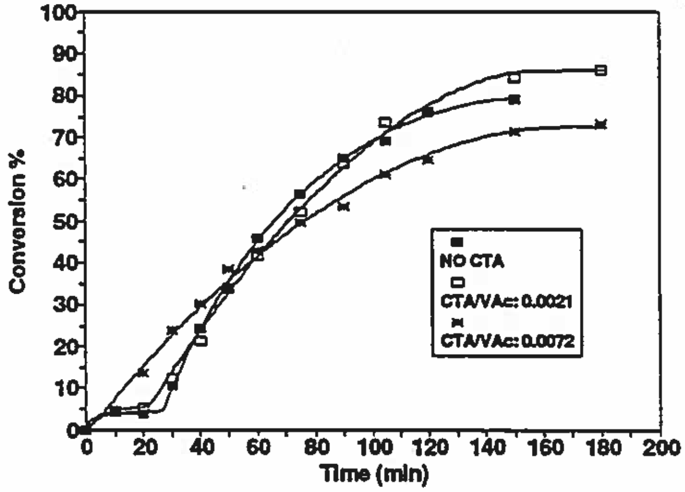

Figure 5. *Conversion-time histories for the emulsion polymerization of vinyl acetate with fully hydrolyzed PVA as emulsifier; with and without CCl_4 chain transfer agent.*

4. Structured Latex Particles for Modification of Polycarbonate (Iris Segall)

In the continuing effort of industry to develop new engineering polymers, commercial rubber-toughened plastics have gained attention. A discrete rubber phase in a continuous plastic matrix provides significant improvement in toughness. However, research indicates further improvement may be gained by the use of polymer blends.

In this project the main concern is the understanding of the basic parameters involved in optimizing the synthesis of "structured" latex particles for use as toughening agents or impact modifiers for composite polymer materials. Core/shell impact modifier particles are designed so that the rubbery core imparts elasticity while the glassy shell provides anchorage and miscibility with the matrix.

The synthesis involves the preparation of slightly crosslinked poly(butyl acrylate) seed and a styrene-methacrylate ester shell. Each of the shell component monomers was closely studied, to better understand their effects on the shell formation. This study covered determination of conversion vs. time behavior, efficiency of various chain transfer agents, influence of temperature, initiation (redox) system, mode of monomer addition (batch vs. semicontinuous), as well as the concentration of chain transfer agent and initiator.

Differential Scanning Calorimetry (DSC) was used to determine the extent of miscibility between the styrene-methacrylate ester copolymer and a polycarbonate matrix. Transmission Electron Microscopy (TEM) applying preferential staining techniques, was employed to study the morphology of the structured rubbery/glassy material.

Electron micrographs of "core/shell" latex particles prepared by batch polymerization show the poly(BuA) seed particles (lighter regions) partially covered by the P(ME) second stage polymer (darker regions). Poly(BuA)/poly(ME) prepared by semicontinuous addition of the ME second stage monomer, yielded a better, though not complete, coverage (Figure 6). The effect of the second stage composition is depicted in Figure 7. It can be concluded that P(ME) yields better coverage than PS, which seems to squeeze out the P(BuA). A 95/5 P(ME)/PS ratio leads to an intermediate morphology consisting of "patches" of shell material spread over the P(BuA) seed surface. Figure 8 is representative of the morphology obtained in the presence and absence of isooctyl mercaptopropionate (IOMP) chain transfer agent. The presence of IOMP causes the second stage monomer to polymerize as a continuous, large patch of shell material, while in the absence of IOMP, smaller patches of shell material are spread throughout the P(BuA) seed surface.

The different morphologies obtained under different polymerization conditions are attributed to thermodynamic and kinetic factors such as polymer/polymer interfacial tensions and viscosity effects. Further work is now being conducted to determine the effect of morphology and the role of the thickness of the interfacial layer between the discrete phase and the polycarbonate matrix in toughening and impact modification of composite materials.

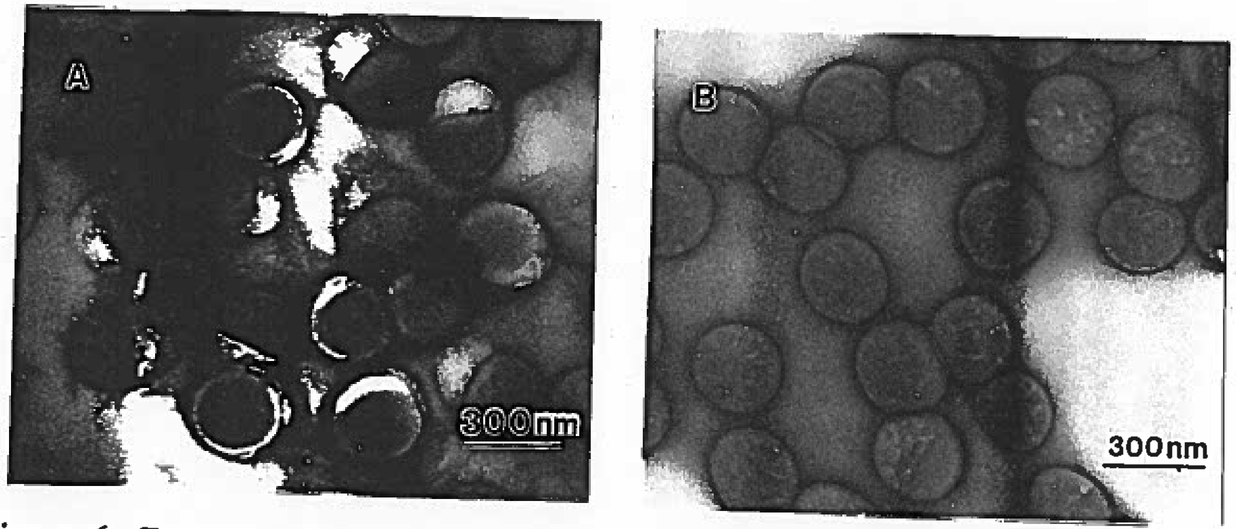

Figure 6. *Transmission electron micrographs of preferentially stained 30/70 P(BuA)/P(ME) core/shell latex particles prepared by: A) batch polymerization; and B) semicontinuous addition of ME second stage monomer.*

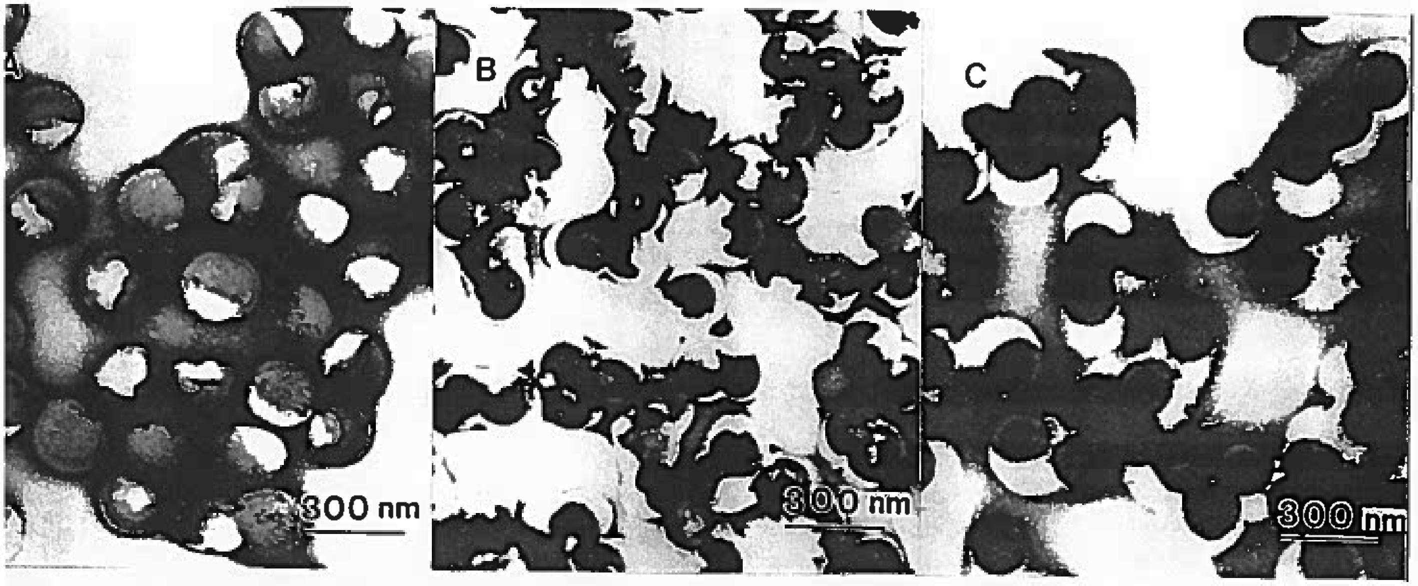

Figure 7. *Transmission electron micrographs of preferentially stained 50/50 core/shell latex particles. Core is P(BuA). Shell is: A) 100% P(ME); B) 95/5 P(ME)/PS; and C) 100% PS.*

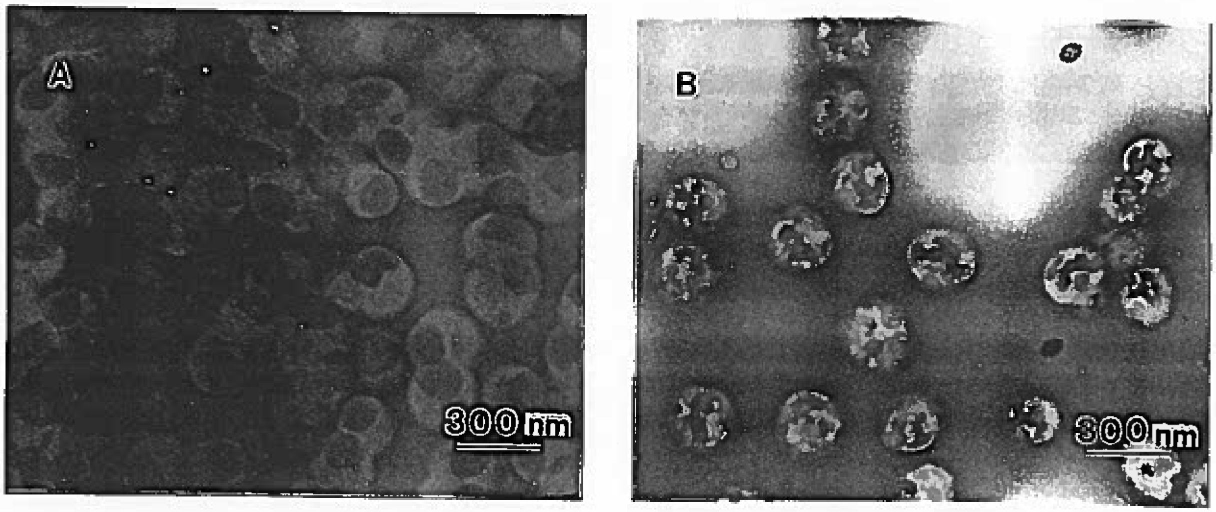

Figure 8. *Transmission electron micrographs of preferentially stained 70/30 P(BuA)/P(ME) core/shell latex particles: A) in the presence of IOMP chain transfer agent; and B) in the absence of IOMP chain transfer agent.*

Recent Presentations

"Development of Morphology of Latex Particles: The Interplay Between Kinetic and Thermodynamic Parameters", M.S. El-Aasser, Y.C. Chen, and V.L. Dimonie, presented at the *International Symposium on Polymeric Microspheres*, Fukui, Japan, October 23 - 26, 1991.

" Morphology of Lamellar Phase Vesicles in the Sodium Dodecyl Sulfate/Dodecanol (Ethylene Glycol)$_n$ Ether/Water Systems", J.F. Hessel and M.S. El-Aasser, presented at the *203rd ACS National Meeting*, San Francisco, April 5 - 10, 1992.

Recent Publications

"Emulsifier-Free Emulsion Copolymerization of Styrene and Sodium Styrene Sulfonate", J.H. Kim, M. Chainey, M.S. El-Aasser, and J.W. Vanderhoff, *J. Polym. Sci.: Part A: Polym. Chem.* **30**, 171-183 (1992).

"Development of Cohesive Strength in Polymer Films from Latices: Effect of Polymer Chain Interdiffusion and Crosslinking", E.S. Daniels and A. Klein, *Progress in Organic Coatings*, **19**, 359-378 (1991).

"Electrokinetic Characterization of Highly Sulfonated Polystyrene Model Colloids", F.J. de las Nieves, E.S. Daniels and M.S. El-Aasser, *Colloids and Surfaces*, **60**, 107-126 (1991).

"Efficiency of Particle Separation in Capillary Hydrodynamic Fractionation (CHDF)", J.G. DosRamos, R.D. Jenkins, and C.A. Silebi, in Particle Size Distribution II, Assessment and Characterization, T. Provder, Ed., *ACS Symposium Series* 472, 264-278, (1991).

"Eluant Composition Effects on the Separation Factor in Capillary Hydrodynamic Fractionation (CHDF)", J. Venkatesan, J.G. DosRamos, and C.A. Silebi, in Particle Size Distribution II, Assessment and Characterization, T. Provder, Ed., *ACS Symposium Series* 472, 279-291, (1991).

"Size Analysis of Simple and Complex Mixtures of Colloids in the Submicrometer Range Using Capillary Hydrodynamic Fractionation", J.G. DosRamos and C.A. Silebi, in Particle Size Distribution II, Assessment and Characterization, T. Provder, Ed., *ACS Symposium Series* **472**, 292-307, (1991).

"Miniemulsion Polymerization - A Comparative Study of Preparative Variables", P.L. Tang, E.D. Sudol, C.A. Silebi, and M.S. El-Aasser, *J. Applied Polym. Sci.*, 43, 1059-1066 (1991).

Recent Ph.D. Dissertations

"Role of the Interphase Region in the Transport of Small Molecules Through Heterogeneous Polymeric Systems" by C. Rodrigo Correa C.

"Preparation and Characterization of Monodisperse Porous Polymer Particles" by Chieh-Min Cheng.

"Electrokinetic, Optical and Rheological Study of Ordered Polymer Colloids and Its Rheological Implications on Printing" by Yann-Per Lee.

"Development of Particle Morphology in Composite Polymer Latexes - Influence of Kinetic and Thermodynamic Parameters" by Yi-Cherng Chen.

"Polymer-Encapsulated Particles with Controlled Morphologies" by Wei-Hsin Hou.

Recent M.S. Reports

"Miniemulsion Polymerization of Divinylbenzene-HP: A Facile Route to Highly Crosslinked Particles" by Samiuddin Mohammed.

"Emulsion Polymerization in an Automated Reaction Calorimeter" by Luis Varela de la Rosa.

"Synthesis and Characterization of Core-Shell Ionomeric Latexes" by Atul Arora.

"Modeling of Latex Particle Size Distribution in Emulsion Polymerization" by Ashwini Sood.

"Preparation of Large-Particle-Size Monodisperse Latexes in Simulated Microgravity Conditions Using a Rotating-Cylinder Reactor" by Vinay Mishra.

"The Role of Compatibilizing Agents in the Development of Particle Morphology in Composite Latexes" by Wichai Chotirotsukon.

