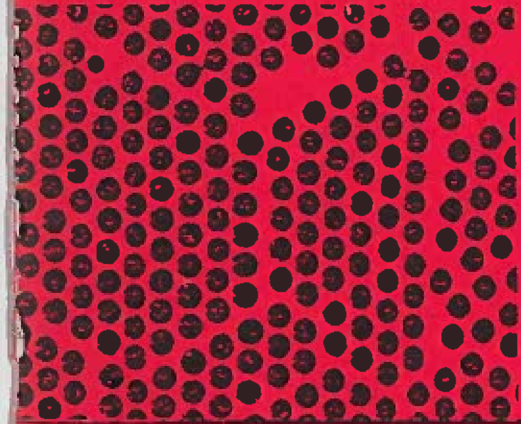

IPCG

INTERNATIONAL POLYMER COLLOIDS GROUP

SEPTEMBER 1990

VOLUME 21

IPCG

INTERNATIONAL POLYMER COLLOIDS GROUP

SEPTEMBER 1990

VOLUME 21 NUMBER 2

NEWSLETTER

INDEX

FROM THE EDITOR'S DESK

CONTRIBUTIONS

Contributions from Drs Dunn, Eliseeva and Pelton arrived too late for inclusion in the May Newsletter and have been held over until this edition. I hope these members will forgive me. To try to overcome this problem, I have delayed slightly the assembly of this Newsletter.

AGMs of the IPCG

Minutes of the two meetings of the IPCG held at Lehigh and Montreal are included in this edition. (Thanks be to my colleague Bob Gilbert for the Montreal minutes.)

NATO ASI BOOKS PUBLISHED

Two books have been published from the 1988 NATO Advanced Study Institute on Polymer Colloids, held in Strasbourg, July 1988. Both are edited by Francoise Candau and Ron Ottewill and published by Kluwer Academic Publishers. The major volume is *Scientific Methods for the Study of Polymer Colloids and their Application*, the first eight chapters being published separately as *An Introduction to Polymer Colloids*.

PRA SEMINAR

Sandy Dunn has supplied a report on the one day seminar on "Advances in Emulsion Polymerization" held in London on 5 April, 1990.

CONFERENCES

Professor Nomura has kindly provided information and registration of interest forms for the October 1991 International Symposium on Polymeric Microspheres (see p iii).

NEXT NEWSLETTER

Please forward your contributions by airmail to reach me by 30 April 1991.

DH Napper
Editor

CONFERENCE SCHEDULE

1991

Conference	Location	Date
201st ACS National Meeting -Latex Particle Nucleation and Morphology (honoring RM Fitch)	Altanta	14-19 April
65th Colloid & Surface Science Symposium	Norman	17-19 June
Emulsions: EUCHEM/NATO Workshop	Bergen	24-26 June
Gordon Research Conference Polymer Colloids	Tilton	1-5 July
7th International Conference Colloids & Surfaces	Compiegne	7-12 July
202nd ACS Natinal Meeting	New York	25-30 August
Polymeric Microspheres Symposium	Fukui	24-27 Oct

LOCATION OF FUKUI

POST CARD

PM Fukui Symp. '91 Secetariat
Professor Mamoru Nomura
Department of Materials Science and Engineering
Fukui University, Fukui, Japan

PARTIAL LIST OF INVITED SPEAKERS AND THEIR PROVISIONAL TITLES

J. Barton, Polymer Inst., Czechoslovakia, "Emulsion Polymerization of monomers with different water solubilities"

F. Candau, CNRS, France, "Micellar polymerization of surface-active monomers"

A.S. Dunn, UMIST, UK, "The kinetics of emulsifier adsorption and the nucleation of latex particles"

M.S. El-Aasser, Lehigh Univ., U.S.A., "Development of morphology in latex particles: an interplay between kinetics and thermodynamic parameters"

V.I. Eliseeva, Academy of Science, USSR, "The role of phase interaction in the structure of latex particles and films"

A. Guyot, CNRS, France, "Very small polystyrene latex from emulsion polymerization in the presence of zwitterionic surfactant"

A.E. Hamielec, McMaster Univ., Canada, "Croslinking kinetics in emulsion polymerization"

K. Higashitani, Kyushu Inst. of Tech. Japan, "Effects of magnetic field on stability of polymeric microspheres"

H. Kawaguchi, Keio Univ., Japan, "Monodisperse hydrogel microspheres: their features and applications"

T. Kitamori, The Univ. of Tokyo, Japan, "Laser photoacoustic and photothermal spectroscopy as a novel characterization method for microparticles"

T. Matsuo, Fukui Univ., Japan, "The role of surfactant in particle nucleation"

N. Mizutani, Tokyo Inst. of Tech., Japan, "Synthesis of narrow-size spherical, fine ceramic particles from organic compound"

D.H. Napper, The Univ. of Sydney, Australia, "The mechanism of entry of free radicals into latex particles"

M. Nomura, Fukui Univ., Japan, "Kinetics and mechanism of emulsion polymerization initiated by oil-soluble initiators"

M. Okubo, Kobe Univ., Japan, "Preparation of micron-size monodisperse polymer microspheres by seeded polymerization utilizing dynamic monomer swelling method"

I. Piirma, The Univ. of Akron, U.S.A. "Surfactant effects in emulsion polymerization"

G.W. Poehlein, Georgia Inst. of Tech., U.S.A., "Emulsion polymerization and copolymerization in continuous reactor systems"

R.E. Riman, Rutgers Univ., U.S.A., "Chemical and physical aspects of multicomponent ceramic oxide precipitation prepared via multicomponent alkoxide hydrosis"

J. Ugelstad, Univ. of Trondheim, Norway, "Monosized magnetic particles for biochemical and biomedical applications"

S. Yoshino, Nagoya Univ., Japan, "Dynamic electric multipole model for super-long-range interaction of colloids"

A. Winnik, Univ. of Tronto, Canada, "Molecular aspects of latex film formation"

Announcement and Call for Papers

高分子ミクロスフェア国際討論会

International Symposium
on
POLYMERIC MICROSPHERES

October 23(Wed)-26(Sat), 1991
Fukui University,
Fukui, JAPAN

HOST ORGANIZATION
主 催
Center for Cooperative Research
in Science & Technology,
Fukui University, Fukui, Japan
福井大学工学共同研究センター

COOPERATIVE ORGANIZATIONS
協 力
Emulsion Polymers Institute,
Lehigh University, U.S.A
McMaster Institute of Polymer
Production Technology,
McMaster University, Canada
Laboratoire des Materiaux Organiques,
CNRS, France

FIRST CIRCULAR

ORGANIZING COMMITTEE

Prof. T. Matuso (Co-Chairman)
Fukui University, JAPAN
Prof. M. Nomura (Co-Chairman)
Fukui University, JAPAN
Prof. M.S. El-Aasser
Lehigh University, U.S.A.
Prof. A.E. Hamielec
McMaster University, CANADA
Dr. A. Guyot
Director, LMO, CNRS, FRANCE

OBJECTIVES AND SCOPE

"Polymeric Microspheres" in submicron range are produced mainly by heterogeneous polymerization such as emulsion, dispersion or similar polymerization processes in the form of aqueous or non-aqueous dispersion. These dispersions of the polymeric microspheres have been used mostly as film-forming materials.

Recently, however, attention has been focused more and more on the use of the polymeric microspheres as speciality materials. Therefore, the investigations on the kinetics and mechanism of particle formation and growth, dispersion properties and modern techniques for characterization are rapidly advancing to enable the production of tailored polymeric microspheres which would meet a wide range of application problems.

The session including the topic of alkoxide method is provided to exchange the informations and ideas among the researchers engaged in both research areas, because alkoxide method which is applied for the preparation of inorganic polymer microspheres seems to have similarity in reaction scheme with dispersion polymerization.

In this symposium, recent advancement in the topics concerning "Polymeric Microspheres" as shown below will be highlighted and discussed extensively. The papers submitted in this symposium will be published in a special issue of some international journal or in a special book.

TOPICS TO BE CONSIDERED

(1) Kinetics and mechanism: Formation and growth of
- Organic polymer microspheres by emulsion, dispersion and other similar polymerization processes, and of
- Inorganic polymer microspheres by alkoxide method

(2) Reactor model and simulation
- Batch, semi-batch and continuous processes, etc.

(3) Characterization and its new technique
- Modern techniques for characterization of polymeric microspheres
- Studies of colloidal properties, etc.

(4) Application of polymeric microspheres
- Biochemical and biomedical applications
- Applications in electrophotographic processes, etc.

OUTLINE OF PROGRAMS

The programs will consist of invited and contributed papers. Two formats are provided for contributed papers: (1) Normal presentations (20 min. presentation + 10 min. discussion), and (2) Short presentations (10 min. presentation + 5 min. discussion).

LANGUAGE

The official language of the symposium is **English**, which will be used for all printed materials, presentations and discussion.

CONTRIBUTIONS

Those wishing to contribute a paper should submit an abstract of 200-300 words written in English together with the Preregistration form by **January 31, 1991** to the Secretariat. The abstract should include the title, authors (specify the speaker with an underline), and organization.

The acceptance of paper will be refereed by the members of the Organizing Committee, if necessary. The authors whose papers are accepted for presentation are requested to submit a 4-6 page camera-ready manuscript by **June 30, 1991** at the latest. Special typing sheets and the "Instructions for Authors" will be provided.

SECOND CIRCULAR

The final list of speakers and their topics together with the detailed informations including accommodations and the registration form will be contained in the second (final) circular to be published by the end of April 1991.

The second circular will be sent only to those who complete and return the attached reply form no later than **March 30, 1991**.

PREREGISTRATION

The number of non-active participants is limited so that the total number of participants is approximately 160. It is, therefore, recommended that you preregister as soon as possible, especially if you are a non-active participant. Pre-registration will be accepted in the order of receipt of the attached pre-registration form. The pre-registered persons will automatically receive the second circular.

REGISTRATION FEE

The registration fee, which includes a copy of the Preprints and Reception, will be ¥20,000 for students and active participants (speakers only), and ¥50,000 for non-active participants.

SECRETARIAT

All correspondence concerning the symposium should be to:

PM Fukui Symp. '91 Secretariat
Prof. Mamoru Nomura
Department of Materials Science and Engineering
Fukui University, Fukui, Japan, 910
Tel: 81-776-23-0500(Ext.2748)
Fax: 81-776-27-8523

……………………………………………… ✂

PM Fukui Symp. '91 - PRERESISTRATION FORM

(No fee is required with preresistration)

I hope to attend PM Fukui Symp.'91 and preregister ··· [ ]

I would appreciate receiving further information(Second circular on "PM Fukui Symp. '91, JAPAN") ·············· [ ]

I intend to present [ ] paper(s).
With provisional title(s): (Please Print or Type)

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……………………………………………………

……………………………………………………

……………………………………………………

[ ] Normal presentation. [ ] Short presentation

Prof./Dr./Mr./Mrs.

Name: ______________________
(Please Print or Type) Last First Middle

Organization: ______________________

Addres: ______________________

____

____

Tel: ______________ Fax: ______________

I suggest that you also send the First Circular to:

Name: ______________________

Address: ______________________

____

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

IPCG

INTERNATIONAL POLYMER COLLOIDS GROUP

Minutes of Meeting of IPCG held on 20 June, 1990 at 12.30 at University Centre, Lehigh, Bethlehem, USA

PRESENT: DHN(Chair), JSD, ME-A, APG, RMF, AK, IMK, RP, IP, RLR, WBR, PRS, JWV, TGMvdV, ALG, FC, FKH, JGHJ, JMA, JU, JWG, PJS

BUSINESS:

1. Membership

(i) The Chair welcomed Ton German to his first meeting. He also reported that Dr L Rios had declined membership as he had transferred to an industrial position. Viv Stannett has retired but wishes to contribute further to the Newsletter.

(ii) It was agreed that the Chair write to Dr Amelia Crux to invite her to membership (in place of Dr Rios).