EMULSION POLYMERS INSTITUTE
Lehigh University

Graduate Research Progress Reports
No. 37 January 1992

CONTENTS

Contributions to the International Polymer Colloids Group Newsletter from Eindhoven University of Technology

The Seeded Emulsion Polymerization of Butadiene, 1
The propagation rate coefficient

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Accepted by *Macromolecules*

SUMMARY

The kinetics of the emulsifier free seeded emulsion polymerization of butadiene at 60°C in Smith-Ewart interval III was investigated using sodium peroxodisulfate as initiator. The aim of this work was to measure the propagation rate coefficient (k_p) of butadiene at 60°C in emulsion polymerization. All experiments were conducted in the presence of tertiary dodecyl mercaptan, as is usual in industrial practice. The fractional conversion was based on gravimetrically calibrated on-line densitometry and was found to be highly accurate. By analogy with the well known Ugelstad plots the product of the propagation rate coefficient (k_p) and the average number of radicals per particle ($\bar{n}$) versus seed latex particle diameter clearly shows Smith-Ewart case I and case II regimes. From a constancy in values of $k_p*\bar{n}$ (case II regime) in this plot, a value for k_p could be calculated that was three times larger than the current literature value. It was found that negligible 'thermal background initiation' is present in the butadiene system. Two linear regions in polymerization rate are observed in interval III. Model calculations are presented in excellent agreement with the experimental data. From these calculations a value of the rate coefficient for transfer to monomer, k_{tr}, could be estimated.

The Seeded Emulsion Polymerization of Butadiene, 2

Effects of persulfate and tertiary dodecyl mercaptan

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To be submitted to *Macromolecules*

SUMMARY

The kinetics of the emulsion polymerization of butadiene at 60°C in Smith-Ewart interval III was investigated using sodium peroxodisulfate (persulfate) as initiator. The aim of this work was to elucidate and model the persulfate initiator efficiency. Monomer conversion was based on gravimetrically calibrated on-line densitometry. Plots of the product of the propagation rate coefficient, k_p, and the average number of radicals per particle ,$\bar{n}$, versus initiator concentration showed minimal dependence of the initiator concentration if tertiary dodecyl mercaptan (TDM) was present during polymerization. These results could not be modelled using normal emulsion polymerization theory. The model used in the absence of TDM fits two separate sets of data, $\bar{n}$ versus particle diameter and initiator concentration. In the absence of TDM, $\bar{n}$ depends strongly on initiator concentration. The significant effect of TDM is asscribed to a decrease in radical desorption. A possible effect on radical absorption is refuted on the basis of theory and experiment.

Partial swelling of latex particles by two monomers

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Submitted to *Macromolecules*

SUMMARY: Partitioning of two monomers between latex particles, monomer droplets and the aqueous phase in an emulsion polymerization is, amongst other things, very important for modelling both the composition drift occurring during reaction and the rate of polymerization. For the monomer combination, methyl acrylate - vinyl acetate, both saturation and partial swelling were determined experimentally. Theories for saturation swelling and partial swelling of the separate monomers were in good agreement with experimental results. Based on previous work an extended thermodynamic model for monomer partitioning at partial swelling of latex particles by two monomers with limited water solubility has been developed. Results predicted by this model are in good agreement with observed monomer partitioning.

Thermodynamics of swelling of latex particles with two monomers: a sensitivity analysis

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Accepted for publication by *Makromolekulare Chemie*

SUMMARY: A sensitivity analysis was performed to determine at what conditions the simplified model for swelling of latex particles by two monomers or two solvents is valid. This model proposes that, inter alia, the fractions of two monomers in the latex particles and in the monomer droplets are equal. The model is a simplified version of that proposed by Ugelstad et al., and results from the use of three assumptions, namely (1) the molar volumes of the monomers are equal, (2) the interaction parameter between the two monomers are equal, and (3) the interaction parameters between each of the monomers and polymer are equal. It is shown by simulation that these assumptions are of algebraic necessity only. The simple model is always valid when utilizing realistic values for all the appropriate parameters for partially water soluble monomers that swell the polymer.

The use of the saturation model for monomer partitioning in simulations of emulsion copolymerizations

Lilian F. J. Noël, Ian A. Maxwell and Anton L. German

Simplification of existing thermodynamic theories for the swelling of latex particles by two monomers has led to simple equations for both saturation swelling[1] and partial swelling[2]. A sensitivity analysis[3] has been performed to check the validity of the simplified model.

The relationships developed for both saturation swelling and partial swelling can be used to predict monomer partitioning in an emulsion copolymerization. Until now only the saturation swelling equations have been programmed in such a way that predictions of, among other things, composition drift can be made. The model for saturation swelling is compared with experimental results for the monomer combination methyl acrylate (MA) and indene (I) in Figure 1. The three reactions between MA and I are performed with a feed composition of 75% MA ($f_{MA} = 0.75$). All reactions are carried out under the same conditions and with the same surfactant, initiator and buffer concentrations. Only the absolute amount of monomer, expressed in the monomer over water ratio (M/W), was varied in this series of reactions.

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[3] Maxwell, I. A.; Noël, L. F. J.; Schoonbrood, H. A. S.; German, A. L. 'Thermodynamics of swelling of latex particles with two monomers: a sensitivity analysis' Accepted for publication by Makromol. Chem., Theory and simulation

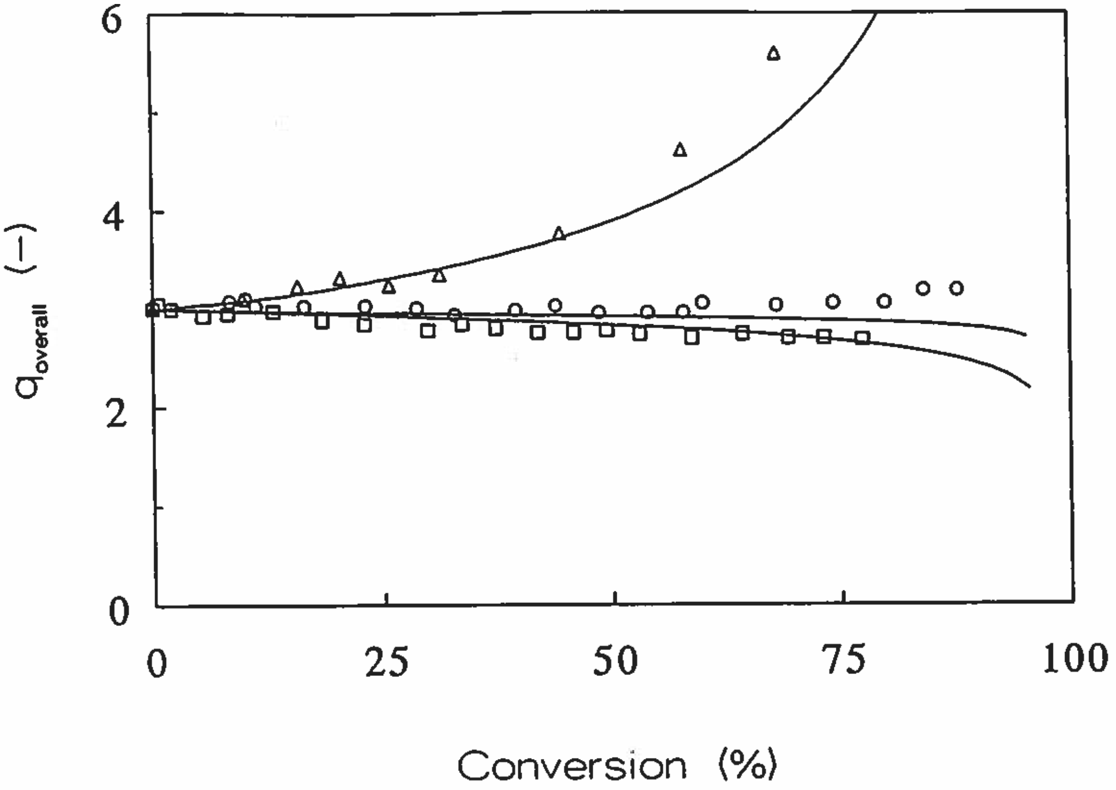

Figure 1. *Comparison of the theoretical predictions based on the saturation swelling model (——) with experimental results. The overall monomer ratio,* $q_{overall}$ = *[MA]/[I], is shown as a function of conversion. The overall monomer feed fraction for the three reactions was* f_{MA} = *0.75, and the M/W ratio varied from 0.1 (△), 0.3 (○) and 0.4 (□).*

From Figure 1 we can conclude:

1 good agreement is reached when comparing the saturation model with experimental results, and

2 monomer partitioning can be used to minimize composition drift for the monomer combination MA - I

The next step in this research project is to also take partial swelling into account to see whether similar results can be obtained. If so, more complete control of composition drift in emulsion polymerization may become possible.

ON-LINE MONITORING AND CONTROL OF THE (CO-)POLYMER ENCAPSULATION OF TiO_2 IN AQUEOUS EMULSION SYSTEMS.

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ABSTRACT

Titanium dioxide (TiO_2) was encapsulated with polymer by means of a 'two-step' process consisting of: 1) modification of the pigment surface with titanates in order to render the surface hydrophobic, followed by 2) an emulsion polymerization-like reaction leading to the actual polymer encapsulation. The emulsion homo-polymerization reactions were carried out with either methyl methacrylate (MMA) or styrene (STY). Compared to reactions carried out with MMA, encapsulation reactions performed with STY generally showed substantial coagulation occurring both during and at the end of the reaction. On-line conductivity measurements are related to surfactant migration because the mobility of the surfactant molecules strongly depends on the state they are in (adsorbed on a surface, dissolved in the aqueous phase, in micelles). These measurements were used to obtain qualitative information concerning the course of the reaction by visualising: the moment of initiation, the moment of droplet disappearance during batch reactions, whether or not monomer starved conditions are obtained during semi-continuous reactions, and the occurrence of coagulation during encapsulation reactions. Furthermore, the conductivity measurements helped to clarify various reaction mechanisms taking place during encapsulation reactions and in principle can serve as a basis for surfactant addition during the reaction in order to prevent coagulation from taking place. Also the possibility of creating multi-layered shells around modified TiO_2 was investigated using MMA and STY as (co-) monomers. The addition of a chain transfer agent (1-dodecyl mercaptan) did not seem to influence the course of the reaction very much, but made removal of the surface polymer (with tetrahydrofuran, THF), for the purpose of analysis, easier.

On-line conductivity measurements during Emulsion Polymerization

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Aim:

On-line monitoring of emulsion (-like) polymerization reactions, especially with relation to surfactant migration.

Experiments:

'Regular' emulsion polymerization
Encapsulation of TiO2: - modification
- emulsion polymerization

Results:

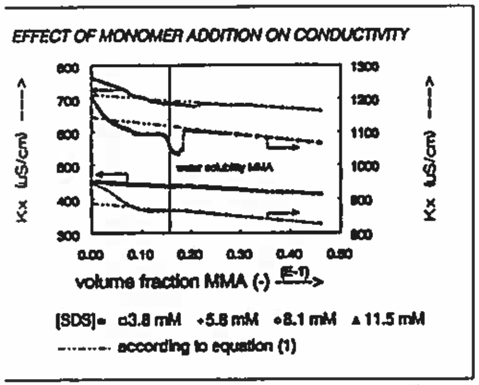

Figure 1

Effect of monomer addition

$$\left.\begin{array}{l}\text{[SDS]} << \text{c.m.c. : dilution of conducting phase with non-conducting phase (monomer).}\\ \text{[SDS]} \approx \text{c.m.c. : monomer behaves like a co-surfactant; micelle formation is enhanced.}\\ \text{[SDS]} >> \text{c.m.c. : micelles are swollen with monomer until total solubility (in both water \& micelles) is exceeded;} \\ \longrightarrow \text{droplets appear.}\end{array}\right\} \text{apparent c.m.c. is decreased.}$$

$$Kx = Kc\,\frac{2\,(1-\phi)}{2+\phi}$$

Equation (1)

ϕ : volume fraction of monomer
Kx: conductivity (μS/cm)
Kc: conductivity of the continuous phase

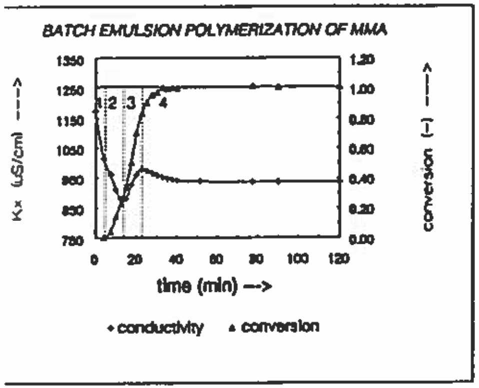

Figure 2

Batch

Section 1: addition of monomer: apparent c.m.c. decreases.
Section 2: particle formation and growth (Smith-Ewart, interval I & II).
Section 3: monomer droplets have disappeared: apparent c.m.c. increases (interval III).
Section 4: shrinking of polymer particles: migration of counter-ions towards particles (interval III).

NOTE: variation in *Kx* is similar during regular emulsion polymerization and encapsulation reactions (MMA).

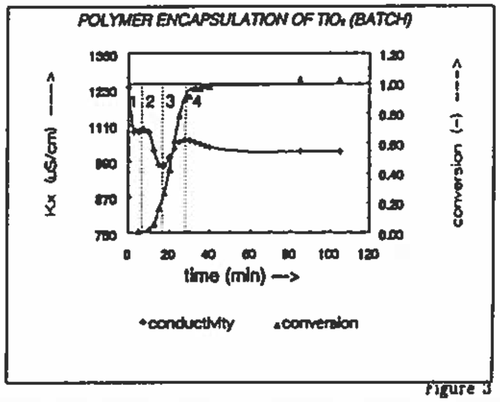

Figure 3

Monomer starved

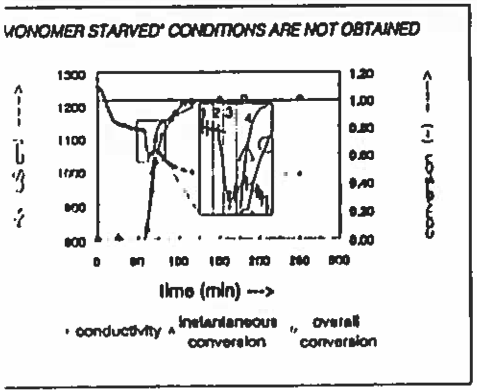

Figure 4

No maximum in *Kx* : no accumulation of monomer
in the aqueous phase.

Negligible coagulation (when using MMA).
Increase in (surface polymer/free polymer) ratio. } encapsulation reactions

NOTES: - figure 4, monomer addition rate: 0.5 ml/min
- figure 5, monomer addition rate: 0.2 ml/min
- variation in *Kx* is similar during regular emulsion polymerization and encapsulation reactions.