(iii) Meeting accepted that the following be invited by the Chair to be alternates for the members named first:

Organization	
Uni of Nth Carolina	Dr Viv Stannett/Dr Dick Gilbert
Uni of Sydney	Dr Don Napper/Dr Bob Gilbert
SC Johnson	Dr Robert Fitch/Dr Sunil Jayasuriya
Wageningen Uni	Dr Hans Lyklema/Dr M A Coken Stuart
Uni of Trondheim	Dr John Ugelstad/Dr Arvin Berge

(iv) Possible future members (to be invivted to contribute to future Gordon conferences):

Dr Maria Santore
Dr Danuy Ou-yang
Dr Harry Ploem

3. Meetings

3.1 Past: F Candau reported that both NATO books now published. Authors of plenary lectures in the smaller (green) book have not received a copy from publisher (FC to check).

3.2 Present: Members complimented Dr Mohamed El-Aasser on both the excellence of the Polymer Colloids program and the exceptionally well-organized 64th Colloid and Surface Science Symposium.

3.3 Future:

(i) Date for NATO meeting is either 1994 or 1996. Standford to host

Colloids meeting in mid-1994, so 1996 may be preferable. JMA reported that a seaside location around San Sebastian was impracticable. A more preferable site would be in the mountains about 100 km away. Cost US$600 - $900 (in 1990$) for 2 weeks. Agreed that this was very reasonable rate. Montreal meeting to consider setting up a technical commettee, using experienced members involved in Strasbourg meeting. Also the possibility of a meeting in 1992.

(ii) Finn Hanson has agreed to give the Plenary Lecture at Atlanta ACS meeting on Latex Nucleation in honour of Robert Fitch.

(iii) Next Gordon conference poster session to have a small panel of members to review/discuss posters after conference dinner.

CLOSURE: The meeting was closed at 1.30 pm.

DH Napper
Minutes Secretary

IPCG Meeting. Tuesday July 10, Montréal.

Chair: T G van de Ven.
Present: P Steniun, K Takamura,, C Pichot, D Sundberg, R Pelton, J Waters, A Gast, I Krieger, R Ottewill, R Gilbert (Secretary), I Piirma, R Rowell, M El-Aasser.

Meeting opened 14:30.

Minutes The minutes of the previous meeting were read and accepted.

Business arising from the minutes. Ottewill reported that the NATO volumes should have been received by all those concerned, and requested members to let him no if they had not received theirs.

Future meetings.
1. It was decided that the proposals from the previous meeting at Lehigh were to be accepted. The NATO meeting in Spain will proceed as planned. Formal application to NATO for funding should not be made until 2 years before the scheduled date. Ottewill has complete records of the submissions prepared for the Strasbourg meeting, with regard to applications for funding for Spain.
2. It was suggested that a IPCG meeting for 1992 might be held in Holland. Ton German was suggested as a possible organizer; he is currently enquiring as to site availablity, etc., and will let the group know by the end of August if it is possible for him to organize something. Funding assistance could be sought from European companies (total funding for a NATO conference is *ca* $45K). Another possibility is the Dahlem Conference trust, which organizes meetings in Berlin. The meeting could be held as a European Gordon Conference; El-Aasser is to check with the Gordon Conference headquarters on this, and on timing. It was decided that a meeting somewhere in Europe would be held in 1992 even if Gordon Conference backing were not forthcoming.

Van de Ven and Waters were thanked for the excellent organization and scientific program for the Montréal conference.

The meeting closed at 5:15 p.m.

[illegible] 'ADVANCES IN [illegible]'
Putney, London, [illegible]

The first of what may become a series of biennial seminars on emulsion polymerisation organised by the Paint Research Association (Waldegrave Road, Teddington, Middlesex, TW11 8LD, U.K.) was held at Whitelands College - a Teachers' Training College with residential accommodation which has an attractive site on a hill in South-West London. Although organised with a short lead time and not publicised extensively outside of the firms in membership of the Association and quite expensive (£161 for non-residents from non-member companies) it attracted 52 participants apart from the speakers etc. including 17 from the continent. The organiser was Dip Dasgupta, Head of the P.R.A. Information Department which has recently taken over publication of Henry Warson's monthly 'Emulsion Polymerisation and Polymer Emulsions' review of the scientific and patent literature which is now edited by Ron Lambourne (formerly of ICI Paints Division) and Norman Morgan. The annual subscription for this service is £220 covering critical notes on about 600 references systematically arranged by subject.

I reviewed 'Problems of Emulsion Polymerisation' along lines which will be familiar to Polymer Colloids Group members but which John Cruden, R & D Director of the Harlow Chemical Company did not think were too relevant to the immediate problems of paint technologists.

John Hearn (Nottingham Polytechnic) reviewed his work on the emulsifier-free emulsion polymerisation of styrene briefly and went on to describe his more recent work on the permeability to solutes or vapours of films formed from model monodisperse surfactant-free butyl methacrylate latices, similar films containing ionic or non-ionic surfactants, and solvent cast films. These experiments were intended to model the type of formulations used for latex automotive finishes where there is a problem of increased permeability compared with films deposited from solutions in organic solvents. Films were found to be asymmetrical: the appearance and properties of the air and substrate sides differed. Curiously the minimum permeability of films formed with surfactants present was found when particles were covered with a monolayer of sodium dodecyl sulphate.

Professor Brian Brooks (Loughborough University) spoke on 'Developments in Modelling Emulsion Polymerisation Processes'. He remarked that we have learned to question almost everything we thought we knew about emulsion polymerisation. We always use models to describe chemical processes: even the established facts we regard as axiomatic are ultimately based on models. But a model which is quite satisfactory for one purpose is not necessarily suitable for another purpose. The importance of coalescence has generally been overlooked but it must be included in any realistic model. In continuous systems more than one time-average conversion may be obtained with one set of reactor conditions depending on start-up procedure. Even when monomer conversion has reached a near-constant value the average particle size and particle size distribution may still be changing. The rate of disociation of emulsifier micelles can be important in continuous systems. It may be necessary to measure as many as 8000 particles to get reliable, reproducible particle size distributions. In practical systems much reliance is placed on evaporative cooling but this can affect copolymerisation systems because of the difference in the composition of the condensate and the bulk of the monomer mixture and because the condensed monomers have to pick up emulsifier.

Henry Warson (Consultant - Solihull Chemical Services, 284 Warwick Road, Solihull, West Midlands, B92 7AF) summarised the contents of his latest report 'Polymerisable Surfactants and Their Applications' (98 pp. $ 99) but he emphasised that very few of the wide range of systems which have been patented seemed to have been commercialised as yet.

David Sykes (Rohm & Haas) presented the results of 7 years development in the Spring House, Pa. Laboratories of 'Multilobe' aggregates of 3 - 6 spherical particles which were only partially coalesced which could be prepared reproducibility although the method for producing them was classified as commercially sensitive information. The objective in developing these latices was to obtain paints which would give such a film thickness that they would have the desired covering power after the application of a single coat. Particle shape influences latex viscosity as well as thickeners, solids volume, average particle size, and particle size distribution, but at high shear rates the solids volume is the most important factor. Because their hydrodynamic volume is much greater than their physical volume, multilobed particles increase the effective solids volume whilst maintaining the same actual solids volume. They do not result from post polymerisation coagulation. Use of the multilobe latex permits a reduction of the amount of thickener required to achieve the requisite viscosity in a formulation which reduces cost and water-sensitivity.

Mathematical calculations show that a tetrahedral particle with four lobes has a hydrodynamic or effective volume 2.5 times that of a spherical particle of the same actual volume. The lobed particle do not break down during normal mixing. Experimentally the dependence of relative viscosity on polymer volume fraction was determined using 0.54, 0.75, and 0.96 μm spheres and lobed particles of which the actual volume was equivalent to that of the 0.75 μm spheres. For the spherical particles a straight line with a slope of 2.56 was obtained in agreement with the Einstein equation

$$\eta_r = 1 + 2.5\phi$$

For the lobed particles the slope was 5.07 (giving a ratio of 1.98 compared with the theoretical value of 2.5). Range of ϕ was up to 0.1.

Exterior wood paints were formulated with pigment volumes of 40% and 52% and with the volume of latex particles in the 20-40 % range adjusted to the same low shear viscosity with hydroxyethyl cellulose thickener. The lobed emulsion provided a higher viscosity at high shear rates than in a similar formulation with spherical particle with actual diameters equal to the hydrodynamic diameter of the lobed particles.

Jeremy Lane (Vinamul Ltd.). Binders (i.e. film forming polymers) for exterior emulsion paints need to be tough but flexible, permeable to water vapour but impermeable to liquid water, with a low dirt pick-up. Ethylene-vinyl acetate emulsion copolymers ('pressure polymers') fulfill these criteria to some extent. Incorporation of ethylene reduces cost of the raw materials compared with a vinyl acetate homopolymer but increases capital outlay because of the necessity of pressure equipment. Incorporation of vinyl chloride improves the hardness of the film and its water resistance and upgrades its pigment binding to give a scrub resistance equal to that of acrylic binders. A further improvement may be achieved by incorporating up to 5% ethyl hexyl acrylate or vinyl versatate as a fourth component. Increase of molecular weight reduces water permeability but optimum mechanical properties are attained at something less than the maximum achievable molecular weight. The distribution of vinyl chloride residues in the copolymer tends to be blocky: elimination of HCl from VC blocks causes yellowing but the tendency to block formation can be reduced by careful control of the method of monomer addition in a semi-continuous process.

Mrs Templeton-Knight (Tioxide and SCI Arthur Marsden Medalist) spoke on 'Encapsulation of Inorganic Particles *in-situ* by Emulsion Polymerisation'. Titanium dioxide is the prime opacifier (n = 2.71 for rutile TiO_2) in use to-day having replaced toxic white lead. Commercial TiO_2 pigments have an inorganic oxide precipitated on to the surface of the particles to improve dispersibility, durability (control of photochemical activity), and opacity (prevention of flocculation). However since the TiO_2 crystals have often to be incorporated in an organic medium (e.g. paint film or plastic) an organic coating could be advantageous. Emulsion polymerisation using TiO_2 crystals as seed particles is an obvious way to achieve this and has already been attempted (cf. Caris, Van Herk, & German, Br.Polym.J. 21 (1989) No. 2) but the particles encapsulated are aggregates of single crystals whereas individual crystals need to be coated to achieve the best effect.

Ultrasonification has proved a useful way for inducing polymerisation on the surface of the TiO_2 crystals. Cavitation on uses high temperatures and pressures locally which accelerate polymerisation. This work was done in collaboration with Drs Tim Mason and Phil Lorimer of Coventry Polytechnic whose book, 'Sonochemistry: Applications and use of ultrasound' was published by Ellis Horwood in 1988. Frequencies between 20 and 50 kHz are used. The project is now being scaled up to a pilot plant. Range of ultrasound in large reactors is not a problem although the rate of stirring and stirrer shape are critical. The average size of aggregates of TiO_2 crystals is drastically reduced by 5 s sonification.

S. K. Emmett (ICI Paints, Slough) presented a paper on 'A Conductometric Technique for the location of Adhesion Promoting Groups on Latex Particles'. Oil paints retain good adhesion in wet conditions (outdoors or in kitchens and bathrooms) but waterborne coatings tend to loose adhesion under these conditions especially when applied over oil paint. Adhesion of acrylic and vinyl acrylic emulsion paints can be improved by incorporation of an Adhesion Promoting Monomer which contains tertiary amino groups (which can be titrated conductometrically) but of which the composition was otherwise undisclosed although it was said to be similar to the cyclic ureide containing monomers developed by Rohm & Haas (B.P. 805 380 (1953)). Such speciality monomers are expensive so it is desirable to investigate where the adhesion promoting monomer is located in latex particles because only groups which are located on the particle surfaces are likely to be effective. The serum replacement technique was used to remove oligomer dissolved in the aqueous phase. Rigorous precautions (nitrogen sparging) are essential in the conductometric titration. With a 0.1 mol dm^{-3} titrant a resolution of 6×10^{-7} mol min^{-1} can be attained. Adhesion tests were claimed to correlate with concentrations of adhesion promoting monomer on particle surfaces but a distressingly large proportion of the monomer was lost in the aqueous phase.

Sandy Dunn,
Chemistry Department,
UMIST

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.

Reported by José M. Asua

Composition Control of Emulsion Copolymers in Reactors with Limited Capacity for Heat Removal

(G. Arzamendi and José M. Asua)

A method for the determination of the optimal monomer addition strategy to produce a homogeneous copolymer under conditions in which the reactor has a limited capacity for heat removal has been developed. The method allows for the calculation of the monomer addition profiles for both constant and time dependent heat removal rates. The approach was applied to the emulsion copolymerization of vinyl acetate and methyl acrylate carried out in a laboratory reactor which had been transformed to reduce its capacity for heat removal. It was found that a homogeneous copolymer composition was obtained when the heat transfer limitations were taken into account in the calculation of the monomer feed rate profile. On the other hand, significant copolymer composition drifts were obtained when the monomer addition rates calculated assuming that all of the reaction heat could be removed from the reactor were used. It was found that, for reactors with poor thermal characteristics (low maximum heat removal rate) the monomer feed rate profiles tend to those corresponding to the starved process. On the other hand, for higher heat removal rates, the use of the monomer addition profiles calculated using the approach presented in this work resulted in an important reduction of the process time. A criteria to discriminate between these two cases was proposed.

On the Main Locus of Radical Formation in Emulsion Polymerization Initiated by Oil-Soluble Initiators

(Juan A. Alduncin, Jacqueline Forcada, María J. Barandiaran and José M. Asúa)

Recently, Asua, Rodríguez, Sudol and El-Aasser (J. Polym. Sci. Part A: Polym. Chem., 27, 3569 (1989)); and Nomura and Fujita (Makromol Chem. Rapid Commun, 10, 581 (1989)) have presented mathematical models for the calculation of the average number of radicals per particle in emulsion polymerization systems using oil-soluble initiators. They reached opposite conclusions. While Asua et al. found that the kinetic similarities between oil-soluble initiators and water-soluble initiators were primarily due to the desorption of initiator radicals from the polymer particles, Nomura and Fujita concluded that the fraction of initiator that dissolves in the aqueous phase is responsible for this behavior.

The effect of the monomer/water ratio on the polymerization rate of both miniemulsion polymerization and seeded emulsion polymerization was used in an attempt to elucidate which is the main locus of radical formation in emulsion polymerization initiated by different oil-soluble initiators. If the oil-soluble initiator was distributed between oil phase and aqueous phase according to the thermodynamic equilibrium and if the amount of initiator dissolved in the aqueous phase was small compared with total amount of initiator, the amount of initiator dissolved in the aqueous phase increased when the monomer/water ratio decreased. Therefore, for a constant number of polymer particles, if the main locus for radical formation was the aqueous phase, $\bar{n}$ and hence, the polymerization rate would increase when the monomer/water ratio decreased. On the other hand, if the oil phase was the main locus for radical formation, the polymerizatin rate would either remain unchanged (negligible termination in the aqueous phase) or decrease (significant termination in the aqueous phase).

The polymerization rates measured for both miniemulsion polymerization and seed emulsion polymerization carried out using different oil-soluble initiators and varying the monomer/water ratio showed that the polymerization rate decreased when the amount of initiator per unit of oil phase dissolved in the aqueous phase increased. This is an evidence against a dominant aqueous phase formation of radicals. On the other hand, these results are consistent with a mechanism in which radicals are mainly produced in the oil-phase with a significant aqueous phase termination.

Emulsion Copolymerization of Styrene and Methyl Methacrylate
II. Molecular Weights

(Jacqueline Forcada and José M. Asua)

A mathematical model for the calculation of the evolution of both $\overline{M}_n$ and $\overline{M}_w$, in emulsion copolymerization has been developed. The model consisted in a set of ordinary differential equations and its application is not limited by the maximum number of radicals per particle. The model has been used to analyze the effect of the St-MMA molar ratio in the initial charge on the weight average molecular weight during the emulsion copolymerization of styrene and methyl methacrylate in a batch reactor. It was found that an almost constant $\overline{M}_w$ was obtained when the St-MMA molar ratio varied from 10/90 to 70/30 but a significant increase of $\overline{M}_w$ was obtained for the 90/10 St-MMA molar ratio. A good agreement between experimental results and model predictions was achieved not only for $\overline{M}_w$ but also for the experimental results reported in part I of this series [J. Polym. Sci., Part A: Polym. Chem. 28, 987 (1990)], i.e., number of polymer particles and time evolution of conversion and copolymer composition.

Estimation of the Reactivity Ratios using Emulsion Copolymerization Data

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

An approach for the estimation of the reactivity ratios based on cumulative copolymer composition-overall conversion data obtained in batch emulsion copolymerization has been presented. The approach, which is based on an algorithm for parameter estimation in ordinary differential equations, uses the whole conversion range and takes into account the partition of the comonomers between the different phases of the system. In addition, both copolymer composition and overall conversion were considered to be affected by experimental errors. Therefore, the appropiate error relationships were included in the objective function. The method was first checked by using simulated experimental data generated with exact values of the parameters. Gaussian random errors were added to the simulated copolymer composition and overall conversion using different levels of experimental errors. Application of the estimation approach to these data showed that accurate values of the reactivity ratios were obtained irrespective of the initial guess used. The approach was able to estimate accurately the reactivity ratios using data that included experimental errors much larger than those expected from careful experimentation.

The parameter estimation approach was used to estimate the reactivity ratios of the styrene-acrylonitrile system based on unseeded batch emulsion copolymerization data. The distribution of monomers in the system was calculated by means of the thermodynamic approach. It was found that good fitting of the experimental data was achieved. Comparison between these reactivity ratios and those estimated considering that the monomer molar ratio in the polymer particles equaled to the overall monomer molar ratio in the reactor showed that significant errors in the values of the estimated reactivity ratios were introduced when the distribution of monomers between phases was not taking into account.

Contribution from the Department of Polymerization Reactions, Polymer Institute, Slovak Academy of Sciences, Dúbravská cesta 10, 842 36 Bratislava, Czechoslovakia.

Reporter : J.Bartoň

Seed emulsion polymerization of methyl methacrylate
(J.Bartoň, Z.Hloušková, V.Juraničová)

The shape of the conversion curves and the rates of the batch emulsion polymerization of methyl methacrylate (MMA) in the presence of poly(butyl acrylate) seed particles (PBA) depends on the mass ratio MMA/PBA and/or the presence and/or absence of 4-octadecanoyloxy-2,2,6,6-tetramethylpiperidinyl-1-oxy (STMPO) in the feed. Irrespective of the presence, and/or absence of STMPO in reaction system the polymer particle diameter experimentally found and calculated under supposition that no new crop of polymer particles was formed agrees well for systems with "low" (0.632) value of the mass ratio MMA/PBA. For systems with "high" (3.16) value of the mass ratio MMA/PBA the calculated diameter is higher than the diameter experimentally measured. This points that for "low" values of MMA/PBA all poly(methyl methacrylate) formed was used only for build up of the shell of poly(butyl acrylate) particles. For "high" values of MMA/PBA approximately 19 mass % (in the absence of STMO) or 11 mass % (in the presence of STMPO) of the poly(methyl methacrylate) formed were used for generation of a crop of poly(methyl methacrylate) particles. The main part of poly(methyl methacrylate) formed was used for the formation of the shell of poly(butyl acrylate) seed particles. Retardation of the polymerization rate in the presence of STMPO is more pronounced for systems characterized by "low" value of the mass ratio MMA/PBA. Only short inhibition periods (up to five minutes) were observed for both "low" and "high" MMA/PBA ratios. It was shown that for "low" mass ratio MMA/PBA the "inner" monomer transport from the PBA particles swollen with MMA to the locus of propagation reaction is decisive. For systems with "high" mass ratio MMA/PBA the "outer" monomer transport from droplets and micelles swollen by monomer to the locus of propagation is of primary importance. For explanation of experimental results the possible reaction mechanism of the seeded emulsion polymerization was proposed.

Kinetics of the emulsion polymerization of styrene in the presence of divinylbenzene.

(J.Bartoň, A.Kleinová)

The emulsion polymerization and copolymerization of ethyl acrylate with a bi-unsaturated comonomer 1) revealed some problems connected with the crosslinking of polymer particles and with the effect of crosslinking on the kinetics of emulsion polymerization. This situation stimulated further research 2) of the effect of divinylbenzene (DVB) on emulsion polymerization of monovinyl compound. In order to exclude possible complications arising from the different nature of comonomer pair (e.g. different water solubility) and different physical properties of the structural units in copolymer chain (cf. ethyl acrylate and divinylbenzene structural units in copolymer) the effect of divinylbenzene on the emulsion polymerization of styrene (S) in the wide range of divinylbenzene concentrations was studied. It was found that by increasing the fraction of DVB in the feed with S the rate of copolymerization decreases and the shape of the conversion curve changes from sigmoidal to the typical shape of the conversion curve of solution polymerization (gradual decrease of the polymerization rate with polymerization time). The lowest polymerization rate was found for emulsion polymerization of divinylbenzene in the absence of styrene. Funke 3) has shown at thermally (spontaneous) initiated emulsion polymerization of 1,4-divinylbenzene that the polymerization of the monomer droplets is responsible for the high initial rate. If monomer is completely solubilized in micelles of emulsifier, the initial rate is distinctly lower. He concluded that two reactions are involved in the thermal emulsion polymerization of 1,4-divinylbenzene: a fast polymerization of the monomer droplets and significantly slower polymerization in the micelles and polymer particles.

Contrary to thermal initiation the initiation of emulsion polymerization by ammonium peroxodisulfate starts in the aqueous phase [4]. Co-oligomer radicals of DVB and S precipitate and form primary particles. Increasing the crosslinking degree of co-oligomer and co-oligomer radicals (by increasing the DVB content in the feed) decreases the swellability of primary particles by monomers. Thus the rate of copolymerization in primary (polymer) particles decreases due to monomer-starved conditions. For the overall rate is then decisive the rate of copolymerization in the aqueous phase (formation of co-oligomer radicals and their propagation in water phase). This mechanism explains the increase of the number of polymer particles in the system with polymerization time up to conversion of 50% and the decrease of the copolymerization rate with increasing concentration of DVB in the system [2]. The existence of trapped radicals in highly crosslinked polymer particles enables the interparticle crosslinking of particles during their agglomeration. This process is responsible for the decrease of polymer particle number at high conversions. In this polymerization model monomer droplets serve only as supply of monomer for the water phase reactions and to a lesser extent (depending on the degree of crosslinking of polymer particles) for swelling of polymer particles.

References

1. I.Capek, J.Kostrubová, J.Bartoň, Makromol.Chem., Macromol. Symp.,31, 213 (1990)
2. J.Bartoň, A.Kleinová, paper in preparation (Makromol.Chem.)
3. H.Kast, W.Funke, Makromol.Chem. 182, 1567 (1981)
4. J.Bartoň, V.Juraničová, Z.Hloušková, Makromol.Chem., 189, 501 (1988)

Effect of emulsifier type and concentration on the aqueous dispersion polymerization of N,N'-methylenebis(acrylamide)

(I. Capek, W. Funke)

The crosslinked macromolecules and polymer particles are formed by the emulsion polymerization and copolymerization of multifunctional monomers. The multifunctional monomers, such as divinylbenzene or alkylenediacrylate, crosslinks and strongly influences the emulsion polymerization via regulation of the equilibrium concentration and pendant unsaturated group concentration within the polymer particles [1,2]. It was concluded that the water-solubility of monomer significantly influences the mechanism of the growth of radicals and particle formation [3].

Little is known, however, about the kinetics in polymerization of water-soluble multifunctional monomers, such as bis(acrylamide)s. In order to clarify the polymerization mechanism of such systems we investigated the polymerization of N,N'-methylenebis(acrylamide) in the absence and presence of emulsifiers, such as sodium dodecylsulfate (SDS), sodium 1,4-bis(2-ethylhexyl)sulfosuccinate (AOT), poly(ethyleneglycol) (PEG), Tween 80 (Tw) and Triton X-15 (Tr). The rate of polymerization is found to be proportional to the 0.4 and 0.2 order with respect to AOT and Tr concentration, respectively. On the other hand it is independent of the concentration of SDS, PEG or Tw. The rate of polymerization is proportional to 0.75, 0.55 and 0.8 order with respect to potassium peroxodisulfate for the system with SDS, AOT and Tw. The rate of polymerization is proportional to the 0.24, 0.23 and 0.5 order with respect to monomer concentration for the system with SDS, Tw and AOT. It is seen that all system deviate from the Smith-Ewart model [4]. The reaction order of initiator is much higher than that for the traditional emulsion polymerization. On the other hand, the reaction order of emulsifier is lower than that for the emulsion polymerization. Besides, in the present systems the rate of polymerization increases with increasing monomer concentration.