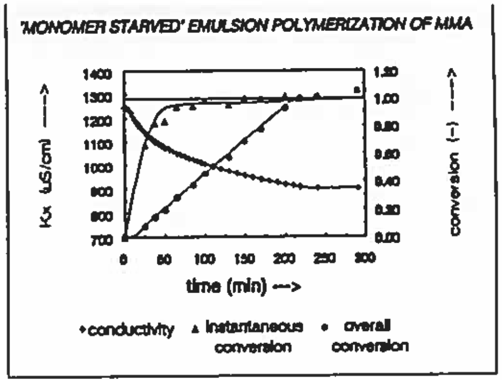

Figure 5

MONOMER STARVED REACTIONS WITH STYRENE

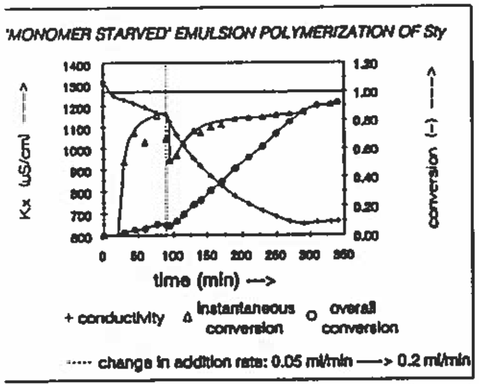

Figure 6

No droplet formation due to
low initial addition rate.

Severe coagulation causes oscillations in conductivity-curve due to surfactant release and consumption.

NOTE: initial addition rate of styrene: 0.05 ml/min,
after 90 minutes the rate is changed to 0.2 ml/min.

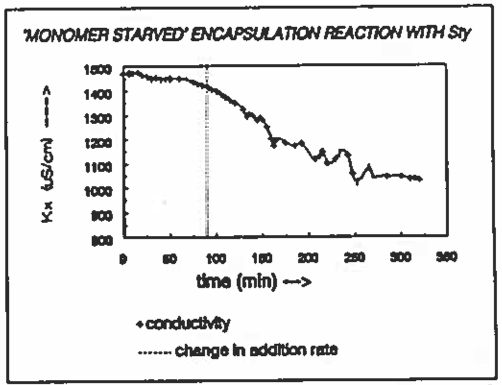

Figure 7

Conclusions:

On-line conductivity measurements provide valuable information during emulsion polymerizations:
- moment of initiation
- moment of droplet disappearance (batch).
- variation in *Kx* is related to surfactant migration (adsorption and desorption).

} the changes in *Kx* during reactions with MMA are not influenced by pigment

The absence of monomer starved conditions manifests itself in a maximum in *Kx* .

During encapsulation reactions with styrene (monomer starved) coagulation is revealed by oscillations in *Kx* .

AKZO This project is being supported financially by
Corporate Research, Arnhem (NL)

Contribution to the International Polymer Colloid Group Newsletter
October 1992

from

Finn Knut Hansen

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P.O.Box 1033 Blindern, 0315 OSLO, Norway

Surface Tension by Image Analysis. Fast and Automatic Measurements of Pendant and Sessile Drops and Bubbles.

The method for surface tension measurement by computer image analysis of a pendant drop as developed at Dyno Industrier was described in the October 1989 Newsletter and published in Journal of Colloid and Interface Sci., **141,** 1 (1991). At the University of Oslo, a new instrument has been built with better hardware and completely rewritten software. The instrument program now has been extended to do general drop shape analysis, thus making possible authomatic measurement of both pendant and sesile drops and bubbles.

The new experimental set-up uses a Ramé-Hart optical bench with the micro syringe attachment and optionally with the environmental chamber. Instead of the standard microscope attachment, an Olympus Auto Bellows is mounted on the microscope stand by a custom made adapter. On the auto bellows is mounted an Olympus 80mm macro lens and a Sony CCD B&W video camera. The camera is connected to a DT2853 (Data Translation) video frame grabber card that has a resolution of 512x512 rectangular pixels with 256 grey levels. The card is mounted in an Olivetti 20 mHz 80386 PC with a 80387 coprocessor. A separate RGB monitor is also connected to the frame grabber board in order to view the drops. The optical bench is placed on a massive stone table to avoid vibrations. The instrument is controlled by a program written entirely in Turbo Pascal. The different functions are accessed through a menu system based on stored Methods that make the running of time-resolved and/or repetitive measurements straightforward. Surface tensions can be measured in real-time, or pictures can be stored to disk and calculated later. The edge tracking procedure is based on local interpolation between intensity values, and is able to give sub-pixel resolution down to ± 0.1 pixel. Interfacial tensions are calculated from the well-known equation

$$\gamma = \Delta\rho g R_0^2/\beta$$

To obtain good initial estimates for the shape parameter, β, and radius of curvature at the apex, R_0, the drop's equatorial height, H, and radius, R, are used in polynomial expressions determined from theoretical profiles that are calculated numerically using the Young-Laplace equation modified for a pendant/sessile drop. A second order optimization procedure gives a residual of 0.1 to 0.4 pixel units in 1-2 runs. The typical time for one measurement of γ is 3-5 seconds.

The surface tension of water was determined by both pendant and sessile drops and sessile bubbles, and give satisfactory consistent results. A mayor source of error in sessile drop measurements was found to be uneven wetting of the substrate, leading to lack of axisymmetry.

An investigation performed with this instrument last year was presented at the XII ECIC Conference in Lund this summer. The abstract is given below.

Surface Tension by Pendant Drop
II. The Influence of Oil Phase on Adsorption in Nonionic Surfactant Systems

F.K.Hansen and G.Trouttet

By means of a new method of computer image analysis of a pendant drop, it is now possible to obtain fast and reliable data on the development of surface and interfacial tensions at the time scale of seconds/minutes. This method has been utilized in order to investigate the effect on interfacial tension, and indirectly on adsorption, of the nature of the oil phase, with and without polar additives. Four different nonionic surfactants, NPEO10, NPEO15, NPEO20 and NPEO40 were used. In addition, also 3 nonionic polymer surfactants of the type PEO-PPO were tested. As oil phase were used toluene and dodecane with addition of 1-pentanol, 3-pentanol, dodecanol, aniline and benzoic acid.

In these systems the interfacial tension of a freshly formed oil/water interface always drops in well-known manner (in milliseconds) from the value of pure oil/water systems to a low initial "steady state" value. From here, the interfacial tension change depends on the nature of the oil phase and the surfactant system. In the pure dodecanol system, interfacial tension is almost constant, and increases with the water solubility of the surfactant as expected. In the pure toluene system, however, it decreases with time, mostly dependent of the hydrophilicity of the surfactant: the surfactant with the lowest hydrophilicity (NPEO10) having the strongest decrease. By means of an "extrapolated zero-time" (EZT) value of the interfacial tension, it is possible to model equilibrium adsorption in these systems both with and without surfactant in the oil phase. The decrease is mostly accounted to the solubility of the surfactant in the oil phase, and the time it takes to saturate the oil drop with surfactant. The EZT-value also shows a minimum in interfacial tension for the NPEO20 surfactant, while NPEO10 has the highest EZT-value.

When low molecular polar additives are added to the oil phase, several effects take place simultaneously. Primarily the surface activity of the additive contributes to the total interfacial tension lowering, while the simultaneous increase of surfactant solubility in the oil phase has the opposite effect. In addition the additive and surfactant may produce mixed micelles in the aqueous phase, sometimes leading to spontaneous emulsification of the oil, or the additive may be precipitated or form inverse micelles in the oil phase, because of incorporation of water from the external phase. These phenomena lead to complex behaviour in these systems and may be monitored by following the interfacial tension and by observing the drop in the video system. By looking at the EZT-values in these systems, the "pure" effect on combined adsorption may be evaluated.

October 23, 1992

CONTRIBUTION TO THE INTERNATIONAL POLYMER COLLOIDS GROUP NEWSLETTER

Do Ik Lee
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The Following Paper Was Presented at The First TAPPI Coating Fundamentals Symposium Which Was Held in Montreal in May, 1991.

The Importance of Electrokinetic Measurements For Understanding The Colloidal Phenomena Occurring in Paper Coating Formulations

Y. Chonde, J. A. Roper, D. I. Lee
Latex R&D

ABSTRACT

A systematic study of the interactions of various components of paper coating formulations was carried out using electrokinetic measurements (electro-sonic amplitude, ESA), sedimentation volume ratio, cryo stage transmission electron microscopy, rheology, and dried coating optical properties. Good correlations were observed between the electrokinetic results, sedimentation volume ratios, results of cryo transmission electron microscopy, yield stresses, and dried coating opacity and brightness. The electrokinetic profile of clay dispersion showed dependency on the type of counter ion and co-ion of added electrolyte. This observed electrokinetic profile was in good agreement with measured sediment volume ratios, yield stress values, and coated Mylar film properties. Similar electrokinetic profiles were observed as function of added electrolytes from a diluted to a semi-concentrated clay dispersions.

In a clay/latex (non-pigment interactive, CP638NA) mixture the electrokinetic and yield stress values decreased with increasing latex addition. These simultaneous decreases were attributed to a result of increased ionic strength and crowding to decrease the electrokinetic values and the possible role of latex particles in modifying the clay particle-particle interactions to lower the yield stress values. However, in a clay/latex/ammonium sulfate dispersion system, a good correlation was observed between the high solid electrokinetic measurements and the yield stress values. In this system, the electrokinetic value decreased with added ammonium sulfate, while the yield stress value increased. In the presence of starch, addition of ammonium sulfate to a clay/latex dispersion showed a unique phenomena. At low level of added ammonium sulfate, a small increase in electrokinetic value was accompanied by a corresponding decrease in the yield stress.

A Paper Submitted For The Second TAPPI Coating Fundamentals Symposium To Be Held In April 30 - May 1, 1993

Latex Film Formation: Determination of Deforming Forces During Coalescence

Charles Kan
Latex R&D

ABSTRACT

The ability of latex particles to deform and coalesce to form a continuous film upon drying is an important property in many end use applications. At temperatures above the minimum film formation temperature, MFFT, the forces generated during drying are sufficient to deform the latex particles to eliminate the voids and form an integral film. Many researchers have speculated about the origin of the forces generated during latex film formation. Theories based on capillary force and adhesive force were proposed to predict the magnitude of the deforming forces. However, no successful experiment has been reported to directly or indirectly measure the forces generated during drying of the latex film.

This paper will describe the experiments carried out to determine the deforming forces exerted unto the latex particles by measuring the moduli of the water saturated latex films at conditions that correspond to the MFFT. The magnitude of the forces is found to be better described by the theory proposed by Kendall and Padget, indicating the importance of adhesive forces in deforming the latex particles during the entire film formation process.

A Paper Submitted For The 1993 TAPPI Coating Conference To Be Held In May, 1993.

RHEOLOGY OF PAPER COATINGS AND ITS IMPACT ON HIGH SPEED BLADE RUNNABILITY

John A. Roper III and Jamel F. Attal
Latex R&D

ABSTRACT

A variety of runnability problems such as blade weeping and scratching occur as paper coating speeds increase. A number of interrelated factors are responsible. This makes it difficult to predict runnability simply from laboratory rheological measurements. However, it was possible to correlate coating rheology with pilot coater performance for certain operating conditions. The coating rheology data were collected using rotational viscometers for low shear measurements and a capillary viscometer for high shear measurements. The viscosity data were combined to generate a single flow curve for each formulation covering shear rates from 1 to 1,000,000 sec^{-1}. This flow curve was fitted with a five parameter model using an extension of the Cross equation to include dilatancy at high shear rates. The rheology model was incorporated into a computational fluid dynamics (CFD) simulation of a short dwell coater which took into consideration differences in coater geometry. By combining laboratory measurements with computer simulations, a better understanding of runnability can be achieved.

On the role of surface conduction in the electrokinetics of latices

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As part of our study of electrical double layers under non -equilibrium conditions we have done experimental work on dielectric relaxation and theoretical work on surface conduction, dielectric dispersion and the influence of double layer disequilibration on colloid stability. Part of this investigation is relevant for polymer colloids. Here I summarise the consequences that surface conduction has for a number of electrokinetic and related phenomena.

Most modern theories that are used to convert electrophoretic mobilities into ζ-potentials, treat the double layer polarization in a rather advanced way, but surface conduction is usually ignored, (surface conduction is excess conduction of ions behind the slip plane). Such theories account for a number of observations, one of them being the maximum through which ζ passes as a function of mobility, which is due to double layer polarization.

There also are a number of recurring observations that cannot be explained in this way. Some of them are

1. When for a given latex ζ-potentials are computed from dielectric relaxation and from electrophoresis the former always tends to exceed the latter.
2. As a function of the electrolyte concentration, ζ often passes through a maximum.

These trends are well-documented. They find their origins in surface conduction. Basically, conduction behind the slip plane tends to lower ζ from electrophoresis, to rise $\Delta\varepsilon$ and to enhance the conductivity of the system. This idea, or parts of it, can be found in the literature[1-8] which contains experimental evidence and theoretical analyses.

Recently, we have developed a quantitative theory for large κa[9] based on Fixman's theory[10].

From this theory it follows that, in the case of non-zero surface conductivity (K^σ) unambiguous establishment of ζ from the electrophoretic mobility *only*, or from $\Delta\varepsilon$ *only* is ambiguous. To establish whether such conduction takes place, one could either measure the static conductivity or the dielectric dielectric response of the sol. From these two pieces of information ζ *and* K^σ are obtained.

Application of this theory to latices shows that very similar ζ's can be obtained from mobility and bulk conductivity by fitting K^σ. The differences are usually less than 10%. The extremely high low frequency dispersion of latices[11] cannot be explained this way, hence that phenomenon must have another origin.

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Contribution to Polymer Colloids Group Newsletter

by
Mamoru Nomura and Hidetaka Tobita

Department of Materials Science and Engineering
Fukui University, Fukui, Japan

Dr. H. Tobita joined our group in July 1, 1991. His research interest is now in the field of Polymer Reaction Engineering. He is interested in crosslinking and grafting kinetics in both homogeneous and heterogeneous polymerization systems. The recent papers of our group concerning emulsion polymerization, which have already been accepted and will soon appear, are as follows:

(1) Control of Network Structure in Emulsion Crosslinking Copolymerization. H. Tobita et al., ***Polymer International.***

(2) Crosslinking Kinetics in Emulsion Copolymerization of Methyl Methacrylate/Ethylene Glycol Dimethacrylate. H. Tobita et al., ***Polymer.***
"This paper shows that the measured development of network formation agree with that predicted by Tobita Model, and that the average crosslinking density is fairly high even from very early stage of polymerization and the produced network tend to be highly heterogeneous"

(3) Particle Nucleation in Emulsion Copolymerization Containing Multi-functional Monomers. M. Nomura et al., ***Polymer International.***
"This paper shows that the number of polymer particles produced in emulsion polymerization increases drastically in the presence of multi-functional monomers. This paper also explains the reason for this"

(4) A New Approach to Continuous Emulsion polymerization. M. Nomura et al., ***Polymer International.***

(5) Kinetics and mechanisms of Emulsion Polymerization Initiated by Oil-Soluble Initiators. IV. Kinetic Modeling of Unseeded Emulsion polymerization of Styrene Initiated by 2,2'-Azobisisobutyronitrille. M. Nomura et al., ***J. Polymer Sci., Polym. Chem. Ed.***

Preprints of "International Symposium on Polymeric Microspheres", which was held in Fukui in October, 1991, consists of 284 pages with 64 papers. The titles of the papers are listed in the following pages. The special issue of *Polymer International*, which contain 39 papers out of 64 papers presented in this symposium, will be soon published. Those who are interested in obtaining the preprints and the special issue of *Polymer International* should write to us.