In the presence of SDS and AOT, it was observed that after a certain reaction time the polymer particles coagulated. The value of this critical conversion increased with increasing emulsifier concentration and decreasing initiator concentration. The highest critical conversion for the system with SDS or AOT was 30% or 50%. In all other systems, the critical conversion was below 10%. It was found that the stability of polymer dispersion increased with decreasing monomer concentration. The dependence of the particle size versus conversion was described by the curve with a maximum at a certain conversion which was close to a critical conversion. The low value of the reaction order of emulsifier was explained by the week interactions of emulsifier with polymer. The high reaction order of initiator indicates the formation of fixed or ocluded macroradicals in polymer particles. The value of reaction order of monomer is result of the low monomer concentration in polymer particles, the low water-swellability of polymer particles and the strong contribution of the intra- and intermolecular crosslinking. In order to increase the stability of polymer particles we used some low-molecular weight additives, such as hexanol. It was observed that these additives did not influence the stability of polymer particles neither the rate of the polymerization.

Literature

1. W.Obrecht, W.Seitz, W.Funke, Makromol.Chem. 177, 1877 (1976)
2. L.Minnema, A.Staverman, J.Polym.Sci.,29, 281 (1958)
3. H.Kawaguchi, Y.Sugi, Y.Ohtsuka, J.Appl.Polym.Sci.,26, 1649 (1981)
4. W.V.Smith, R.H.Ewart, J.Chem.Phys. 16, 592 (1948)

HEAT-SENSITISATION OF LATICES BY POLYVINYLMETHYL ETHER

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A detailed investigation of the heat-sensitisation of polymer latices by polyvinylmethyl ether, which we completed a few years ago, has now been published in three papers which appeared recently in a single issue of the Journal of Dispersion Science and Technology. The titles and references are as follows:

1. "Heat-sensitisation of ammonia-preserved centrifuged natural rubber latex concentrate by polyvinylmethyl ether. I. Effects of maturation, former temperature, dwell time, latex pH, level of zinc oxide, dilution, and concentration and molecular weight of polyvinylmethyl ether", D. C. Blackley, A. D. T. Gorton and L. Sivagurunathan, J. Disp. Sci. Technol., 1990, 11(3), 215-248
2. "Heat-sensitisation of ammonia-preserved centrifuged natural rubber latex concentrate by polyvinylmethyl ether. II. Effects of addition of inorganic electrolytes, urea, carboxylate soaps and fatty-alcohol ethoxylates", D. C. Blackley, A. D. T. Gorton and L. Sivagurunathan, J. Disp. Sci. Technol., 1990, 11(3), 249-278
3. "Effect of polyvinylmethyl ether upon synthetic polystyrene latices", D. C. Blackley, A. D. T. Gorton and L. Sivagurunathan, J. Disp. Sci. Technol., 1990, 11(3), 279-306.

The titles of these papers give some indication of the contents. The first paper is concerned with the effects of some of the more obvious processing variables upon the thickness of deposit which is obtained when a heated former is immersed in a natural rubber latex concentrate which contains polyvinylmethyl ether. It is to facilitate the formation of thick latex deposits by dipping and casting using heated formers and moulds that polyvinylmethyl ether finds its principal application in latex technology. The second paper reports the effects of certain variables which were investigated in an attempt to gain further insight into the mechanism of the heat-sensitisation of natural rubber latex by polyvinylmethyl ether. The third paper describes attempts which were made to reproduce in carboxylate-stabilised synthetic latices the heat-sensitisation effect observed when polyvinylmethyl ether is incorporated in natural rubber latex. It was not found possible to obtain thick deposits from any synthetic latices containing polyvinylmethyl ether by using heated formers. Instead, increases in viscosity at ambient temperatures were sometimes observed. These are thought to have their origin in the physical effects which lead to the heat-sensitisation of natural rubber latex by polyvinylmethyl ether.

It is known that several water-soluble polymers, of which polyvinylmethyl ether is the best known, are able to impart heat-sensitivity to natural rubber latex. The ability of such polymers to heat-sensitise latices is believed to be associated with their inverse solubility behaviour. Possible heat-sensitisation mechanisms can be classified under two broad headings, and then under various sub-headings, as follows:

A. Mechanisms which depend upon the presence of water-soluble polymer dissolved in the aqueous phase of the latex

According to these mechanisms, heat-sensitisation is a consequence of reduction of the solubility of the polymer in the aqueous phase of the latex as the temperature is raised. These mechanisms sub-divide into:

- i) those in which heat-sensitisation is due to the precipitation of water-soluble polymer in the aqueous phase, *i.e.*,
    - a) a mechanism in which the latex particles become entrapped in a gel of precipitated water-soluble polymer;
    - b) a mechanism in which the precipitated water-soluble polymer adsorbs the colloid stabilisers from the latex particles and so reduces colloidal stability;
- ii) those in which heat-sensitisation is a consequence of adsorption of the dissolved polymer at the polymer-aqueous phase interface as the temperature of the latex is raised, gelation then occurring by one or other of the processes listed under B below.

B. <u>Mechanisms which depend upon the presence of water-soluble polymer adsorbed at the polymer-aqueous phase interface of the latex</u>

According to these mechanisms, heat-sensitisation is a consequence of changes in the nature of water-soluble polymer which is initially adsorbed at the surface of the latex particles. The polymer remains adsorbed as the temperature of the latex is raised, but the condition of the adsorbed molecules changes as a consequence of factors such as loss of hydration by the polymer. These mechanisms sub-divide into:

- i) those in which heat-sensitisation is due to reduction in the colloid stability of the latex because the adsorbed polymer is no longer able to function as a steric stabiliser;
- ii) those in which heat-sensitisation is due to interparticle bridging by the adsorbed polymer molecules, there being two types of process by which interparticle bridging could occur:
    - a) bridging by single polymer molecules initially adsorbed upon a single particle, but which subsequently also adsorb upon a second particle;
    - b) bridging by association in the aqueous phase between pairs of polymer molecules adsorbed on different particles;
- iii) those in which heat-sensitisation is due to interactions between the adsorbed polymer molecules and other colloid stabilisers in the latex.

The results which have been obtained in this investigation are consistent with heat-sensitisation being primarily a consequence of the effect of increased temperature upon polyvinylmethyl ether which is adsorbed at the surface of the latex particles, rather than of precipitation of polyvinylmethyl ether in the aqueous phase of the latex as the temperature is raised. Interparticle bridging by adsorbed polyvinylmethyl ether molecules as the temperature of the latex is raised may also be a significant factor.

One question which immediately arises from this investigation, and to which we have no answer at present, is why natural rubber latex should behave so differently from carboxylate-stabilised synthetic latices when polyvinylmethyl ether is present. Whereas natural rubber latex which contains polyvinylmethyl ether appears to be colloidally stable at ambient temperatures, but gels rapidly when the temperature is raised above a certain critical value, carboxylate-stabilised synthetic latices are either unaffected by the presence of polyvinylmethyl ether or undergo pronounced thickening at ambient temperatures. One obvious possible explanation is that the unusual behaviour of natural rubber latex is a consequence of the presence of substances derived from the non-rubber constituents of the fresh latex. This hypothesis could be tested by investigating the behaviour of natural rubber latex concentrate from which as much as possible of the non-rubber material has been removed. However, this is an investigation which will now have to be left to others!

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AQUEOUS SOLUTION PROPERTIES OF HYDROPHOBICALLY ASSOCIATING COPOLYMERS.

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(abstract presented at the 64th Symposium
on Colloids and Surface Science Symposium : Lehigh
June 18-20. 1990)

Water-soluble polymers containing a small amount of hydrophobic groups hav been prepared in aqueous medium by radical copolymerization of acrylamide and ethylphenylacrylamide as the hydrophobic comonomer. Two methods of synthesis have been used : a "micellar" process in which the use of a surfactant ensures the solubilization of the water insoluble monomer and a "heterogeneous" process wherein the insoluble monomer is simply dispersed in water. The copolymer compositions have been determined by UV spectrophotometry and the molecular weights by light scattering.

Rheological properties in dilute and semi-dilute aqueous solutions have been studied as a function of polymer concentration, shear rate, content in hydrophobic groups, and concentration of added surfactant. The effect of sample preparation on the rheological behavior is discussed. The more pronounced thickening effect observed for copolymers compared to homopolyacrylamide results from intermolecular hydrophobic associations. Under shear, associations are disrupted and a strong but reversible shear-thinning effect is observed. This dissociation process is relatively slow as indicated by the thixotropic behavior at high-shear rates. On the contrary, a rheopexic behavior can be observed at low-shear rates.

Recent publications

Polymerization in microemulsions : Formulation and structural properties of microemulsions containing a cationic monomer.
P. BUCHERT and F. CANDAU
J. Colloid Interface Sci., **136**, 527 (1990).

Properties of copolymer latexes prepared in inverse microemulsions.
F. CANDAU, D. COLLIN and F. KERN
in "*Copolymerization and Copolymers in Dispersed Media*" (J. Guillot and C. Pichot Eds.) Makromol. Chem. Makromol. Symp., Hüthig Wepf Verlag, Basel, Heidelberg, New York, 35/36, 105 (1990).

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The Importance of the Adsorption Kinetics of the Emulsifier in Particle Nucleation

The evidence for the occurence of particle coalescence during the emulsion polymerisation even of monomers which have a very low solubility in water - typically styrene - which has been recognised in recent years tends to discredit the micellar nucleation of latex particles as being important in such cases because it is difficult to see why a monomer-swollen micelle with a saturated monolayer of emulsifier at its interface with the water phase can become unstable during its transformation to a latex particle which is generally stable even when the amount of emulsifier present is significantly less than that required to form a saturated monolayer at the polymer/water interface. Consequently it seems more likely that particles are nucleated by oligomeric precipitation in the aqueous phase when the polymer/water interface would not be saturated with adsorbed emulsifier initially. Limited coalescence undoubtedly accounts for the larger latex particles which are formed in absence of emulsifier or at low emulsifier concentrations below the c.m.c. which produce monodisperse particle size distributions. Conventionally it would be supposed that the width of the particle size distribution formed above the c.m.c. should correlate with the duration of Interval I but this correlation is not actually observed: equal micellar concentrations of homologous emulsifiers produce latices with the same average particle size and the same breadth of particle size distribution even although the duration of Interval I is much longer for the more weakly adsorbed emulsifiers (cf. Dunn & Al-Shahib in Fitch ed. 'Polymer Colloids II' (1980) p. 624, Fig. 2).

Non-ionic emulsifiers are well known to produce latices with much larger average particle sizes than equivalent concentrations of ionic emulsifiers even though the amounts adsorbed at the polymer/water interface at equilibrium may be similar.

These observations are explicable if the rate at which the surface area of a latex particle is increasing when it is growing can exceed the rate at which emulsifier is adsorbed at the newly formed polymer/water interface so that the interparticle repulsive energy may periodically fall to a value low enough to permit particles to coalesce: it appears that this will be the case for very small latex particles (not much larger than the size of monomer-swollen micelles) and, moreover, that the rate of emulsifier adsorption will usually be proportional to the concentration of emulsifier in molecular solution (which is much lower for non-ionics which have much lower c.m.c.s than ionics so that they are adsorbed more slowly allowing more extensive coalescence to occur producing a latex with a larger average particle size).

It is generally accepted that termination is instantaneous when a second radical enters a latex particle which has a sufficiently small volume because the instantaneous radical concentration in the particle is then much higher than it ever is in bulk polymerisations. Curiously, it seems to have escaped attention that the radical concentration is also very high when a very small particle contains only a single radical and that consequently the propagation rate should also be expected to be abnormally high with the rate of increase of particle surface area being, correspondingly, extremely rapid for small particles.

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MECHANISM OF PARTICLE FORMATION IN THE EMULSION POLYMERISATION OF VINYL ACETATE

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Results obtained in investigating particle formation in the emulsion polymerisation of vinyl acetate are discussed in terms of an appropriate model.