ORAL PRESENTATION

01 The Mechanism of Entry of Free Radicals into Latex Particles. D.H. Napper, R.G. Gilbert, I.A. Maxwell, B.R. Morrison, (University of Sydney, Australia).
02 The Kinetics of Emulsifier Adsorption and the Nucleation of Latex Particles. A.S. Dunn (University of Manchester, U.K.)
03 Particle Nucleation in Emulsion Copolymerization Containing Multifunctional Monomers. M. Nomura, K. Fujita (Fukui University, Jpn)
04 Studies on Mechanism and Kinetics of Emulsion Copolymerization of Vinylidene Chloride. Yu Zaizhang, Jia Hongbing, Li Bogeng, Li Baofang (Zhejiang University, P.R. China).
05 Reactant Partitioning in Free-Radical Heterophase Polymerization. J. Barton (Polymer Institute, Slovak Academy of Science, C.S.F.R.)
06 Chain Transfer to Styrene Monomer to Produce Stable Radicals: Analysis of Seeded Microemulsion Polymerization of Styrene. M. Litt (Case Western Reserve University, U.S.A.)
07 Soapless Emulsion polymerization of MMA in the presence of $CaSO_3$. J.F. Lee and W.Y. Chiu (National Taiwan University, R.O. China)
08 Synthesis, Characterization and Application of Surface Active Initiator. K. Tauer, S. Kosmella (Institute for Polymer Chemistry, Germany)
09 The Role of Surfactant in Particle Nucleation in Emulsion Polymerization. T. Matsuo, S. Hashiya (Fukui University, Jpn.)
10 Shell Growth Mechanism in Emulsifier-Free Emulsion Polymerization: Morphological and Kinetic Studies. S-A. Chen, S-T. Lee (National Tsing-Hua University, R.O. China)
11 Development of Morphology in Latex Particles: The Interplay Between Kinetic and Thermodynamic Parameters. Y-C. Chen, V. Dimonie, M.S. El-Aasser (Lehigh University, U.S.A.)
12 Emulsion Polymerization of Vinyl Esters. P.S. Martin, O.W. Smith, D.R. Bassett (Union Carbide Chemicals and Plastics Co. Inc., U.S.A.)
13 Miniemulsion Formation and Polymerization of Styrene. Z. Pan, H. Fan, Z. Weng, Z. Huang (Zhejiang University, P.R. China)
14 Use of a ^{13}C NMR Chemical Shielding Technique to Investigate the Polymerization of Styrene Oil-in-Water Microemulsions. H.J. Yue (Air Product and Chemicals, Inc., U.S.A.), J.S. Guo, E.D. Sudol, J.W. Vanderhoff, M.S. El-Aasser (Lehigh University, U.S.A.)
15 Very Small Polystyrene Latexes from Emulsion Polymerization in the Presence of Zwitterionic Surfactants. A. Guyot, C. Graillat, H. Essaddam, C. Pichot (CNRS-LMO, France)
16 Mechanism and Kinetics of the Polymerization of Surface-Active Monomers. D. Cochin, R. Zana, F. Candau (CNRS-ULP, France).
17 Preparation of Reactive Latices by Emulsifier-Free Emulsion Copolymerization of Styrene with a Novel, Water-Soluble Monomer Having an Active Ester Group. K. Nagai, Y. Itoh, H. Obata, N. Muraoka (Yamagata University, Jpn.)
18 The Role of Polyvinyl Alcohol in Emulsion Polymerization. K. Yuki, T. Sato, H. Maruyama, J. Yamauchi, T. Okaya (Kuraray, Co., Ltd., Jpn.)
19 Triblock Copolymers of Polyisobutylene-Block-Polyoxyethylene-Block-Polyisobutylene(PIB-b-POE-b-PIB) as Stabilizers in Aqueous Emulsion Polymerization. I. Piirma, Bidulate Sar (The University of Akron, U.S.A.)
20 Preparation of Micron-Size Monodisperse Polymer Microspheres by Seeded Polymerization Utilizing Dynamic Monomer Swelling Method (II). M. Okubo, S. Masaya, Y. Tsukuda, T. Nakagawa (Kobe University, Jpn.)
21 Preparation of Monodisperse Polymer Particles by Dispersion Copolymerization of MMA with Poly(2-Oxazoline) Macromonomer. S. Kobayashi, H. Uyama, J.H. Choi, Y. Matsumoto (Tohoku University, Jpn.)
22 Preparation of Polyperfluoroalkylmethacrylate Microspheres by Dispersion Polymerization Using Graftcopolymers for the Dispersant. T. Arai, Y. Takizawa, S. Kawase (Soken Chem. & Eng. Co., Ltd., Jpn.

23 Characterization of Latices Prepared by Surfactant-Free Emulsion Polymerization Using Vinylidene Fluoride. T. Shimizu, N. Tsuda T. Aoyama (Daikin Ind.,Jpn.)

24 Monodisperse Ellipsoidal Polystyrene Latex Particles: Preparation and Characterization. C.C. Ho (University of Malaya, Malaysia), A. Keller, R.H. Ottewill and J.A. Odell (University of Bristol, U.K.)

25 Intramoleculary Crosslinked Macromolecules - Characterization and Particle Properties. W. Funke, H. Bauer, B. Joos, O. Okay (Stuttgart University, Germany)

26 Fluorescence Analysis for Thermo-Sensitive Hydrogel Microspheres. K. Fujimoto, Y. Nakajima, H. Kawaguchi (Keio University, Jpn.)

27 Characteristics of Highly Water Absorbent Polymer Emulsion. N. Watanabe, Y. Hosoya, A. Tamura, H. Kosuge (Mitsui-Cyanamid, Ltd., Jpn.)

28 Molecular Aspects of Latex Film Formation. M.A. Winnik, Y. Wang (University of Tronto, Canada)

29 Water Vapor Permeability, Diffusion and Solubility in Latex Films. J. Richard, C. Mignaud, K. Wong (Rhone-Poulenc Recherches, France)

30 Model Prediction, Experimental Determination and Control of Emulsion Copolymer Microstructure. G.H.J. van Doremaele, A. German (Eindhoven University of Technology, The Netherlands)

31 Copolymer Composition Control in Emulsion Polymerization Using Technical Grade Monomers. J.R. Leiza, G. Arzamendi, J.M. Asua, (Universidad del Pais Vasco, Spain)

32 Emulsion Polymerization and Copolymerization in Continuous Reaction Systems. G.W. Poehlein, D.M. Lange. (Georgia Institute of Technology, U.S.A.)

33 A New Approach to Continuous Emulsion Polymerization. T. Imamura, K. Saito, S. Ishikura (Nippon Paint Co.,Ltd., Jpn.) M. Nomura (Fukui University, Jpn.)

34 A Fundamental Investigation of the Synthesis of Polybutadiene Seed and Further Grafting Emulsion Copolymerization of Styrene/Acrylonitrile Mixture. J. Guillot, P. Mathey-Muller (CNRS-LMO, France)

35 Crosslinking Kinetics in Emulsion Polymerization. A. Hamielec (McMaster University, Canada)

36 Control of Network Structure in Emulsion Crosslinking Copolymerization H. Tobita (Kao Co., Ltd., Jpn.)

37 Chemical and Physical Aspects of Multicomponent Ceramic Oxide Precipitation Prepared via Multicomponent Alkoxide Hydrosis. R.E. Riman (Rutgers, The State University, U.S.A.)

38 Precipitation of Uniform Inorganic Particles: Growth Mechanism and Colloidal Stability. C.F. Zukoski, J-L. Look (University of Illinois, U.S.A.)

39 Preparation of Polymeric Microsphere-Silica Hybrid Materials by Alkoxide Process. T. Inoue, A. Kimi, Y. Kataoka (Nippon Zeon Co., Ltd., Jpn.), S. Yamazaki(National Chemical Laboratory for Industry, Jpn.)

40 Chemical Reactor System for Preparation of Monosized Colloidal Oxide Particles. T. Ogihara (Fukui University, Jpn.)

41 Laser Photoacoustic and Photothermal Spectroscopy as a Novel Characterization Method for Microparticles. T. Kitamori, T. Sawada (The University of Tokyo, Jpn.)

42 Submicron Particle Size Analysis by Capillary Hydrodynamic Fractionation (CHDF) J.G. Dos Ramos (Matec Applied Sciences, U.S.A.), C.A. Silebi (Lehigh University, U.S.A.)

43 Flow Profile of Electro-Endosmosis and Effect of Chemical Coatings on the Cell Surface for Electrophoretic Light Scattering Measurement. K. Oka, W. Otani, M. Akagi, H. Kita (Otsuka Electronics Co., Ltd., Jpn.)

44 Laser Manipulation and Ablation of an Individual Latex Particle in Solution. H. Misawa, M. Koshioka, K. Sasaki, N. Kitamura, H. Masuhara (Microphotoconversion Project, JRDC)

45 Dielectric Spectroscopic Characterization of Weak Acid Polystyrene Colloids. L.S. Su, S. Jayasuriya (S.C. Johnson Wax, U.S.A.), R.M. Fitch (Fitch & Associate and the University of Wisconsin, U.S.A.)

46 Depletion Effect of Excess Polymer on latex Suspension. K. Furusawa (University of Tsukuba, Jpn.)

47 Electroviscus Effect in Dilute Suspensions of Ionic Polymer Latices. J. Yamanaka, S. Hashimoto, T. Yamaguchi, S. Saeki, M. Tubokawa (Fukui University, Jpn.), H. Matsuoka, H. Kitano, N. Ise (Kyoto University)

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Poly(N-isopropylacrylamide) latexes prepared with SDS.

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October 19, 1992

Abstract

Stable aqueous colloidal dispersions of cross-linked poly(N-isopropylacrylamide), polyNIPAM, were prepared by aqueous dispersion copolymerization of NIPAM with methylenebisacrylamide, BA, in the presence of sodium dodecyl sulfate, SDS. Below 32 ^{o}C the particles were highly swollen with water and had average diameters in the range 400-800 nm. Above 32 ^{o}C the average diameters decreased by a factor of two. Swelling showed the expected trends with cross-linker density, the presence of methanol, and the presence of urea. Also observed was the expected decrease in average particle size with increasing SDS concentration during the polymerization. Flory χ values were estimated from the swelling data.

Unexpectedly, the average diameter at 25 ^{o}C and the electrophoretic mobility of a cleaned latex were greater in 1x 10^{-5} M KCl than in higher electrolyte concentrations. Also unexpected was the observation that colloidal particles were obtained without BA. The presence of particles rather than isolated linear polyNIPAM chains was explained by chain entanglement.

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Poly(N-isopropylacrylamide) 1: Interactions with sodium dodecyl sulfate measured by conductivity.

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October 19, 1992

Abstract

Conductometric titration of poly(N-isopropylacrylamide) (polyNIPAM) with sodium dodecyl sulfate (SDS) gave two apparent transitions labeled C1 and C2. The C1 transition was independent of polyNIPAM concentration in the range 0.05 to 0.3 wt % whereas C2 was proportional to the polymer concentration. C1 corresponded to onset of binding of surfactant with polymer. Arguments based on a simple mass action model for micellization are presented to show that C2, the second transition, is not due to any simple explanation such as being the point above which only free micelles are formed with surfactant addition The cloud point of polyNIPAM increased with the amount of bound surfactant. This was attributed to electrostatic contribution of bound sulfate groups to the increased solubility of polyNIPAM

Keywords:

poly(N-isopropylacrylamide), sodium dodecyl sulfate, polymer-surfactant complex formation, micelle formation, phase separation temperature.

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Poly(N-isopropylacrylamide) 2: Effect of polymer concentration, temperature and surfactant on the viscosity of aqueous solutions.

K. C. Tam[1], X. Y. Wu[2] and R. H. Pelton[2*]

The effects of polymer concentration, temperature and surfactant on the rheological properties of poly(N-isopropylacrylamide) were studied. Below 28 ^{O}C the viscosity decreased with increasing temperature according to the Arrhenius expression. However, at 29 ^{O}C the viscosity increased to a maximum value at 32 ^{O}C, the Lower Critical Solution Temperature (LCST) for aqueous polyNIPAM. Higher temperatures gave a much lower viscosity. This unusual rheological behavior was explained by the phase behavior of the polymer. Sodium dodecyl sulfate (SDS) binding to polyNIPAM increased the cloud point temperature (CPT) and attenuated the unusual rheological behavior of polyNIPAM in water.

Keywords:

viscosity, poly(N-isopropylacrylamide), sodium dodecyl sulfate, polymer-surfactant complex formation, phase separation, temperature sensitive conformation.

The kinetics of poly(N-isopropylacrylamide) microgel latex formation

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October 19, 1992

Abstract

Conversion versus time curves were measured for poly(N-isopropylacrylamide) microgel latexes prepared by polymerization in water with sodium dodecyl sulfate, SDS. Polymerization rates increased with temperature but were independent of particle size and SDS concentration. By contrast the particle diameter decreased with increasing concentrations of SDS in the polymerization. This confirmed that the main role of SDS was to confer colloidal stability. Particle was by homogeneous nucleation and not micellar nucleation because of the absence of micelles .

Comparison of particle size distributions from dynamic light scattering to those from a centrifugal sizer led to the conclusion that larger particles within a specific latex were less swollen with acetonitrile than were the smaller ones.

Keywords: N-isopropylacrylamide polymerization, nucleation mechanisms, polymerization kinetics, gel swelling.

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Contribution to Polymer Colloids Group Newsletter

from CNRS/Lyon

submitted by C. Pichot
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Suspended emulsion polymerization: Application to acrylonitrile-methyl acrylate system (Ph. Vindevoghel, A. Guyot -LMO-Solaize)

The suspended emulsion process consists in a monomer polymerization in an aqueous phase containing a water-soluble initiator system . The aqueous phase which is the polymerization locus is dispersed as droplets in the monomeric continuous medium.

The final beads obtained by this new polymerization process have a mean diameter of 100mm and contain primary particles of size 0.5mm-2mm. The influence of various parameters on the external and internal morphology have been studied. The addition of different surfactants in the aqueous phase enables to control the internal morphology: small primary particles (0.5mm) with a narrow size distribution are obtained with an anionic surfactant (SDS) whereas larger particles are synthesized when non ionic (NP30) or cationic surfactants are used. The addition of surfactants involves kinetics changes whatever the nature of the emulsifier.

A study of initiator decomposition by two different methods (potentiometric titration and capillary electrophoresis) enables to quantify the influence of different additives (emulsifier, monomer...) on the kinetics of decomposition. The influence of monomers on the different surfactants cmc's have also been investigated. All these studies should lead to a better understanding of the polymerization process.

Investigations of persulfate decomposition and the effect of some parameters : Temperature, pH and other reagents (C. Graillat, Ph. Vindevoghel, J. Guillot - LMO - Solaize)

Initiator decomposition is a key parameter in emulsion polymerization. However, even the effect of experimental conditions on persulfate dissociation is an object of controversy. As a contribution to this field, a study of potassium persulfate decomposition has been carried out by various techniques :
- pH-metry,
- potentiometric titration of sulfate ions($SO_4^{=}$)with a specific electrode (calomel electrode as reference - lead perchlorate as titration solution),
- capillary electrophoresis for ions titration.

The fisrt results with the specific electrode tend to show that :
- at acidic pH, the pH of the solution decreases versus time(decomposition) and that the effect of initial pH is low if pH ≈2 at beginning. However, the accuracy of pH-metry is poor at pH < 3.
- the presence of sulfate ions does not significantly modify the persulfate decomposition, as expected if the decomposition does not obey an equilibrium equation.
- the rate of decomposition is increased in the presence of a reductor($Na_2S_2O_5$). Emulsifiers, as sodium dodecyl sulfate (SDS), seem to lower the rate.
- at basic pH (≈10), the half-life time is twice larger than at initial neutral pH.

In the presence of sulfate ions, it is observed a much lower rate of decomposition at the beginning as if $SO_4^{=}$ ions participate in an equilibrium reaction, as a "buffer".
Electrophoresis data are in good agreement for persulfate decomposition, what is promising as a novel technique for such investigations.

Synthesis of nonionic surface active initiators, and application to emulsion polymerization (F. Vidal, J. Guillot, A. Guyot - LMO/Solaize)

The aim of this study is to prepare stable latices without ionic charges using surface active initiators (inisurf). The initiators are diesters resulting from the reaction between the 4,4' azobis (4-cyanopentanoic acid) (ACPA) and:

- either a polyethylene glycol methyl ether 550. The esterification reaction was carried out by treatment of the corresponding diacide chloride of ACPA with the alcool.
- or a polyethylene glycol (n=30) dodecanol. This inisurf was prepared in collaboration with J.M.H. Kusters (Laboratory of Polymer Technology and Chemistry, T.U. Eindhoven).

All these inisurfs have been found to be able to initiate polymerization of styrene. Only with the second kind of inisurf it is possible to prepare stable latices.
Futher investigations, such as temperature (cloud point), amount of inisurf, the solid content and polymerization mechanism will be carried out.

Emulsion polymerization of nonionic surface active monomers (A.Filet, J.Guillot,A.Guyot -LMO/CNRS)

This work is devoted to the synthesis and characterisation of surface active monomers.and their study in emulsion polymerisation Their structure consists in 3 parts : a polymerisable function (styrene or methacrylate), an hydrophobic part (alkyl chains, with n=6 or 12), an hydrophilic part (ethylene oxyde chains, n=10 or 25). After determination of some physiochemical properties (cmc, molecular weight, cloud points..;), they are currently applied in various types of polymerisation :
- solution polymerisation, for the determination of reactivity rates.
- emulsion polymerisation, where such surfactants should allow to confer a long term steric stability to the particles, because they should be chemically bounded by polymerisation.

Different parameters, such as process (batch, semi continuous...), surfactant concentration, and its HLB, the ratio surfactant/monomer..) are being investigated in order to optimize the location of the hydrophilic part at the surface of the particles.

Synthesis and characterization of lipopeptide-type monomers bearing various terminal bioreactive groups (X.Revilla C.Pichot (UM CNRS/bioMERIEUX), B. Gallot (LMO-CNRS/Solaize))

A series of new monomers of general formula ($C_6H_4CH_2NH(CH_2)_{10}NH$-CO-R) have been designed with the objective to functionalize polystyrene- based latex particles so as to be used in biomedical applications . The preparation of such monomers is based on a five- step synthesis, starting from aminomethylstyrene (providing the polymerizable end group) and further reacted with a N- protected aminoacid; after recovering the amine function, a terminal bioreactive is coupled.Two monomers with the lipogluconamide and lipomaltonolactone, respectively have been obtained and their physiochemical properties (especially the surface activity) and kinetic behavior in homo and copolymerization were recently studied. Much work is currently investigated on the properties of the various solution (co)polymers as well as on the functionalization of latexes with such monomers.

Recent Publications and Thesis

* Crosslinking ability of styrene-butyl acrylate copolymer latices functionalized with glycidyl methacrylate, S. Magnet, J. Guillot, A. Guyot, C. Pichot - Prog. in Org. Coatings 20,73,1992

* B. Charleux: Synthesis and characterization of monomers and macromonomers bearing a terminal reactive function . Kinetic studies on solution and emulsion (co)polymerization.
Thesis . Univ. Claude Bernard - Lyon I - Nov 1991

* M. Hidalgo: Synthesis, physiochemical and thermomechanical characterization of films issued from functionalized styrene- butyl acrylate copolymer latexes.
Thesis . Univ. Claude Bernard - Lyon I - Fev 1992

Newsletter Contribution from The University of Akron

by Irja Piirma
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Polymerization of Butadiene and Acrylonitrile.

Report by Svetlana Karova

As has been reported previously, it is the gel content of the PBD-PAN seed that is the most important factor in controlling the morphology of the particles when AN-MA monomers are polymerized in the presence of that seed. When the seed latex is only slightly crosslinked, the second stage monomers penetrate the seed, swell it, and polymerize inside the particle. On an electron microscope picture this particle appears homogeneous. When the seed is highly crosslinked, as not to allow much swelling, the core and shell of the particles look like two separate phases. Sometimes new, PAN-PAM appear, totally separate from the seed particles.

Further study of the effect of the polymerization variables on the morphology in this system has revealed that the addition of mercaptan in the second stage of the polymerization leads to the following changes: the core is dislocated from the center to one end of the particle creating an acorn-shape morphology, instead the usually observed core-shell. Depending on the mercaptan concentration, any intermediate positions can be observed. The addition of mercaptan chain transfer agent will create shorter, more hydrophilic PAN-PMA chains as the AN-MA monomers polymerize inside and around the seed particles. Hence, the mercaptan addition can change the location the PBD-PAN core and create different morphologies of final particles.

Newsletter Contribution from The University of Akron

by H. Michael Cheung

Polymerization in Bicontinuous Microemulsions

Bicontinuous microemulsions offer a unique environment for polymerization. Several projects are underway which utilize this enviroment:

Microemulsion Pathway to Elastomers : Microemulsion of methylmethacrylate, ethylene glycol, and acrylic acid were characterized and polymerized. The phase diagram of the unpolymerized system was determined. The Winsor-IV region was identified and characterized using viscometry and laser light scattering. Winsor-IV region microemulsions were polymerized to yield polymeric solids. Selective solvents were used to estimate the amount of ethylene glycol incorporated in the polymer chains. DSC was used to measure the T_g and the enthalpy of relaxation of the polymer. Mechanical testing was performed to investigate the elastomeric properties of the polymer.

Synthesis and Characterization of Hydrogels Formed by Microemulsion Polymerization:
Polymerization of bicontinuous microemulsions has been used to create porous hydrogels. Studies were conducted to relate the characteristics of the precursor bicontinuous microemulsions to the morphology of the porous hydrogels. The porous hydrogels obtained were characterized and their properties compared to those of non-porous hydrogels of similar composition. This technique has the potential of being applied to form hydrogels when control of the porous structure and surface composition is required.

Synthesis of Interpenetrating Polymer Networks by Microemulsion Polymerization:
Polymerization of bicontinuous microemulsions can be used to form open-cell, porous polymeric networks. This process has been applied as the first step in a two step procedure to form interpenetrating polymer networks. The characteristics of the precursor microemulsions have been studied. The interpenetrating polymer networks formed were characterized with respect to their morphology and physical properties. The relationship between the properties of the interpenetrating polymer networks and the structural feactures of the precursor microemulsions was examined.

Microemulsion Route to Polymer Blends using Polymerizable Surfactants:
The application of various polymerizable surfactants for polymerization in microemulsions creates polymeric materials with modified surface properties. This is achieved by incorporation of the surfactant at the polymer surface. The modification of surface properties by this technique has been utilized to achieve compatibilization in polymer blends. The precursor microemulsions and intermediate polymer latices were characterized using laser light scattering and SEM. The final polymer blends were characterized using SEM, thermal analysis, and mechanical measurements. Considerable potential exists for the application of microemulsions in the production of precursor latices for polymer blend formation.

Characterization of Water-Soluble Oligomer in Acrylic Acid-Styrene Emulsion Copolymerization

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Summary

Low molecular weight species formed during the emulsion copolymerization of styrene and acrylic acid were isolated and characterized. Samples of the reaction mixture were taken at different times during seeded and unseeded batch reactions. The reactions in the samples were stopped via injection into hydroquinone solutions and cooling with dry ice. Low molecular weight copolymers were separated and FTIR spectroscopy, mass spectroscopy and ^{13}C-NmR spectroscopy techniques were used to measure the oligomer composition, molecular weight and copolymer sequence distribution respectively.

The molecular size measurements should relate to the size of oligomeric radicals that enter polymer particle and to any water-soluble polymer that is formed by termination in the aqueous phase.

The molecules found for copolymers formed from 90/10 weight ratios of styrene and acrylic acid were comprised of 6-9 monomer units. Those formed from 60/40 styrene/AA ratios contained 13-16 monomer units. Differences were observed between seeded and unseeded systems, especially in the amount and nature of the water-soluble material formed early in the reaction. Brief information on the experimental systems used and the results are provided on the attached table.

Table 1. Recipe and reaction conditions for preparation of styrene-divinylbenzene seeds*

Recipe:	Styrene	98.28 g
	55% Divinylbenzene**	1.82 g
	Sodium dodecyl sulfate (SDS)	3.00 g
	Potassium persulfate	1.00 g
	Deionized water	200 g

Reaction conditions:

55°C for 3 h, 70°C for 3 h, 80°C for 3 h

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* 25 g mixed bed ion exchanger was added to 100 g seeds to remove the emulsifier when the seeds were used.

** Other components are ethylstyrene and diethylbenzene.

Table 2. Recipe for unseeded and seeded emulsion copolymerization of styrene and acrylic acid at 50°C

Unseeded copolymerization, SA-10 and SA-40:	
Styrene+acrylic acid	100 g
Acrylic acid in monomers (wt %)	10, 40
SDS	2.5 g
$K_2S_2O_8$	1.0 g
Deionized water*	300 g
Seeded Copolymerization, SAS-10 and SAS-40:	
Solid polymer of styrene-divinylbenzene seed	50 g
Styrene+ acrylic acid	50 g
Acrylic acid in monomers (%)	10, 40
SDS	0.3 g
$K_2S_2O_8$	1 g
Deionized water*	300 g

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* The water contains KCl (0.1 mol/L) and HCl (0.2 mol/L).

Table 3. Largest MS ion peaks of selected samples at different conversion

Sample code	Conversion (%)	Largest M^+/e
SA-10	9.19	804
	16.99	716
SA-40	16.33	1251
	26.32	1205
SAS-10	7.00	992
	21.16	972
SAS-40	9.11	1318
	22.00	1380

Table 4. Critical free radical size for entry and their composition

Sample code	Conversion (%)	M_w*	Composition			
			AA/S (mol/mol)	N_{AA}	N_S	Z
SA-10	9.19	599	3.26	6 (5.8)**	2 (1.8)**	8
	16.99	511	1.69	4 (3.8)	2 (2.3)	6
SA-40	16.33	1046	14.89	13 (13.2)	1 (0.9)	14
	26.32	1000	9.91	12 (12.1)	1 (1.2)	13
SAS-10	7.00	787	1.99	6 (6.3)	3 (3.2)	9
	21.16	767	1.93	6 (6.1)	3 (3.2)	9
SAS-40	9.11	1113	10.64	14 (13.6)	1 (1.3)	15
	22.00	1175	14.67	15 (14.8)	1 (1.0)	16

* $M_w = M^+/e - 205$, where M^+/e is the ion weight divided by its charge number in MS, 205 is added group weight of the sulfate and oxided hydroquinone in oligomer.

** The number bracketed are that calculated before integer.

International Polymer Colloids Group

Polybutadiene-poly(methyl methacrylate) core-shell latexes studied by high-resolution solid-state ^{13}C-NMR: interphase formation as a function of the surface coverage of the polybutadiene seed latex.

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Abstract : High resolution solid-state ^{13}C-NMR has been used to examine the effect of the surface coverage of the polybutadiene seed latex on the interphase formation of PBut-PMMA core-shell latexes. On the basis of $T_{1\rho}$(H) measurements information on the interphase has been obtained.

Keywords: Pulsed NMR ; Interphase ; core-shell ; latex.

1. INTRODUCTION

Pulsed solid-state NMR has previously been used to investigate the molecular and dimensional level of homogeneity for a number of polymer blends including compatible systems as well as two phase materials (1-12). Their interface has been also investigated (13-18). From pulsed NMR measurement one can obtain information on the microscopic structure and dynamics or degree of molecular motion through the spin-spin relaxation time T_2, the spin-lattice relaxation time T_1, and that in the rotating frame, $T_{1\rho}$.

Schaefer et all have shown for blends that individual spin lattice relaxation times in the rotating frame for protons attached to different carbons can be measured using high resolution ^{13}C-NMR (6, 11, 19). The homogeneity of a blend can be characterized by the proton spin lattice parameters, which are sensitive to the short range spatial proximity of interacting dipole moments of the protons and thus to the spin diffusion phenomena.

Our recent studies (21-23) have demonstrated that solid-state ^{13}C-NMR can be used to study core-shell latexes having a polybutadiene (PBut) core and a thermoplastic shell such as poly (methyl methacrylate) (PMMA), polystyrene and styrene-acrylonitrile copolymer which are of practical importance as "impact improvers" for various thermoplastics (25,26). The two phase characteristics and the interphase of these systems have been investigated by the $T_{1\rho}$(H) measurement directly on the polymer in the latex form, in contrast to Llauro (24) , who has studied such latexes after filmification.

By this type of approach it becomes possible to have a better understanding of the degree of phase separation and the interactions between polymers in the interphase of a core-shell latex particle. In this respect we have shown recently that the interphase thickness and the average composition can be obtained by solid state NMR as a function of the various parameters, e.g. synthesis process, reaction temperature, particle size of the rubber seed latex, etc ... (23).

In order to extend this kind of investigation, we have examined in the present work the influence of the surface coverage of the seed latex on the interphase characteristics of PBut-PMMA core-shell latexes.

2. EXPERIMENTAL

2.1. *Synthesis and characterization of latexes*

PBut latex stabilized by anionic surfactant (SDS), as a starting material, has been kindly supplied by ROHM-HAAS. It has an average particle size of 55.5 nm and a solid content of 15 weight%. The surface coverage of this PBut seed latex is 0.17, which means that 17% of the particle surface is covered by the surfactant. SDS was added in order to vary the initial surface coverage between 17 and 94%. The latex of PMMA homopolymer, with an average particle size of 63.2 nm, was obtained by emulsion polymerization in a batch process at 60°C. Different samples of core-shell latexes have been prepared by a "semi-continuous" emulsion polymerization at 60°C by adding MMA monomer to the seed latex at an addition rate of 5.8 ml/h which is lower than the polymerization rate of MMA monomer. The concentration of the initiator, $K_2S_2O_8$, was in all cases 0.45 weight% (with respect to PBut solid content).

The size of latex particles, determined by photon correlation spectroscopy (Coulter N4), and their number determined from these values as a function of the surface coverage of PBut seed latex particles are given in Table 1.

The latex samples were then precipitated with a solution of concentrated sodium chloride, filtered, washed with distilled water and finally dried under vacuum at room temperature.

	surface coverage of the PBut seed latex						
	0.17	0.27	0.36	0.45	0.55	0.68	0.94
Dw (nm)	78.4±2.7	72.8±0.4	68.6±0.8	71.1±1.8	69.5±0.8	53.7±2.5	54.6±3.5
$Np.10^{-18}$	0.98±0.10	1.22±0.02	1.46±0.05	1.31±0.10	1.41±0.05	3.05±0.43	2.90±0.56

PBut seed latex: Dw = (55.5±3) nm ; Np = (1.74±0.29) $.10^{18}$

Table1: Particle size (Dw) and particle number (Np) of the core-shell latexes synthesized with PBut seed latexes with variable surface coverage.