1. Introduction

Amongst the numerous property parameters of polymer dispersions which are important for their manufacture and technical application the average particle size and the particle size distribution are particularly important. Consequently these have been the object of many previous investigations (summarised in references (1-3)). Despite this the models and theories presently available lack general validity so that the precise prediction of the course of a polymerisation is problematical as a rule. From the literature and our own results it appears that the particle size (or the specific particle number n) obtained in the emulsion polymerisation of vinyl acetate depends on the kind and concentration c_I of initiator, the kind and concentration c_e of emulsifier, on the temperature during the polymerisation T, on the rate of shear in the reaction mixture $\dot{\gamma}$, on the conversion c, and also on the pH value of the dispersion medium. Further batch processes are influenced by the phase ratio c_m (monomer used to dispersion medium) and processes with continuous addition of monomer by the monomer addition rate v_z. The specific particle number obtained

$$n = n(c_I, c_e, T, \dot{\gamma}, c, pH, c_m, v_z) \qquad (1)$$

Fig. 1 and 2 show the dependence of the number of particles on single factors in this complex expression. Little can be inferred on the mechanisms of particle formation and growth from the final result. The purpose of the following work is to reach conclusions on the vinyl acetate emulsion polymerisation which will be of general validity and to describe them so far as possible.

2. Experimental

The polymerisations were carried out in a 500 cm^3 stirred reaction vessel with continuous addition of monomer as well as with all the monomer initially present. Twice distilled water was used as the dispersion medium; its conductivity $\leq 2 \times 10^{-6}\,\Omega^{-1}\,cm^{-1}$. The initiator was A.R. potassium peroxydisulphate and the emulsifier was the half ester of sulphosuccinic acid. The specific particle number was generally lower both at low and very high shear rates in the reaction mixture and depended very strongly on shear rate; polymerisations were conducted in the medium shear rate region ($\dot{\gamma} \approx 80\ s^{-1}$) in which the dependence of specific particle number on shear rate is slight.

Fig. 3 shows the dependence of the specific particle number of the polymerised latex on emulsifier concentration $c_{e1} = 0$ mol dm^{-3} (1), $c_{e2} = 0.28 \times 10^{-3}$ mol dm^{-3} (2), and $c_{e3} = 5 \times 10^{-3}$ mol dm^{-3} (3) where the critical micelle concentration $c_e = 0.3 \times 10^{-3}$ mol dm^{-3}. The curves are qualitatively similar in this region. At the beginning of the reaction a very large number of particles are formed - the primary particles - of which the specific number is rapidly reduced by aggregation in the course of the reaction. Subsequent to this aggregation (described as primary aggregation) the specific particle number remains sensibly constant for the rest of the polymerisation.

When the particle number is constant the average diameter of the solid particles increases (Fig. 4) in accordance with the function:

$$\overline{d} = \left(\frac{6c\rho_D}{\pi n_2 \rho_T}\right)^{1/3} \qquad (2)$$

where ρ_D is the density of the dispersion, ρ_T the density of the particles, and n_2 the specific number of the aggregates. From these results it can be seen

immediately that aggregated nuclei are formed by the primary aggregation with which particle formed later coalesce. The primary aggregation process will be described as the nucleation phase of the polymerisation reaction.

The influence of the emulsifier on the nucleation phase and on the growth of the particles can be quantified. As shown in Fig. 3 the degree of aggregation of the primary particles decreases with increasing emulsifier concentration. The specific particle number (number of nuclei) obtained increases with increasing emulsifier concentration when higher conversions are attained. Thus the size diminishes when t emulsifier concentration is increased. More aggregates (nuclei) are formed at highe emulsifier concentrations consisting of a smaller number of primary particles.

In further experiments the rate of monomer addition, the pH value, and the temper were varied as well as the emulsifier concentration. In all cases the results were qualitatively consistent with those found by varying the emulsifier concentration. There are differences only in respect of the stationary specific particle number (aggregation number) and the conversion at which the specific particle number is reached (Fig. 1,2).

It is of the greatest interest to find the size of the primary particles and the molecular weight of the polymer in the primary particles under these conditions. Electron microscopy (Fig.5), soap titration, and light scattering show the size of the primary particles to be 10 nm varying between 7 nm and 15 nm. It is not possible to find how the size of the primary particles depends on the recipe and the condition for the process because the methods used do not acieve the precision (better than 10 which would be needed.

To obtain information on the average molecular weight of the polymer in the primar particles, it should be noted that van den Hul abd Vanlerhoff (4) found that electric charged initiator residues at chain ends were preferentially located on the surface of particles. With this assumption and assuming disproportionation the product of th surface charge density σ_o and the surface area $4\pi r_o^2$ immediately gives the number of polymer molecules in a primary particle. Then the mass m_T of a primary particle can easily be calculated from the total mass of polymer M and the number of primary parti n_1, whence the average molecular weight of the polymer in primary particles:

$$\overline{M}_p = \frac{M}{n_1 4\pi r_o^2 \sigma_o} \qquad (3$$

With the experimental value of the surface charge density $\sigma_o \approx 7\,\mu C\,cm^{-2}$ (5) this g an average molecular weight of 1900. This may be compared with the value found by Kakuschke (6) using GPC in parallel work when agreement is satisfactory.

Fig. 6 shows the dependence of the specific particle number of the polymerised material extended to higher conversions. It can be seen that the specific particle number from the primary aggregation process either remains constant or falls with increasing conversion. In (7) the decrease of the specific particle number at higher conversions was investigated. This showed that the decrease in the specific particle number at higher conversions was the result of a secondary aggregation process which results from insufficient stabilisation of the particles. Secondary aggregation is promoted particularly by high concentrations of ions, high rates of shear, large excess of monomer, low pH values, and lack of emulsifier.

Whereas the decrease of the specific particle number with conversion can be treated by itself no renucleation of particles was detected after the nucleation phase in the previous work. This shows that there is no tendency to form new particles after the nucleation phase. However renucleation can be induced by addition of the dispersion medium (dilution effect) or by addition of emulsifier and sometimes also of initiator (stabilisation effect). This permits the degree of stability of the number of particl already in the reaction mixture to be evaluated.

In the case of an emulsifier-free polymerisation addition of the dispersion medium can be used when renucleation occurs when the particle number $n < 10$ [illegible] cm^{-3} after dilution. Renucleation due to emulsifier addition can be detected in an initially emulsifier-free polymerisation when the particle number $n < 3 \times 10$ [illegible] cm^{-3} when the final emulsifier concentration $c_n > 3 \times 10^{-3}$ mol dm^{-3}. When particle numbers in the reaction mixture are low renucleation begins at lower emulsifier concentrations (Fig.

When the results are summarised, the following picture of particle formation processes in the vinyl acetate emulsion polymerisation is obtained.

- At the beginning of the polymerisation primary particles 10 nm in diameter are formed by association of relatively low molecular weight polymer (oligomer) in the reaction mixture.
- The primary particles aggregate as the polymerisation proceeds to form the nuclei of the ultimate latex particles.
- The number of primary particle which aggregate to form the average nucleus depends on the recipe and the procedure.
- To achieve sufficient particle stability (no secondary aggregation) the specific particle number and consequently the particle size of the final latex is determined by the primary aggregation process.

3. Calculation of the number of nuclei in the reaction mixture

According to this concept the calculation of the number of particles in the final latex must depend on the aggregation of primary particles to form nuclei. The calculation of the particle number proceeds from the experimental observation that primary particles are formed at least at the beginning of the polymerisation. If n_1 be the number of primary particles; then by analogy the formation of a new phase a saturation value for particle aggregation can be postulated.

The number of primary particles formed per unit time is:

$$\left(\frac{dn_1}{dt}\right)_0 = \frac{3}{4\pi r_0^3 \rho_P}\frac{dM}{dt} \qquad (4)$$

(r_0 - radius of the primary particles; M moles monomer reacted). The number of primary particles in the reaction mixture is the result of aggregation either of primary particle with each other

$$-\left(\frac{dn_1}{dt}\right)_1 = 8\pi D_1 r_0 n_1^2 \theta_{11} = k_{11}n_1^2 \qquad (5)$$

or else with previously formed aggregates

$$-\left(\frac{dn_1}{dt}\right)_2 = 4\pi (D_1 + D_2) r\, n_1 n_2 \theta_{12} = k_{12}n_1 n_2 \qquad (6)$$

(D_1, D_2 - diffusion coefficients of primary particles and aggregates respectively; r - effective radius; n_2 specific number of aggregates; k_{11}, k_{12} rate constants for the aggregation of primary particles with each other or for primary particles with aggregates. The constant θ indicates the interaction of primary particles with each other θ_{11} or primary particles with previously formed aggregates θ_{12}. They give the probability that collisions between particles will lead to aggregation.

In the stationary state the number of primary particles formed is equal to the number lost by aggregation. From (4), (5), and (6) it follows that

$$\left(\frac{dn_1}{dt}\right)_0 = \left(\frac{dn_1}{dt}\right)_1 + \left(\frac{dn_1}{dt}\right)_2 \qquad (7)$$

In real cases

$$\left(\frac{dn_1}{dt}\right)_1 \ll \left(\frac{dn_1}{dt}\right)_2 \qquad (8)$$

which is equivalent to

$$n_1\frac{k_{11}}{k_{12}} \ll n_2 \qquad (8a)$$

When the number of aggregates already present n_2 is so large that primary particles formed preferentially aggregates with the aggregates present. New aggregates form only when n_2 is below the particle number in the later stage of the polymerisation.

From the stationary state condition (7) the number of primary particles which exist in the reaction mixture as a function of the number of aggregates already present is

$$\left(\left(\frac{1}{2}\frac{k_{12}}{k_{11}}n_2\right)^2 + \frac{3}{4 r_0^3 \pi \rho_T}\frac{dM}{dt}\frac{1}{k_{11}}\right)^{\frac{1}{2}} - \frac{k_{12}n_2}{2k_{11}} \qquad (9)$$

substitution in (8) gives the criterion

$$\frac{n_1 k_{11}}{n_2 k_{12}} = \left(\frac{1}{4} + \frac{3k_{11}}{4\pi r_0^3 \rho_T k_{12}^2 n_2^2}\frac{dM}{dt}\right)^{\frac{1}{2}} - \frac{1}{2} \ll 1 \qquad (10)$$

All the quantities in (10) are known in principle either theoretically or experimentally so that it is possible to calculate the number of particles in the final latex.

The interaction function θ is given generally by

$$\theta = \exp\left(-\frac{V_0 - V_D}{kT}\right) \qquad (11)$$

where V_e is the repulsive and V_D the attractive interaction energy. According to (8) the attractive interaction energy is given by

$$V_D = -\frac{A}{6}\left(\frac{2r_0^2}{h^2 + 4r_0h} + \frac{2r_0^2}{h^2 + 4r_0h + 4r_0^2} + \ln\frac{h^2 + 4r_0h}{h^2 + 4r_0h + 4r_0^2}\right)$$

where A is the van der Waals-Hamaker constant and h is the distance between particles.

If it is supposed that the repulsive interaction energy results only from the electrical charge on the surface (no steric repulsion), the repulsive energy of the relatively small primary particles can be described to a good approximation by (9,10)

$$V_e = \frac{2r_0\varepsilon_0\varepsilon}{e^2z^2}(kT)^2\left((1 - \sin^2\gamma)K^2 + 2K\sin\gamma - 2KE + \int_{\sin\gamma}^{1}\frac{KE}{\sin\gamma}\,d(\sin\gamma)\right) \qquad (13)$$

$$\frac{\kappa h}{2} = K\sin\gamma = \frac{1}{\cosh\left(\frac{ze\psi_\delta}{2kT}\right)}$$

K, E - complete elliptical integrals of the first or second kind; ε_0 - permittivity of a vacuum; ε - dielectric constant; k - Boltzmann constant; e - elementary charge; z - valency of ion; κ - Debye-Hückel parameter; ψ_δ - Stern potential. For the calculation rate constant k_{12} the interaction energies between particles of unequal size must be used.

With the assumption that aggregation does not occur preferentially in any direction so that spherical aggregates are formed, the radius of an aggregate is:

$$r = r_0\sqrt[3]{j} \qquad (14)$$

where j gives the number of primary particles constituting the aggregate.