2.2 *NMR measurements*

Solid-state ^{13}C-NMR experiments using cross-polarization, dipolar decoupling, and magic angle spinning (CP/DD/MAS) were run on the samples with a ^{13}C frequency of 75.47 MHz on a Bruker MSL300 spectrometer. The cross-polarization experiments (21-23) with variable contact times were used to determine $T_{1\rho}(H)$. The relaxation time of the proton spin is observed from its effect on the carbon nucleus to which the proton is bonded. Magnetic field strenghts of 50 KHz were used for the matched spin-lock cross-polarization transfers. Contact times from 2 ms to 24 ms were used with delays of 2.5 s between scans (recycle time). About 80 mg of powder were packed in 4 mn zirconia spinners with Kelf-F caps and were spun at the magic angle at 6 KHz. Depending on the composition, 200-800 scans were necessary per contact time value for a satisfactory signal-to-noise ratio. All spectra were obtained at a temperature of 20°C.

3. RESULTS AND DISCUSSION

The main features of the solid state ^{13}C-NMR spectra of PMMA are the peaks due to the α-methyl carbons (C9) at 15-27 ppm, the quaternary carbons (C6) at 45 ppm, the methoxy carbons (C5) at 52 ppm and the carbonyl carbons (C1) at 177 ppm. The methylene carbon peak is a broad underlying peak at 55-60 ppm.

By plotting the ln(carbon magnetization) versus contact time, the relaxation time $T_{1\rho}(H)$ is obtained from the negative of the inverse of the slope (-1/slope) (1). Duplicate experiments have previously shown a reproductibility of ±1% for carbons C1, C5 and C6, and ±10% for carbon C9 . The most precise $T_{1\rho}(H)$ values are determined for the protons linked to carbons C5 and C6 giving the most intensive signal. For the pure PMMA these relaxation times are respectively 13.8 ms and 13.1 ms for the carbon C5 and C6.

3.1 Influence of the surface coverage on $T_{1\rho}(H)$

A number of core-shell latexes have been prepared using PBut RH55 seed latex by varying the surface coverage of particles between 0.17 and 0.94. The PMMA content is 50 weight% in all cases. The corresponding $T_{1\rho}(H)$ values of PMMA in the core-shell latex are listed in table 2. The variation of the particle number (Np) and the $T_{1\rho}(H)$ relaxation time as a function of surface coverage of the PBut seed latex is shown in figure 1 for the methoxy carbon C5.

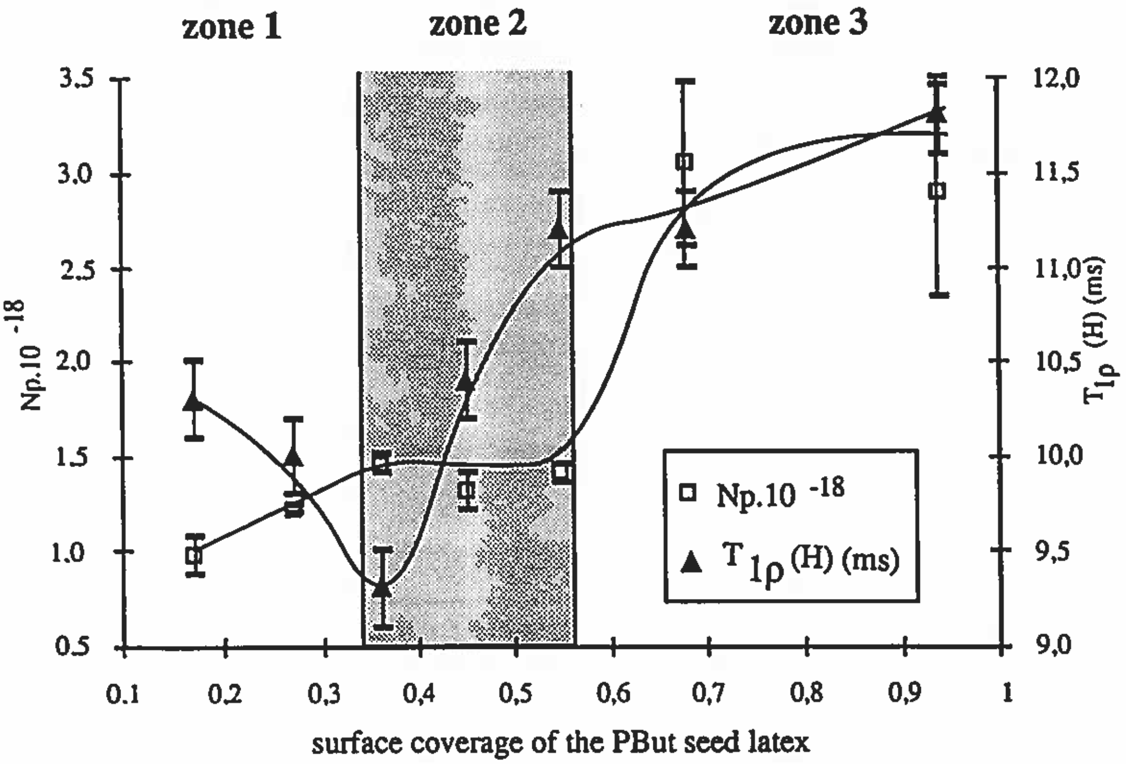

Figure 1 : Particle number (Np) and PMMA $T_{1\rho}(H)$ relaxation time (methoxy carbon C5) of the core-shell latexes versus the surface coverage of the PBut seed latex.

	surface coverage of the PBut seed latex						
	0.17	0.27	0.36	0.45	0.55	0.68	0.94
C5 carbon (52 ppm)	10.3	10.0	9.3	10.4	11.2	11.2	11.8
C6 carbon (45 pmm)	9.9	9.5	9.3	10.2	10.7	11.2	11.5

Table 2: PMMA carbon (C5, C6) $T_{1\rho}(H)$ relaxation times of the core-shell latexes synthesized with PBut seed latexes with variable surface coverage.

As shown in our recent studies (21-23), the decrease of $T_{1\rho}(H)$ in the core-shell latex particles with respect to pure PMMA may have two reasons. The PMMA protons can either interact with neighbouring PBut nuclei by direct dipole-dipole interactions, or the mobility of PMMA chains may be increased in the contact area between those two polymers; PMMA protons might have sufficient PBut near-neighbours to alter the molecular motion of the PMMA chains (2).

From table 2 and figure 1, it appears that the relaxation time for a given PMMA carbon depends on the surface coverage of the PBut seed latex used to prepare the core-shell latex. Three zones of surface coverage can thus be distinguished:

A first zone (zone 1 of figure 1) concerns samples corresponding to a surface coverage between 0.17 and 0.27, which have low particle numbers (or high particle sizes) due to a partial agglomeration of latex particles during the polymerization; there is not sufficient surfactant available to stabilize latex particles when their size increases. Because of partial agglomeration phenomena, particles area of PBut in contact with PMMA decreases so that dipole-dipole interactions between PMMA protons and PBut nuclei are lower (high PMMA $T_{1\rho}(H)$ value) than the same interactions in the core-shell latex having no agglomerated particles, as the one corresponding to a surface coverage of 0.36. The lowest PMMA $T_{1\rho}(H)$ value obtained for this last case suggests the highest PMMA fraction in the interphase or the strongest dipole-dipole interactions.

The second zone (zone 2) concerns core-shell latex samples with PBut latex having a surface coverage between 0.36 and 0.55. The difference observed in the PMMA $T_{1\rho}(H)$ values may be due to the difference of morphology of core-shell latexes.

The samples corresponding to a surface coverage of the seed latex above 0.55 form the zone 3. The higher particle numbers is an indication that PMMA homopolymer particles and core-shell latexes are formed simultaneously during the polymerization. PMMA in the interphase is decreased due to the presence of PMMA homopolymer particles and consequently PMMA $T_{1\rho}(H)$ are less perturbated than in zone 2.

3.2 *Determination of PMMA content in the interphase*

We have previously shown the linear variation of PMMA $T_{1\rho}(H)$ relaxation time with the PMMA content in the core-shell latexes (figure 2 and table 3). This linear $T_{1\rho}(H)$ behaviour can be used to determine the PMMA content in the interphase.

	PMMA content in the core-shell latexe (weight%)					
	15	30	40	57	75	100
C5 carbon (55 pmm)	7.2	8.6	9.0	10.6	11.9	13.8
C6 carbon (45 pmm)	6.8	8.3	9.1	9.9	11.4	13.1

Table 3 : PMMA relaxation time in the core-shell latexes with variable composition.

Surface coverage of the seed latex : 0.36

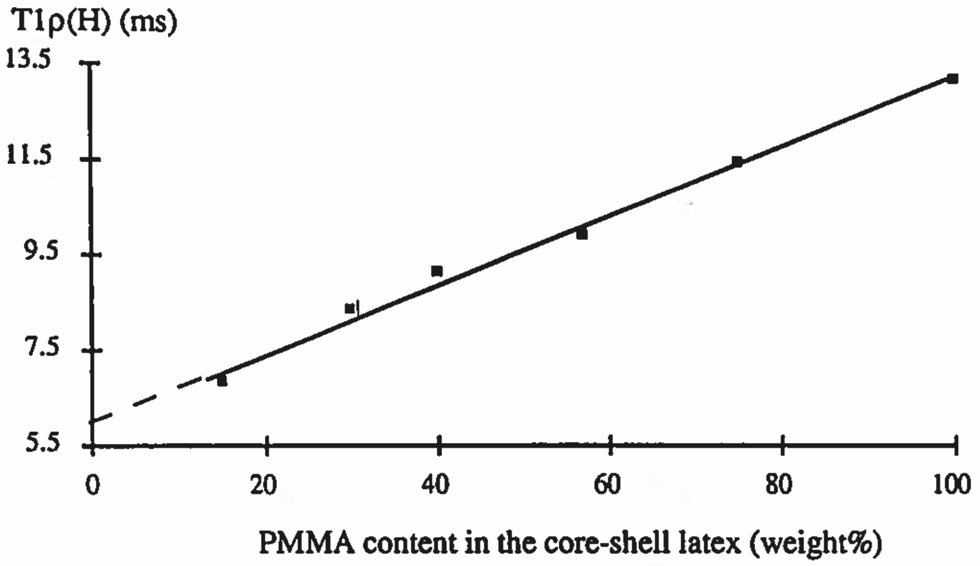

Figure 2 : PMMA $T_{1\rho}(H)$ relaxation time (quaternary carbon C6) versus PMMA content in the core-shell latex

In a compatible system, the protons of the two components have the same relaxation time indicating an efficient spin diffusion as a consequence of an intimately interconnection of the two phase protons via dipolar interactions.

The situation is quite different for the incompatible PBut-PMMA system having a pure PMMA and a pure PBut phase as well as the interfacial domain (figure 3). However the whole PMMA in the core-shell sample can be considered as a blend of two compatible polymers:

- the interfacial PMMA or "perturbated" PMMA which interacts directly with nearby PBut having a relaxation time $T_{1\rho}(H)_1$; as a first approximation this value can be considered as the one obtained by extrapolation to zero PMMA concentration, e. g. 6.1 ms and 6.0 ms respectively for the carbon C5 and C6 (figure 2).

- the "unperturbated" PMMA having no interaction with PBut for which the relaxation time $T_{1\rho}(H)_2$ is the same as for pure PMMA, e. g. 13.8 ms and 13.1 ms respectively for the carbon C5 and C6.

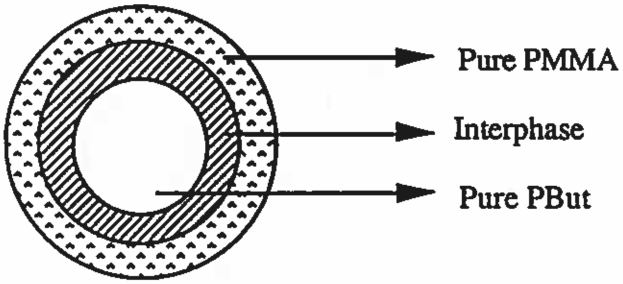

Figure 3 : schematical representation of the core-shell latex particle

Spin diffusion phenomena averages these two relaxation times and one measures by ^{13}C solid-state NMR only one average relaxation time $T_{1\rho}(H)_m$ depending on the relative amount of the two components, e. g perturbated and unperturbated PMMA.

A model has been proposed for compatible blend systems having a relaxation time which changes with the composition (8, 27). On this basis we can apply this model to the core-shell system:

$$1/T_{1\rho}(H)_m = [N_1M_1/N]\,[1/T_{1\rho}(H)_1] + [N_2M_2/N]\,[1/T_{1\rho}(H)_2] \quad (a)$$

Where

$T_{1\rho}(H)_m$ is the experimental determined $T_{1\rho}(H)$ value of the core-shell latex

$T_{1\rho}(H)_2$ is the relaxation time for pure PMMA latex

$T_{1\rho}(H)_1$ is the extrapolated values of the $T_{1\rho}(H)$ relaxation time

with 1 and 2 being the two PMMA components. Mi is the mole fraction of phase i, Ni is the number of protons in one mole of phase i, and $N=N_1.M_1+N_2.M_2$. From reduction of equation (a) it becomes:

$$M_1 = [(1/T_{1\rho}(H)_m) - (1/T_{1\rho}(H)_2)]\,/\,[(1/T_{1\rho}(H)_1) - (1/T_{1\rho}(H)_2)] \quad (b)$$

The proportion of the interfacial PMMA, determined by this approach and given in mole % with respect to the total PMMA, is listed in table 4.

	surface coverage of the PBut seed latex						
	0.17	0.27	0.36	0.45	0.55	0.68	0.94
% of interfacial PMMA	27±4	31±4	37±5	25±3	19±3	16±2	11±2

Table 4: Proportion of the interfacial PMMA in the the core-shell latexes synthesized with PBut seed latexes with variable surface coverage.

The PMMA content in the interphase of core-shell latex samples depends on the surface coverage of the PBut particles seed latex used to prepare the core-shell latex. A surface coverage of 0.3 - 0.4 leads to the maximum of interphase.

4. CONCLUSION

These results show that the influence of the surface coverage of the PBut seed latex on the formation of the interphase in the core-shell latex particles can be studied by high resolution solid-state ^{13}C-NMR. It has also been demonstrated that this surface coverage has an effect on the PMMA $T_{1\rho}(H)$ relaxation time. This has been explained by the interactions between PMMA and PBut in the interphase which can be correlated to the proportion of the interfacial PMMA. An optimum surface coverage of PBut seed latex particles has been found which leads to the highest amount of interphase.

Acknowlegements

The authors express their thanks to ROHM and HAAS Co.(Lauterburg) for providing samples of polybutadiene latex.

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Recent Publications:

F.E. Torres, W.R. Schowalter, & W.B. Russel, "Simulations of coagulation in viscous flows", *Journal of Colloid and Interface Science* **145**, 51 (1991).

W.B. Russel, "Concentrated colloidal dispersions", *MRS Bulletin* **16**(8), 27 (1991).

W.B. Russel, "Dynamics of concentrated colloidal dispersions: Statistical mechanical approaches", *Particulate Two-Phase Flows* (ed. M.C. Roco), Butterworths, Chapter 17, 1991.

W.B. Russel, D.A. Saville, & W.R. Schowalter, *Colloidal Dispersions*, Cambridge University Press, paperback edition, 1991.