Model calculations show that the energy-distance functions (12) and (13) which are applicable to particles of equal size describe the interaction energies of particle of unequal size very well when these functions are multiplied by the expression $2r/(r_0 + r)$ (11). The interaction function between the primary particles and the aggregates can therefore with the assumption of equal surface charge densities and equal Hamaker constants be derived from the following expression:

$$\theta_{12} = \theta_{11}^{\frac{2r}{r_0 + r}} = \theta_{11}^{\frac{2\sqrt[3]{j}}{1 + \sqrt[3]{j}}} \qquad (15)$$

To assess the realism of the model described the following example will be considered: the emulsifier-free polymerisation of vinyl acetate with T = 353 K, $c(K_2S_2O_8) = 7 \times 10^{-3}$ mol dm^{-3}, $dM/dt = 3.05 \times 10^{-5}$ g s^{-1}cm^{-3}, producing in the reaction mixture primary particles with a radius r_0 = 6 nm with a Stern potential ψ_δ = 140 mV. For the Hamaker constant the value $A = 2.9 \times 10^{-21}$ J (8) was used producing an energy barrier of 0.1 kT = $(V_0 - V_D)$ in the energy-distance behaviour between primary particles. For these parameters and j = 10, Fig. 8 shows

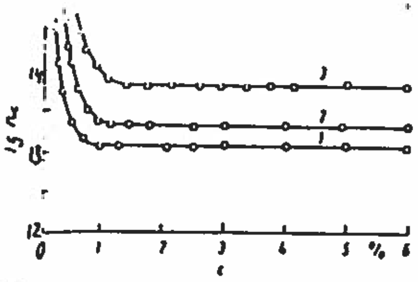

Fig. 3. Dependence of specific particle number on conversion for different emulsifier concentrations; 0 (1), 0.[illegible]8 x 10^{-3} mol dm^{-3} (2) [illegible] mol dm^{-3} [illegible]

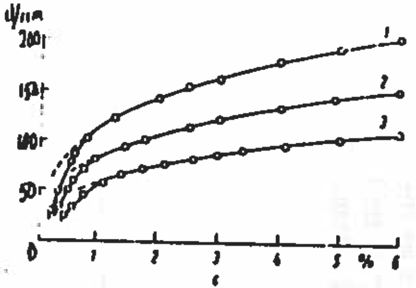

Fig. 4 Dependence of particle size on conversion at different emulsifier concentrations (emulsifier concentrations as in Fig, 3).

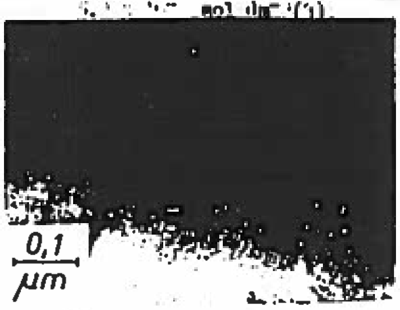

Fig. 5 Electron micrograph of primary particles

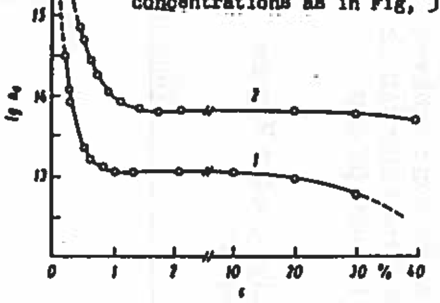

Fig.6. Dependence of specific particle number on conversion. Curve 1 with c_3 = 0 and Curve 2 with c_3 = 5 x 10^{-3} mol dm^{-3}.

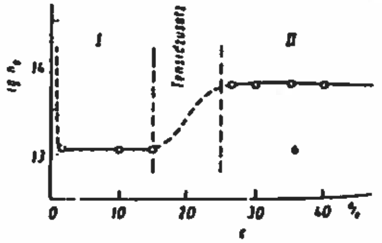

Fig. 7. Renucleation by emulsifier addition, Region I c_3 = 0; Region II; c_3 = 5 x 10^{-3} mol dm^{-3}

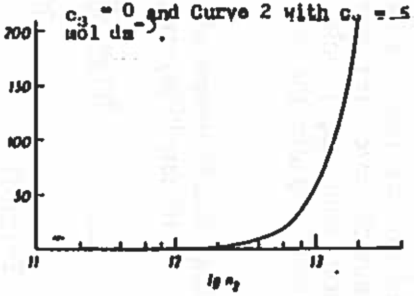

Fig. 8. Dependence of the reciprocal of KR on number of aggregates present.

the dependence of the reciprocal of the value of the criterion ([illegible] number of aggregates n_g. As may be seen from the graph, the rec[illegible] very rapidly for $n_g > 10^{13}$. Consequently under these conditions renucleation need only be considered when the number of aggregates falls below n < [illegible] because the criterion (10) is very well satisfied for $n_g > 10^{13}$.

To verify these conclusions polymerisations using a seed latex [illegible] were carried to 0% conversion. The particle numbers of the seed latices were: I: n_2 = 6 x 10^{13} cm^{-3}, II: n_2 = 2 x 10^{13} cm^{-3}, III: n_2 = 8 x 10^{14} cm^{-3}. No renucleation occurred in experiment I and II. The average particle size increas with conversion in accordance with equation (2). Renucleation was detected in experiment III; the particle size distribution of the final latex was clearly bi

References

(1) V.I.Eliseeva 'Emulsion polymerisation and its application in Industry' Mosco (English translation; Plenum, New York
(2) D.C.Blackley 'Emulsion polymerisation' London, Applied Science ([illegible]),
(3) S.S.Ivanchev & S.I.Kuchanov, Plast. Kautschuk 24 (1977) 225.
(4) H.J.van den Hul & J.W.Vanderhoff, Br.Polym.J. 2 (1970) 121.
(5) H.Kienitz, W.-D.Hergeth, & K.Schmutzler, Wiss.Zeit. Tech.Hochschule Leuna-Mer [illegible] (1981) 61.
(6) H.Kakuschke, Dissertation, Tech.Hochschule Leuna-Merseburg.
(7) W.-D.Hergeth, H.Kienitz, & K.Schmutzler, Acta Polym. [illegible] ([illegible]) [illegible].
(8) H.Sonntag, Lehrbuch der Kolloidwissenschaft, VEB Deutscher Verl[illegible] (1977)
(9) V.M.Muller in 'Research on Surface Forces' (Russian) Moscow, [illegible] (1967)
(10) G.A.Martynov & V.M.Muller in 'Surface forces in thin films and [illegible] syst (Russian), Moscow, Izd.Nauka (1972).
(11) B.V.Derjaguin, Koll.Z. 69 (1934) 155.

Received [illegible] November [illegible]

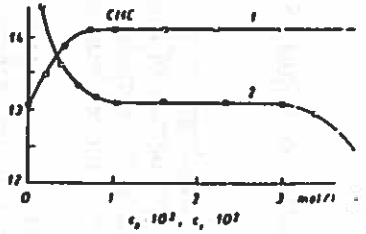

Fig. [illegible] Dependence of the specific particle number on surfactant concentration (Curve 1) and initiator concentration (Curve 2); conversion

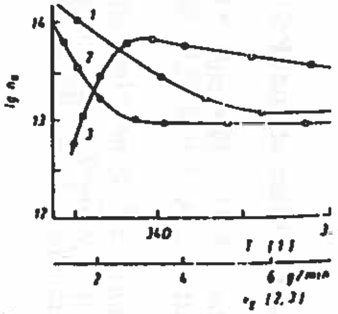

Fig. [illegible] Dependence of specific pa number on temperature of polymerisation (Curve 1) rate of addition of monome [illegible] for c_3 = 0 and Curve [illegible] c 5 x 10^{-3} mol dm^{-3}; convers

Contribution to the International Polymer Colloids Group Newsletter

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The titles of our current research projects are given in the enclosed Contents of our Graduate Research Progress Reports, No. 34, July, 1990. Copies of any of these reports can be obtained by contacting Ms. Debra Nyby at the above address. Summaries of progress in several research areas are presented.

1. Electrokinetic Characterization of Highly Sulfonated Polystyrene Model Colloids
(F. Javier de las Nieves)

The objectives of this research program are three-fold: 1) to determine the influence of the cleaning process on the surface properties of highly sulfonated polystyrene model colloids; 2) to study the electrokinetic behavior of these model colloids; and 3) to use these particles as substrates to study the adsorption behavior of model biomolecules.

Highly sulfonated polystyrene latex particles were prepared by a two-stage "shot-growth" emulsion polymerization process in the absence of emulsifier. Sodium styrene sulfonate (NaSS) was used as an ionic comonomer to produce a series of latex particles with nearly the same particle size but with different surface charge densitites. Table I shows the standard polymerization recipe used to prepare this type of latex. A long and comprehensive cleaning process comprised of repeated centrifugation and sonication, heating, and ion-exchange or serum replacement cycles was followed to achieve reproducible surface charge density values obtained by conductometric titration measurements. The cleaning process proved to exert a strong influence on the final surface charge density of these particles. The surface charge density values were found to change with time unless these rigorous cleaning cycles were followed. This phenomenon was attributed to the desorption of physically adsorbed oligomers (formed during the shot growth phase of the polymerization) from the surface of these latex particles which were removed by the repeated centrifugation-redispersion (strong sonication) cycles. Table II shows the particle size and surface charge density of these latexes obtained after the extensive cleaning process.

TABLE I: Standard Polymerization Recipe Used to Prepare Sulfonated Polystyrene Latexes

Component	Initial Charge	Shot Injection
Styrene (g)	20	4
Sodium Styrene Sulfonate (NaSS) (mM)	1.5	Variable
Potassium Persulfate (mM)	4	4
Sodium Bisulfite (mM)	4	4
Sodium Bicarbonate (mM)	8	8
Distilled-Deionized Water (ml)	140	14

TABLE II: Particle Size and Surface Charge Density (σ) of Model Sulfonated Polystyrene Latexes Obtained after Extensive Cleaning [a]

Latex	FJN-20	FJN-21	FJN-22
% conversion at shot injection	87	89	95
NaSS (g)	0.4	0.8	1.2
D_n (nm)	248	263	244
D_w	250	264	245
PDI	1.008	1.004	1.004
σ(μC/cm^2)	13.9	16.3	19.4

[a] NaSS: Sodium Styrene Sulfonate; D_n: number average diameter; D_w: weight average diameter; PDI: Polydispersity Index (D_n/D_w); σ: surface charge density

The electrokinetic properties of these cleaned latexes were measured at 25°C under different ionic strength and pH conditions using a PenKem 3000 instrument. Figure 1 shows the electrophoretic mobilities (μ_e) for the three latexes with different surface charge densities characterized in Table II as a function of electrolyte concentration. This figure shows that there was little difference in the μ_e values for these latexes regardless of the surface charge density. A maximum in the value for μ_e was also observed when measuring the electrophoretic mobility of these three latexes, regardless of the surface charge density. These same result were observed when measuring the electrophoretic mobility of these latexes as a function of pH.

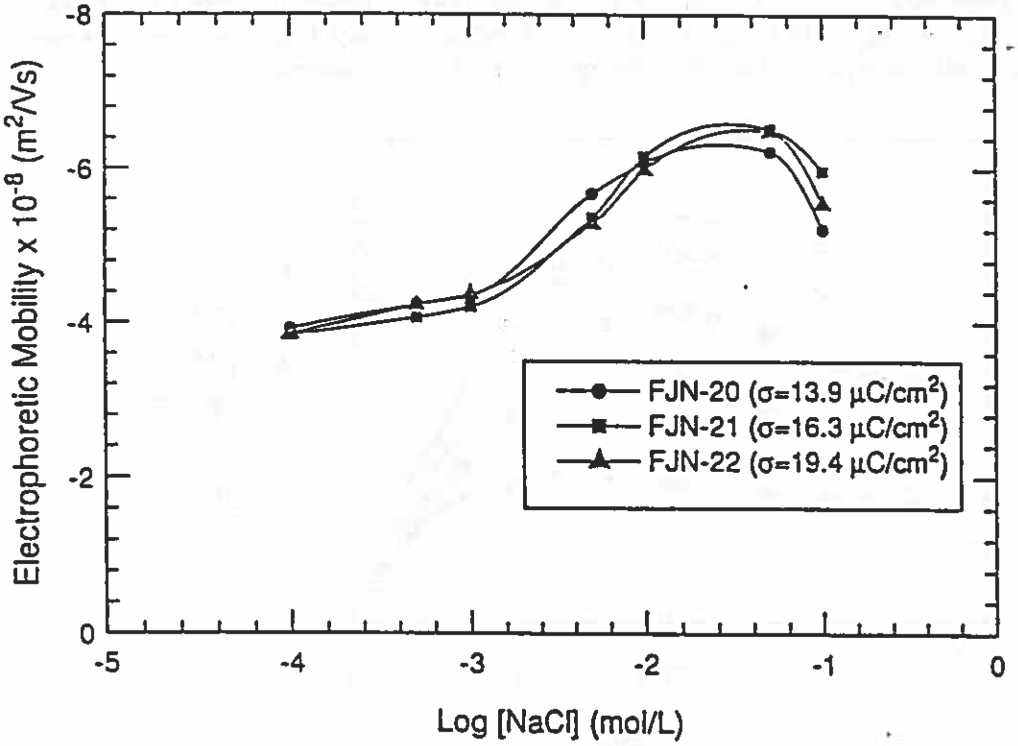

Figure 1: *Electrophoretic mobility as a function of electrolyte concentration for the three highly sulfonated model latexes.*

2. Effect of Electrolyte on the Electrokinetic Potentials of Toluene-in-Water Miniemulsions

(Richard J. Goetz)

Electroacoustics is a new technique that permits the electrokinetic potentials of concentrated dispersions to be measured at their formulation concentration. Standard electrokinetic experiments, i.e., microelectrophoresis, require that the dispersion be substantially diluted to approximately 100ppm. Thus, this technique is particularly useful for the study of emulsions and polymer colloids that have unique properties at high dispersion concentrations. Diluting an emulsion can change the chemical nature of the continuous phase, shift the surfactant adsorption equilibrium and ultimately affect the stability of the emulsion. In this report, the effect of electrolyte on the electrokinetic sonic amplitude (ESA) of toluene-in-water miniemulsions prepared with sodium lauryl sulfate (SLS) and cetyl alcohol (CA) are examined.

The ESA is measured by applying a high frequency (1 MHz) electric field across the dispersion that forces the charged particles to undergo oscillatory motion. The motion of the particles in the dispersion generates an acoustic wave with the same frequency as the applied field. The ESA is defined as the pressure amplitude per unit electric field and has units of mPa m/V. The amplitude of this acoustic wave is proportional to the concentration of the colloid and the zeta-potential. Thus, at a given dispersion concentration the effects of electrolyte on the surface charge properties of the miniemulsion can be investigated. Figure 2 shows the ESA as a function of NaCl concentration for miniemulsions prepared with 10mM SLS and 30mM CA at six different toluene phase volumes. Surprisingly, the data show an increase in the surface charge of the emulsion droplets as the concentration of NaCl increases, reaching a maximum near 10mM NaCl. Beyond the maxima the surface potential decreases with the collapse of the double layer to the point of coagulation. Although not shown in Figure 1, maxima are not observed for emulsions prepared solely with SLS. Increases in the zeta-potentials of emulsion droplets, prior to the point of charge reversal, have been observed in other emulsion systems although an explanation has never been given [Usui, S. and Imamura, Y., *J. Disp. Sci. Techn.*, 8, 359 (1987); Prakash, C. and Srivastava, C., *Bull. Chem. Soc. Japan*, 40, 1756 (1967)]. However, similar behavior has also been observed in polystyrene latexes with several explanations being offered for the maxima.

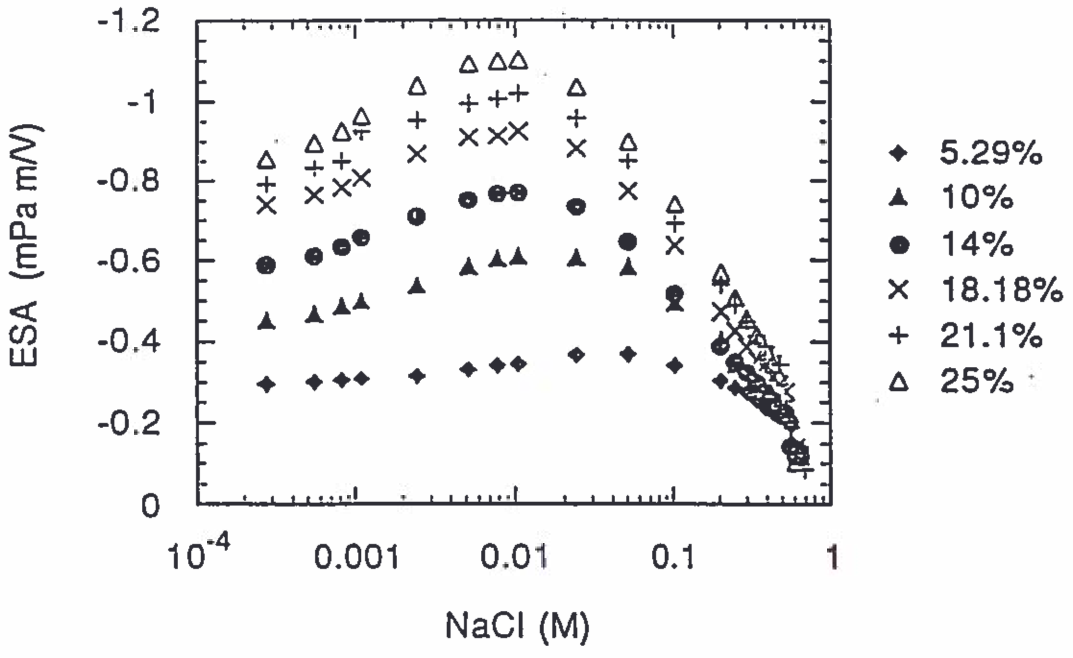

Figure 2: *ESA as a function of added NaCl for miniemulsions prepared with 10mM SLS and 30Mm CA at six different toluene phase volumes.*

One explanation for the ESA/electrolyte maxima originates from the effect of added electrolyte to decrease the solubility of SLS in the continuous phase, favoring adsorption. Since SLS is a stronger amphiphile than CA, the adsorbed CA is displaced by SLS. This displacement mechanism would also explain the absence of an ESA/electrolyte maximum when CA is not present in the emulsion. For emulsions prepared without CA, the interfacial area would need to increase for the surface excess of SLS to increase, which is energetically unfavorable. However, it is possible that the addition of electrolyte would decrease the adsorption area of adsorbed SLS by partially neutralizing the electrostatic headgroup repulsive forces. However, added electrolyte also tends to dehydrate charged surfaces. Figure 3 shows a plot of the concentration of SLS adsorbed on the miniemulsion droplets as a function of added NaCl for miniemulsions prepared at 10mM SLS and 30mM CA at 25vol% toluene. The data in Figure 3 clearly show that the addition of NaCl shifts the surfactant adsorption equilibrium, increasing the surface excess of SLS. Thus, the increase in the electrokinetic potential can in part be attributed to a higher surface concentration of SLS. Additional studies have shown that the position of the maximum is also affected by the type of anion, suggesting co-ion adsorption as another mechanism for explaining the maximum. However, different electrolytes will also affect the solubility of SLS to a different degree and shift the position of the maximum. Nevertheless, co-ion adsorption cannot be ruled out as a possible mechanism until further experiments are conducted.

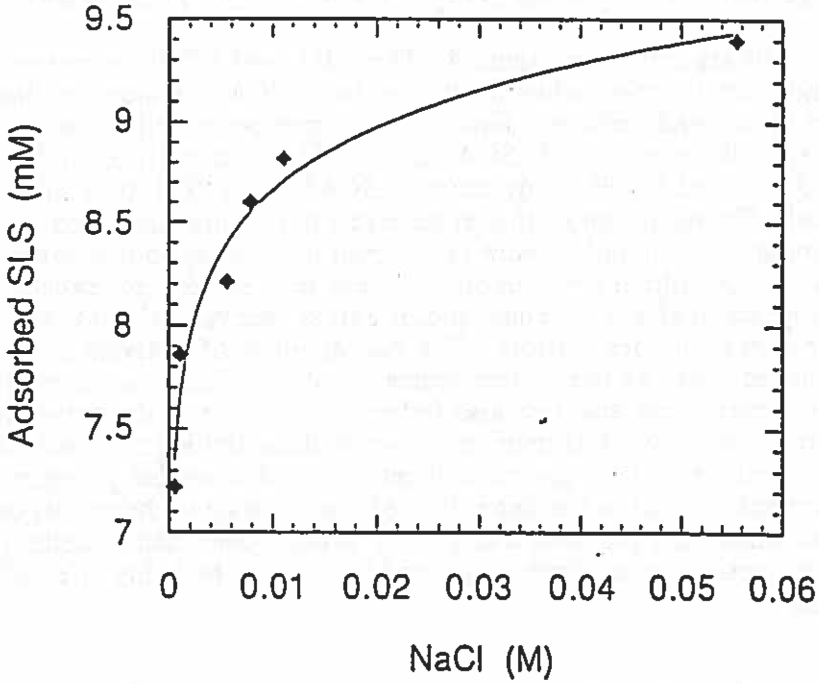

Figure 3: *Concentration of adsorbed SLS as a function of added NaCl for a miniemulsion prepared with 10mM SLS and 30mM CA with 25vol% toluene.*

3. Effect of Cetyl Alcohol on the Kinetics of Miniemulsion Polymerization

. (Phan L. Tang)

The enhanced stability of miniemulsions prepared with SLS/CA has been attributed to the formation of "intermolecular complexes" at the oil/water interface. A common feature of miniemulsion polymerizations is the relatively slow nucleation stage of the reaction [Y.T. Choi, M.S. El-Aasser, E.D. Sudol and J.W. Vanderhoff, *J. Polym. Sci., Polym. Chem. Ed.*, 23, 2973 (1985)]. This has been attributed to a reduced radical absorption rate possibly caused by this interfacial layer formed by the mixed emulsifier systems at the droplet-water interface. Another possible cause for the reduced radical absorption rate is that the presence of cetyl alcohol may interfere with the initiator decomposition in the aqueous phase.

To obtain the entry and exit rate coefficients, the number of polymer particles have to be known. Therefore, seeded emulsion polymerization was use to study the effect of cetyl alcohol on the polymerization kinetics. A monodisperse polystyrene seed of approximately 100 nm diameter was used with various amounts of surfactant (sodium lauryl sulfate) and co-surfactant (cetyl alcohol) added to mimic the miniemulsion oil-water interface. A comparison was carried out between cases with and without cetyl alcohol at various initiator concentrations to evaluate the effect of cetyl alcohol on the entry and exit of radicals.

Polymerization kinetics were obtained via dilatometry. Reactions were begun by addition of initiator (potassium persulfate) solution to the swollen latex at the polymerization temperature (50^{o}C). Two similar methods were used to evaluate the data: 1) that developed by the Sydney Group [R. G. Gilbert and D. H. Napper, *Rev. Macromol. Chem. Phys.*, C23(1), 127 (1983)] by which free radical entry and exit rate coefficients are inferred from the approach of the rate of polymerization to a steady-state (slope/intercept method); and 2) that developed at Lehigh which estimates parameters using all the conversion-time data in the approach to steady-state [J. M. Asua, M. E. Adams and E. D. Sudol, *J. Polym. Sci., Polym. Chem. Ed.*, 39, 1183 (1990)].

The experimental results are shown in Figure 4. The solid lines (SNO) represent the results from experiments without cetyl alcohol while the dashed lines (SCA) are those obtained with cetyl alcohol on the surface of the seed particles. Four sets of experiments with varying initiator concentration are represented in these results: 1) SCA1 and SNO1 employed 1.33 mM initiator (potassium persulfate); 2) SCA4 and SNO6, 0.66 mM; 3) SCA2 and SNO2, 0.13 mM; and 4) SCA3 and SNO3, 0.013 mM. The results show that at all levels of initiator, the reaction rates in the cases in which cetyl alcohol was included were faster than the corresponding cases (at the same level of initiator) that had no added cetyl alcohol. These results were not expected. The presence of cetyl alcohol appears to affect the entry and/or exit of free radicals, favoring an increased $\bar{n}$ (average number of radicals per particle). The two methods of analysis are in rough agreement indicating that indeed the entry rate of free radicals is slightly increased in the systems containing cetyl alcohol. However, these analyses also indicate a decrease in the desorption rate constant in the same systems. Further work is required to verify these findings. Nonetheless, the conversion histories clearly illustrate that the presence of cetyl alcohol in seeded polymerizations does not decrease the polymerization rate but rather enhances it in contrast to the results obtained in the polymerization of miniemulsions prepared using cetyl alcohol. One suspect being investigated at this time is the decomposition rate of persulfate and how it may be being affected by the differences in the two systems.