Abstracts:

M. Chen and W.B. Russel, "Gel Transition in Colloidal Silica Dispersions"

Dispersing colloidal silica spheres bearing grafted octadecyl chains in hexadecane can produce strong attractions between the particles. Hence, a silica/hexadecane gel undergoes a sol-gel transition with decreasing temperature. For samples of volume fractions ϕ higher than the critical gelation value $\phi_{gel}(T)$, the elastic moduli vary as $(\phi - \phi_{gel})^S$ with the prefactor and index independent of temperature. Though this form resembles the predictions from static percolation theories, the power law index lies significantly below those expected and the transition volume fraction varies with temperature.

The relationship of the gelation transition to dynamic percolation and phase transitions predicted by equilibrium statistical mechanics has also been addressed. Matching the calculated structure factor for adhesive spheres with that measured by static light scattering yields the unknown strength of the interparticle attraction as a function of temperature. Though an imperfect fit introduces considerable uncertainty, this empirical relationship demonstrates the colloidal silica gel transition to lie well below the dynamic percolation threshold but above the spinodal curve associated with the fluid-fluid transition for adhesive spheres. Thus we conclude that gelation in this colloidal dispersion corresponds to a metastable state lying beyond the fluid-solid phase boundary.

Contribution to International Polymer Colloids Group
Fall, 1992

Polymer Research Group
University of New Hampshire

- Recent papers published

  "Conversion Dependent Morphology Predictions for Composite Emulsion Polymers. I. Synthetic Latices", C.L. Winzor and D.C. Sundberg, Polymer, 33, 3797 (1992).

  "Conversion Dependent Morphology Predictions for Composite Emulsion Polymers. 2. Artificial Latices", C.L. Winzor and D.C. Sundberg to appear in December 1992 issue of Polymer.

  "Morphology Development for Three Component Emulsion Polymers. Theory and Experiments", E.J. Sundberg and D.C. Sundberg, to appear in 1992 in J. Appld. Poly. Sci.

- Emulsion Polymerization Kinetics for Two Component Latex Particles

  Work has continued on the enhancement of polymerization kinetic models for core-shell, inverted core-shell, hemispherical (or half moon-like), and occluded latex particles. The reaction rates within latex particles are predicted to be significantly different for the various particle morphologies, especially when a glassy polymer resides in the shell phase. An experimental kinetic study has been initiated using PSty, PMMA and Pn-BA as both seed and second stage polymers. $K_2S_2O_8$ and AIBN have been used as initiators and SLS has been used as the surfactant. All experiments utilize a 2:1 second stage monomer to seed polymer ratio and are run as batch reactions. Analyses of the particle morphologies are by TEM. Using combinations of these parameters, a data base of kinetic and morphology results is being constructed and subsequently used to test the kinetic models.

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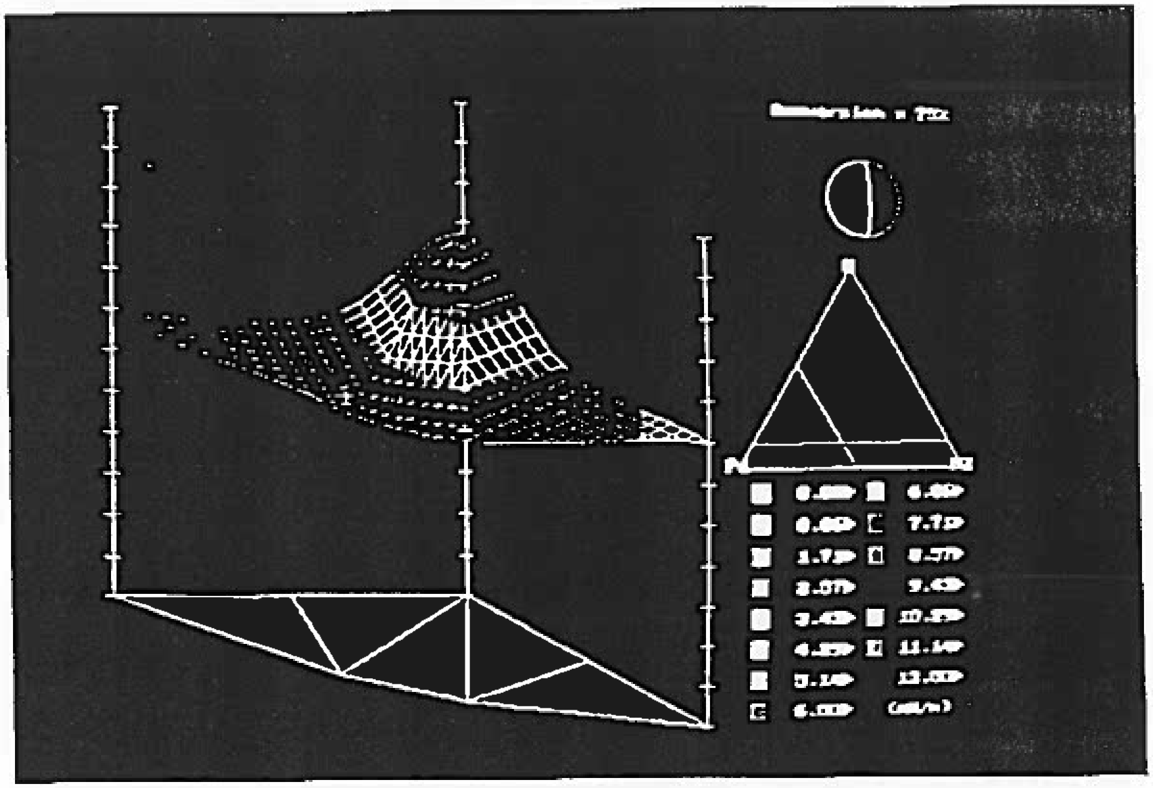
To Don Napper	From Don Sundberg
Co. U. of Sydney	Co. U. of New Hampshire
Dept. Chemistry	Phone # OSR
Fax # 011-61-2-692-3329	Fax # 603-862-3750

Contribution to International Polymer Colloids Group (Continued)

* Software Development for Conversion Dependent Latex Morphology Predictions

A new, rapid algorithm has been developed to make predictions of phase equilibria and particle morphology as a function of conversion level. The computer output graphically displays the entire free energy topological map for all possible morphologies, shows the location of the preferred morphology and draws its structure with correct phase volumes, and displays the equilibrium phase diagram with the appropriate tie line at the conversion level of interest. The computational speed is essentially instantaneous on a 486-33MHz computer which allows the operator to advance the simulated conversion level with a key stroke and obtain nearly instantaneous graphical results. Inputs required are the various interfacial tensions and polymer/monomer interaction parameters, and may be predicted or supplied from experimental data. The graphical output shown below is typical of the results for simple systems.

D.C. Sundberg



CONTRIBUTIONS TO THE INTERNATIONAL POLYMER COLLOIDS GROUP NEWSLETTER

Reporter: Klaus Tauer

Max-Planck-Institut für Kolloid-und Grenzflächenforschung
Kantstraße 55, D-O-1530 Teltow-Seehof, Germany

Changes of the research scenery in Teltow-Seehof

A lot of changes took place in all life fields of the eastern states in Germany after the reunification in 1990. Within this it was necessary to change the research scenery of the former GDR, too.
All institutes of the former Academy of Sciences of the GDR have been dissolved at the end of 1991. However, a lot of new institutes have been founded with the beginning of 1992. Most of the scientists have the chance to continue their research in new institutes.
Following institutes are existing since the beginning of 1992 in Teltow-Seehof:

- Max-Planck-Institute for Colloid and Interface Research
- Fraunhofer Institute for Applied Polymer Research
- Branch offices of two other research institutes - one for Applied Materieal Research and one for Membrane Research
- 4 research groups of the Brandenburg State University at Potsdam.

Our research group for "Heterophase Polymerization" is a part of the MPI for Colloid and Interface Research.

Heterophase Copolymerization of MMA and a Nitro-Group Containing Azo-Dye Comonomer

Introduction

Over the last years nitro-group containing side-chain copolymers have been found much attention as materials for nonlinear optical (NLO) applications /1/. Organic polymers possess several advantages compared with inorganic NLO materials as for instance $LiNbO_3$ crystals.
The molecular weight of NLO polymers is important for many of

their application properties such like mechanic strength, water resistance and dielectric strength during the poling process in an electric field . There are also some references to that the magnitude of NLO effects depends on the molecular weight of the polymers employed /2/.

All known NLO vinyl copolymers have been synthesized by radical solution polymerization (see for instance Ref. 1). However, by this way the molecular weight of the copolymers is limited to some 10^4 g /mole.

Two other effects affect the molecular weight in the case of nitro group containing azo benzene derivatives as comonomers: (1) retardation effect by the nitro group /3/ and (2) retardation effect by the azo benzene unit /4/.

The aim of this work was to prepare NLO copolymers with considerable higher molecular weights than those obtained by solution polymerization.

Experimental part

We started with the copolymerization of MMA and N-methyl-N[4-(2-methoxy-4-nitro phenyl)azo phenyl]-2-amino ethyl methacrylate (Formula 1).

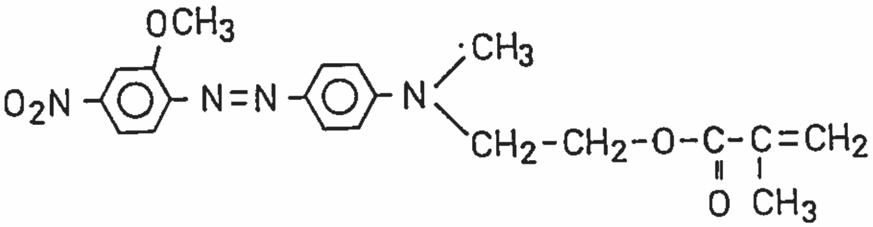
The emulsion polymerizations were carried out at 80 °C in a normal manner with our surface active initiator PEGAS 200 without additional emulsifiers.

The solution polymerizations were carried out at 70 °C in benzene or dimethylformamide as solvents also with the PEGAS 200 initiator.

The initiator concentration was balanced in such a way that the same rate of free radical production was achieved in both polymerization systems.

The molecular weights of the copolymers were determined by viscometry in benzene at 25 °C.

Additional informations about the retardation behavior of the dye comonomers were obtained from the final conversions after a fixed polymerization time.



Formula 1

Results

The results show clearly the differences regarding the monomer conversion as well as regarding the copolymerization behavior and the molecular weights of the copolymers between both polymerization techniques.

Figure 1 shows the change of the monomer conversion with increasing amount of dye comonomer in the starting monomer mixture in dependence on the different polymerization systems. The final conversion remains practically unchanged with increasing dye content in the emulsion polymerization system. Whereas an inhibition effect of the dye comonomer is clearly to be seen in the solution polymerization systems regarding the monomer conversion. The reason for this difference is not yet well understood. Comparable results with this were obtained regarding the copolymerization behavior, e.g. the ratio of the comonomers in the final copolymers. Table 1 summarizes the comonomer ratios in the starting monomer mixture and in the copolymers. The solution polymerization leads to a higher dye content in the copolymers than in the starting comonomer composition. Whereas the dye content is lower in the copolymers prepared by emulsion polymerization than in the starting monomer mixture. It is necessary to remark that the dye comonomer is only sparingly soluble in MMA. Thats why the dye content is limited which can be achieved by emulsion polymerization compared to solution polymerization.

Table 1: Comparison of the copolymerization behavior of MMA and the azo dye monomer (Formula 1) in solution and emulsion poymerization

Solution polymerization				Emulsion polymerization			
Run	MoFs (%)	MFs (%)	MoFs/MFs	Run	MoFs (%)	MFs (%)	MoFs/MFs
L2	0,994	1,83	0,543	D2	0,0126	0,0075	1,68
L3	2,450	8,64	0,284	D3	0,1250	0,0579	2,16
L4	4,780	10,50	0,455	D4	0,2500	0,1338	1,87
L5	9,120	31,34	0,291	D5	1,9700	1,2450	1,58

MoFs - Mol% azo dye monomer in the starting monomer mixture
MFs - Mol% azo dye monomer in the copolymer

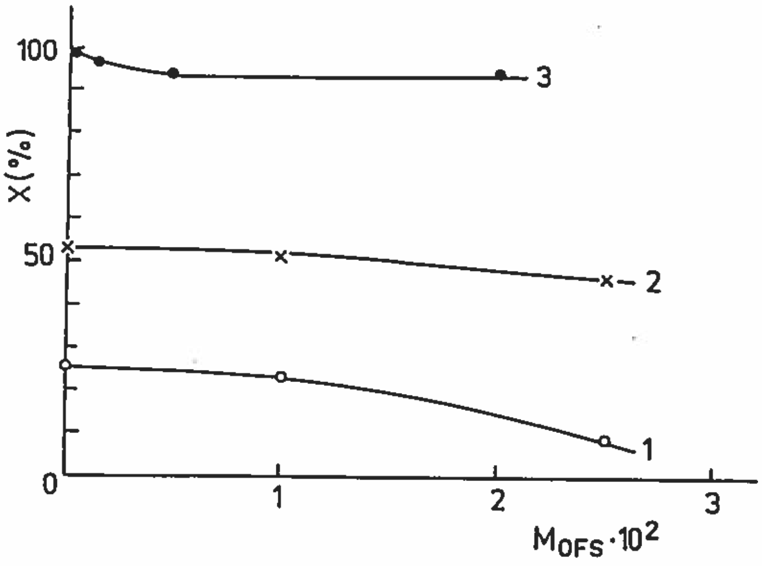


Fig. 1 Dependence of the final conversion on the dye monomer content in the starting monomer mixture

1 - Solution polymerization in benzene
2 - Solution polymerization in DMF
3 - Emulsion polymerization

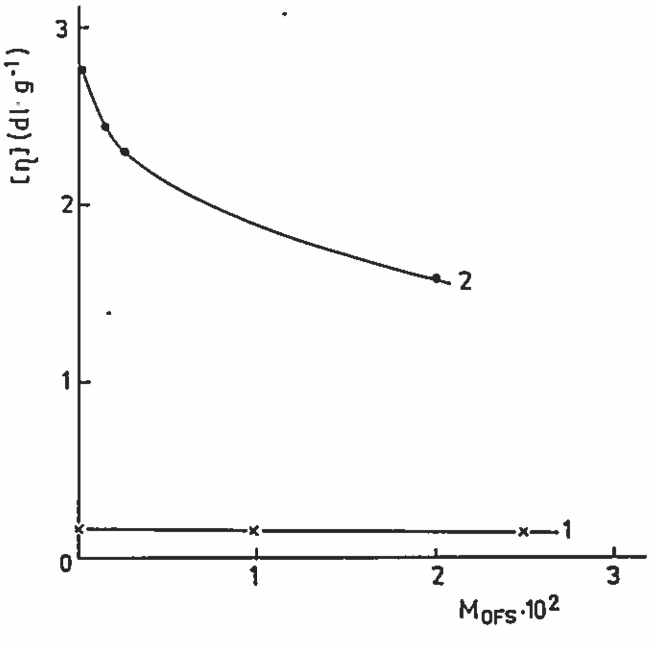


Fig. 2 Dependence of the intrinsic visosities of the copolymers on the dye monomer content in the starting monomer mixture

1 - Solution polymerization in DMF
2 - Emulsion polymerization

Figure 2 compares the intrinsic viscosities of the copolymers prepared by the different polymerization techniques in dependence on the dye monomer content in the starting monomer mixtures. The copolymers prepared by emulsion polymerization possess much higher molecular weights than those prepared by solution polymerization. The dependence of the molecular weights on the dye content reflects contraray to the monomer conversion an inhibition effect of the dye comonomer regarding the molecular weights in both polymerization systems.
However, the copolymers from the emulsion polymerization possess molecular weights high enough to form mechanical stable coatings on different substrates by spin coating or even stable free films. Different kinds of manipulations are possible with these films or coatings like for instance coating with thin metal layers by vacuum evaporation and corona poling. Contrary to this it was not possible to obtain stable coatings with the copolymers prepared by solution polymerization.

The results clearly show, that emulsion copolymerization of MMA and an azo dye comonomer offers the possibility to prepare high molecular weight NLO copolymers with better mechanical properties than those prepared by the mostly employed solution copolymerization.

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The complete paper is submitted to "Makromolekulare Chemie" for a publication. Authors: K. Tauer, E. M. Morozova, A. Wedel

Another paper regarding the NLO and optical properties of these copolymers is submitted to "Molecular Crystals and Liquid Crystals". Authors: A. Wedel, R. Danz, W. Künstler, K. Tauer

"Conductivity study on micellization of surface active maleic acid derivatives"

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The use of polymerizable emulsifiers in emulsion polymerization is of large practical importance because these emulsifiers will be incorporated into the product and thus have not to be removed from it, as it is done with conventionally synthesized products.

The homologous series of sodium sulfopropyl alkyl maleates $H_{2m+1}C_mOOC\text{-}CH{=}CH\text{-}COO(CH_2)_3SO_3Na$ with m = 12,14,18 investigated in this study belongs to this group of emulsifiers. Their physico-chemical properties are mostly unknown at present. In this short note we report on first measurements on micellization of these surfactants in aqueous solution by conductivity methods.

The surfactants were synthesized according to the procedure described in [1] and purified by recrystallization from acetone. Highly deionized water (conductivity $< 10^{-6}$ S cm^{-1}) was used in all measurements.

A typical conductivity versus concentration curve æ(c) for the C_{14} alkyl maleate is represented in Fig. 1. In all measurements of this study the plots are slightly curved towards the concentration axis and it is thus always possible to draw two or more straight lines through the experimental points. The concentration at the first intersection point is taken as the critical micellization concentration (cmc), although this procedure introduces significant uncertainty into the cmc value, since the value obtained depends on the data used in this graphical extrapolation. The curvature of the æ(c) plots obviously points to a changing of micelles with rising surfactant concentration. The following cmc values were estimated (T = 21 °C):

$m = 12$: cmc $= 1.61 \cdot 10^{-3}\ Ml^{-1}$
$m = 14$: $= 0.52 \cdot 10^{-3}\ Ml^{-1}$
$m = 18$: $= 52.0 \cdot 10^{-6}\ Ml^{-1}$.

The cmc rises with rising temperature according to a parabolic relation independent of the length of the alkyl chain. The cmc(T) curve for tetradecyl maleate is shown in Fig. 2. This dependence means, that the stability of micelles decreases with increasing

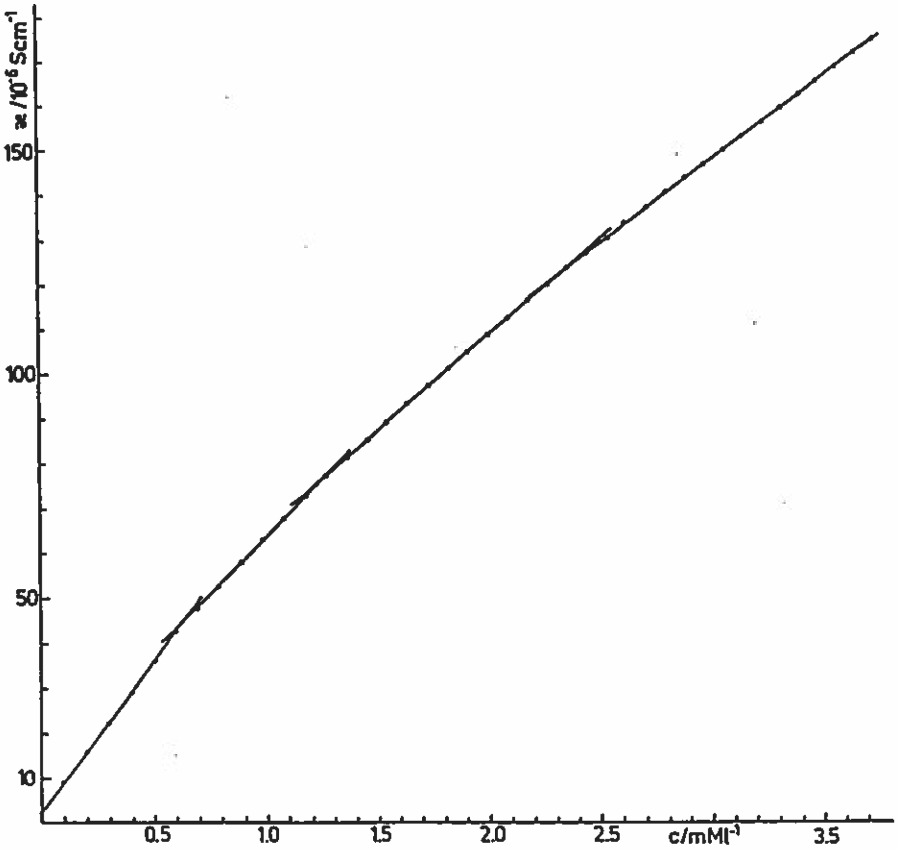

Fig. 1: Conductivity æ as a function of surfactant concentration c for tetradecyl maleate. T = 34 °C.

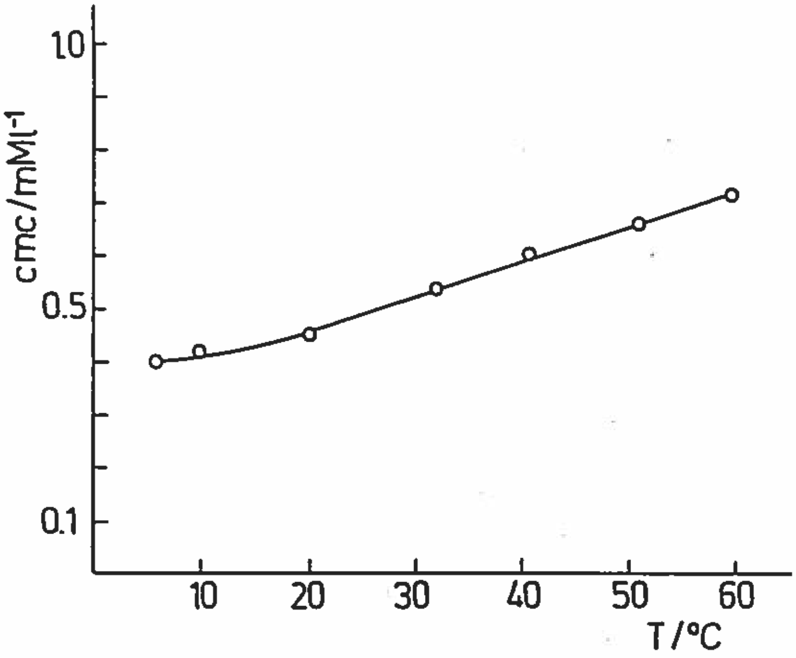

Fig. 2: cmc as a function of temperature for tetradecyl maleate.

Within the framework of mass action model of aggregation [2] the standard free enthalpy change ΔG for the addition of one more monomer to an aggregate having n monomers follows from

$$\frac{\Delta G}{RT} = (2-\alpha)\ln \mathrm{cmc} \qquad (1),$$

with the gas constant R and the micelle ionization degree α. For a completely ionized micelle, $\alpha = 1$, and for a neutral micelle, $\alpha = 0$. α was taken in first approximation as the ratio of the slopes of the æ(c) curves above and below the cmc [3]. The calculations yield a decrease of ΔG with rising chain length, i. e. the stability of micelles increases.

The standard differential heat of micelle formation ΔH is given by [2] the expression

$$\Delta H = -RT^2\left[(2-\alpha)\frac{\partial \ln \mathrm{cmc}}{\partial T}\bigg|_p - \frac{\partial \alpha}{\partial T}\bigg|_p \ln \mathrm{cmc}\right]. \qquad (2)$$

ΔH is found to be negative and decreasing with temperature. Thus its contribution to ΔG is exothermic. The corresponding standard entropy change ΔS is positive, but diminishes with rising temperature. Thus our results confirm the wellknown characteristic of compensating changes in enthalpy and entropy in the course of micellization. To illustrate the just discussed behaviour the calculated thermodynamic functions for tetradecyl maleate are plotted in Fig. 3.

The degree of ionization estimated from the æ(c) plots increases with chain length as well as with temperature ($m = 12$: $\alpha = 0.68$; $m = 14$: $\alpha = 0.73$; $m = 18$: $\alpha = 0.82$; $T = 21$ °C; $\partial\alpha/\partial T|_{m=14} = 0.0019$ grd^{-1}).

Presumably this behaviour has to be connected with a falling micelle aggregation number [4].

The effect of added salt, in our case NaCl, on the cmc was investigated in a further series of experiments on tetradecyl maleate. The cmc changes with the concentration of counterions c_{Na} according to the relation

$$\ln \mathrm{cmc} = A - (1-\alpha_{coun})\ln(\mathrm{cmc} + c_{Na}) \qquad (3),$$

where A and α_{coun} are empirical constants. α_{coun} is usually interpreted [5] as micelle ionization degree. Its value of $\alpha_{coun} = 0.27$ (T = 33 °C) strongly differs from that, determined from the conductivity slopes. The big difference we can´t explain at present, but it clearly appears that the procedure to estimate α has to be applied with caution [6].

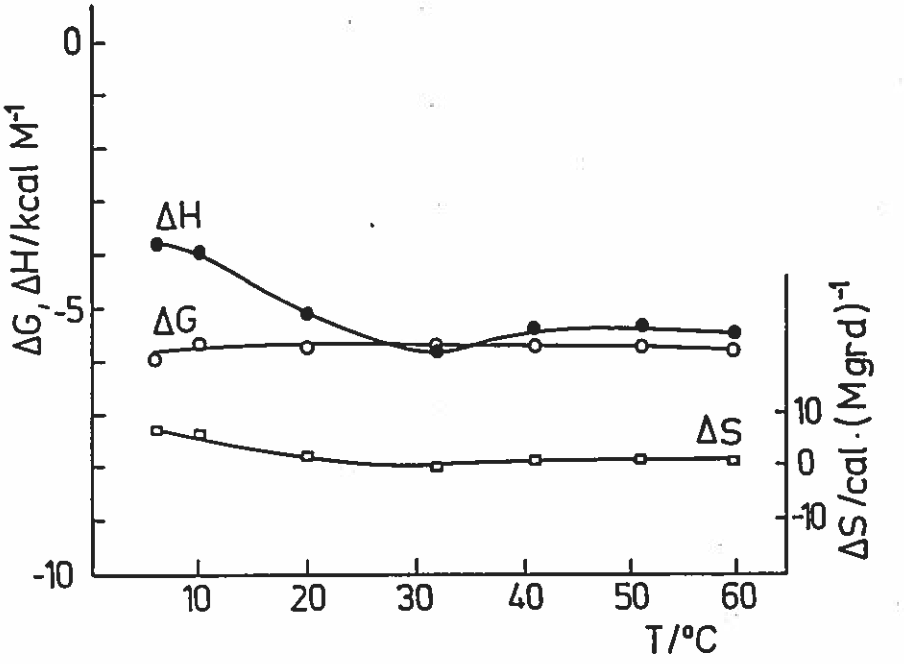

Fig. 3: ΔG, ΔH and ΔS as a function of temperature for tetradecyl maleate.

It is well established that for a homologous series of alkyl surfactants, the cmc varies with chain length m according to

$$\log cmc = a - bm \qquad (4)$$

with empirical constants a and b. We found this relation to hold also for the surfactants under investigation and estimated a value b = 0.25 at T = 22 °C. This is a typical value for ionic surfactants [7].

At the end of this short note let´s add some remarks to the so-called Krafft phenomenon. All prepared solutions of the surfactants with m = 12 and m = 14 were completely clear down to T = 5 °C in the investigated concentration range. That means, that the Krafft point lies obviously below 5 °C. Contrary to this finding the octadecyl maleate solutions were turbid below a certain temperature. This temperature is a strong function of surfactant concentration. We estimated the apparent Krafft point conductometrically and found ≃35 °C for $c = 1.5 \cdot 10^{-3} Ml^{-1}$. For concentrations in the cmc range we obtained ≃15 °C. This result is in accordance with the expected impossibility to estimate a cmc below this characteristic temperature.

Summarizing the results of this study, we can state, that the unsaturated surfactants under investigation behave similar to other kinds of ionic surfactants.

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Monosized polymer particles.

1. Particles for chromatography.

We have developed recipies for macroporous polymer particles to be used in size exclusion chromatography in organic solvents. Such particles have been described by us previously, (L.I. Kulin, P.J. Flodin,T. ELlingsen and John Ugelstad, J. Chromatogr.514, 147 (1990).
These particles were useful up to molecular weight of about 10^6 Our new particles have been successfully applied up to 10^7.
The requirement to these particles are besides a high degree of monodispersity that they should swell very little even in hot organic liquids. This call for a relatively very high amount of crosslinker which in turn tend to give relatively small pores.
We have succeeded in the combination of the requirements of high crosslinking and large pores by use of a carefully controlled mixture of organic solvents as porogens. In the table given below are given some results of various particles. As will be seen we have prepared particles with various pore size distributions including particles with very large pores.
These particles have also been modified to get a strongly hydrophillic surface for use in separation of biochemicals in aqueous solution. Preliminary results of this work was presented at the IUPAC meeting in Prague this summer and will be published in a book from the meeting.

Tab. 1: Pore size distribution for several 15µm macroporous particles

Particle	Surface area [m²/g]	Pore volume [ml/g]	Pore size distribution (radius in Å) <50	50-100	100-200	200-500	500-2000	2000-5000
A	828	1.50	0.50	0.14	0.19	0.35	0.32	0.00
B	613	1.72	0.35	0.20	0.20	0.41	0.42	0.14
C	413	2.40	0.21	0.14	0.32	0.55	0.74	0.44
D	387	2.55	0.18	0.08	0.09	0.32	1.26	0.62
E	100	2.15	0.02	0.06	0.10	0.28	1.09	0.60
F*	68	1.50	0.00	0.00	0.13	0.47	0.90	-
G	28	2.00	0.00	0.00	0.10	0.06	0.34	1.50

* 3.3µm

2. Monosized polymer particles for immuno assays by flow cytometry.

The use of highly monodisperse particles in different sizes, combined with fluorescence labelling makes it possible to carry out multiple analysis in one run i.e. a simultaneous determination of different antigens. Recently macroporous polyacrylate particles with epoxy groups on them have been especially designed and investigated in assays for carcino embryonic antigen (CEA) and alpha phoeto protein (AFP)

4. Publication.

I have recently written a rather comprehensive paper on PREPARATION AND APPLICATION OF MONOSIZED POLYMER PARTICLES in "PROGRESS IN POLYMER SCIENCE".

I include a list of content of this paper. Reprint of this paper may be obtained by request to J.U.

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