4. Preparation of Water Absorbent Poly(Acrylamide-co-Acrylic Acid Salts) by Inverse Suspension Polymerization (Yin-Shen Chang)

In the early 1970's, the so-called "superabsorbents" were developed as materials which could absorb as well as retain a substantial quantity of fluid even under a compressive force. These absorbents are primarily a type of polyelectrolyte gel and have found use in many fields, e.g., in disposable diapers, water reservoir materials in agriculture and horticulture, coagulants in the sedimentation of sludges, and drying agents in the dehydration of oils. Although these materials have been in large-scale production, little is known of the mechanism by which they absorb and hold such large amounts of water.

In this work, poly(acrylamide-co-acrylic acid salts) with low crosslinking levels were prepared by inverse suspension polymerization for use as model polymers. The products are in the form of easily separable beads. The first part of this work was aimed at clarifying the relationship

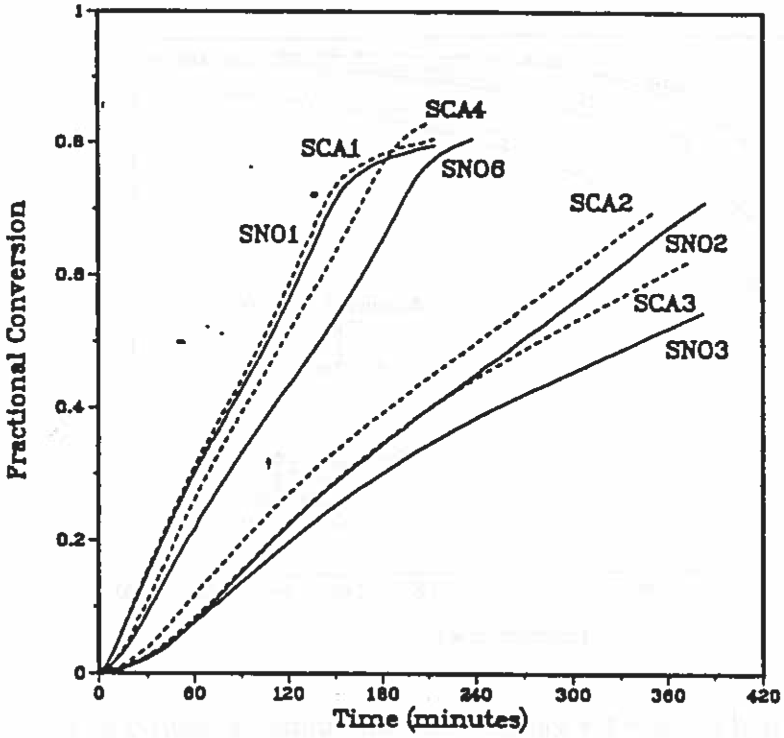

Figure 4: *Conversion-time curves for seeded emulsion polymerizations with (SCA) and without (SNO) cetyl alcohol at various levels of persulfate initiator.*

between the structure properties of the 71:29 molar ratio poly(acrylamide-co-sodium acrylate) [71:29 PACSA] beads and the kinetic swelling process through the diffusion process.

The kinetic swelling of the 71:29 PACSA beads was observed by two techniques: optical microscopy and environmental scanning electron microscopy [ESEM]. By using these two techniques, the diffusion mechanism and kinetic swelling were characterized. According to the observations via optical microscopy, the diffusion of water into these glassy 71:29 PACSA beads proceeds by means of anomalous diffusion which is a combination of Fickian and Case II diffusion. The kinetic swelling ratio increases with decreasing particle size. According to the kinetic swelling theory, the diffusion coefficient is in the range of 1.6 - 2.0×10^{-7} cm^2/s which is independent of the particle size as shown in Figure 5. Using the ESEM, water vapor can be introduced and removed from the environs of the microscope chamber allowing close observation of the swelling process. In this case, the water transport is dominated by Case II diffusion rather than anomalous diffusion. The physical and chemical structures of the 71:29 PACSA were investigated to provide a better understanding of their relationship to the swelling phenomena. A core/shell structure with a higher carboxylate content in the shell and the gel structure were characterized using ESEM, NMR and DSC. The ESEM showed that the shell can be peeled off the core during the re-swelling process. The existence of the core/shell structure prevents the occurrence of gel blocking due to significant cross-linking in the shell. The network structure of the gel matrix provides a great capacity to hold a large amount of water even under compression.

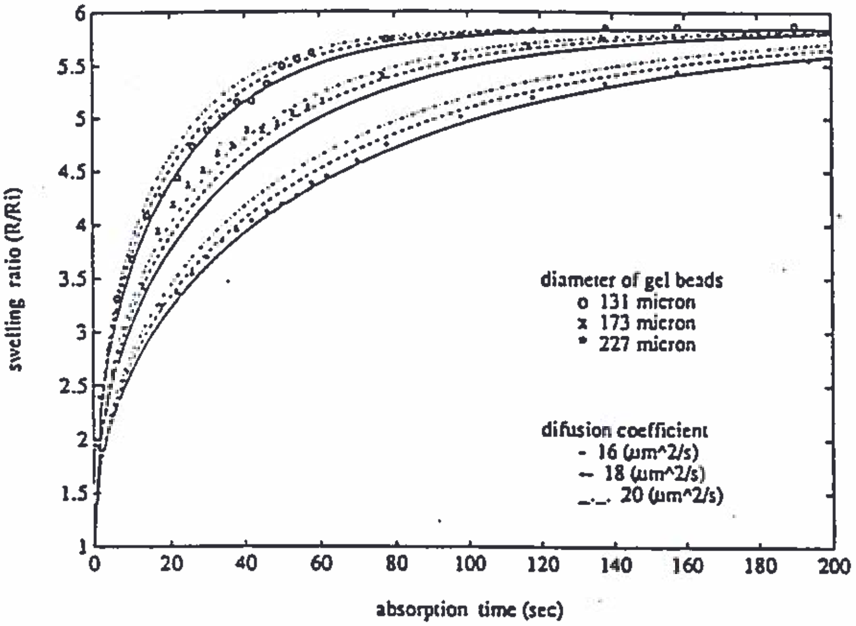

Figure 5: *Swelling ratio (R/R_i) vs. time for gel particles with initial diameters of 131, 173, and 227 μm; the symbols are the experimental data and the lines represent simulations using various diffusion coefficients.*

Papers Recently Presented

The following were presented at the 64th Colloid and Surface Science Symposium held at Lehigh University, June 1990:

"Preparation and Morphological Characterization of Microscopic Composite Particles", S. Shen, V.L. Dimonie, M.S. El-Aasser and J.W. Vanderhoff.

"Graduated Core-Shell Supramolecular Structure in Polystyrene Latexes", S.I. Yang, A. Klein and L.H. Sperling.

"Molecular Interdiffusion During Film Formation From Polystyrene Latexes", J.N. Yoo, A. Klein and L.H. Sperling.

"Synthesis of Monodisperse Porous Polymer Particles", C.M. Cheng, M.S. El-Aasser and J.W. Vanderhoff.

"Evaluation of Diphenyl Ether Disulfonate Surfactants and Polycarboxylated Surfactants in Emulsion Polymerization Systems", E.S. Daniels and M.S. El-Aasser.

"Electro-Acoustic Properties of Concentrated O/W Miniemulsions", R.J. Goetz and M.S. El-Aasser.

"Adsorption, Stability, and Rheological Behavior of Latexes that Contain Model Associative Polymer", R.D. Jenkins, M. Durali, C.A. Silebi and M.S. El-Aasser.

The following papers were presented at the 33rd IUPAC International Symposium on Macromolecules held in Montreal, CANADA, July 1990:

"Development of Particle Morphology in Composite Latexes", M.S. El-Aasser, Y.C. Chen, and V.L. Dimonie.

"Synthesis and Characterization of Core/Shell Type Ionomeric Latexes", E.S. Daniels, R. Jourdan, M.S. El-Aasser and J.W. Vanderhoff.

"Role of Surfactants in Emulsion Polymerization of Vinyl Acetate", V.L. Dimonie, O.L. Shaffer, M.S. El-Aasser and J.W. Vanderhoff.

The following was presented at the Fall Meeting of the ACS Division of Polymeric Materials: Science and Engineering held in Washington, D.C., August, 1990:

"The Morphology of Microscopic Composite Particles Prepared by Two-Stage Polymerization", S.Shen, V.L. Dimonie, E.D. Sudol, M.S. El-Aasser and J.W. Vanderhoff.

Recent Publications

"Miniemulsion Copolymerization of Styrene-Methyl Methacrylate: Effect of Transport Phenomena", J.M. Asua, V.S. Rodriguez, C.A. Silebi and M.S. El-Aasser, Makromol. Chem., Macromol. Symp., 35/36, 59 (1990).

"Effect of Alkyl Substitution of Dowfax^{TM} Surfactants in Styrene-Butadiene Emulsion Copolymerization", V.L. Dimonie, M.S. El-Aasser, J.W. Vanderhoff and L.A. Settlemeyer, Makromol. Chem., Macromol. Symp., 35/36, 447 (1990).

"Batch Emulsion Copolymerization of 50/50 Vinyl Acetate/n-Butyl Acrylate Using Poly(vinyl Alcohol) Emulsifier", J.W. Vanderhoff, N.J. Earhart, V.L. Dimonie and M.S. El-Aasser, Makromol. Chem., Macromol. Symp., 35/36, 477 (1990).

"Investigation of the Persulfate/Itaconic Acid Interaction and Implication for Emulsion Polymerization", M.R. Lock, M.S. El-Aasser, A. Klein and J.W. Vanderhoff., J. Appl. Polym. Sci., 39, 2129 (1990).

"Pseudosteady States in Semicontinuous Emulsion Copolymerization", J. Dimitratos, M.S. El-Aasser, C. Georgakis and A. Klein, J. Appl. Polym. Sci., 40, 1005 (1990).

"FT PGSE NMR Investigation of the Supramolecular Structure of a Dilute Gel Phase", R.J. Goetz, A. Khan and M.S. El-Aasser, J. Colloid Interface Sci., 137, 395 (1990).

"Characterization of Film Formation from Polystyrene Latex Particles via SANS. 1. Moderate Molecular Weight", J.N. Yoo, L.H. Sperling and A. Klein, Macromolecules, 23, 3962 (1990).

Recent Ph.D. Dissertations and M.S. Reports

"Polymerization of Styrene Oil-in-Water Microemulsions", Ph.D. Dissertation by Jong-Shing Guo.

"Preparation of Model Solid Rocket Propellant by Emulsification", PhD. Dissertation by Tom W. Hawkins.

"Preparation and Characterization of High T_g Core/Shell Copolymer Latex Particles", M.S. Report by Connie Heck.

Copies of the Abstracts are available upon request.

The Emulsion Polymers Institute's 22nd Annual Short Course "Advances in Emulsion Polymerization and Latex Technology" will be held at Lehigh on June 3-7, 1991.

EMULSION POLYMERS INSTITUTE
Lehigh University

Graduate Research Progress Reports
No. 34 July 1990

CONTENTS

THE FACTORS OF STABILITY OF CARBOXYLCONTAINING FREE EMULSIFIER LATEXES

Eliseeva V.I., Aslamazova T.R., Bogdanova S.V.

It is known that the including of carboxyl groups and other hydrophilic groups into a polymer composition promotes the increase of colloid stability of latex obtained in the absence of emulsifier by persulfate initiation.

With the purpose of clearing up the factors which determine the stabilization of carboxylcontaining free emulsifier latexes we have made experiments on copolymerizing monomers of different composition with variable concentrations of undissociated acrylic acid (AA) and have been researched physico-chemical properties of obtained latexes. It has been studied the stability in the process of copolymerization (the formation of coagulate-C), diameter D and ξ - particle potential, surface tension of latexes (σ), area per one COOH group S_{COOH}. The concentration of initiator - potassium persulfate (PPS)-was the same in all compared experiments. pH of latex was varying in the value range of 2.1-2.3 under which COOH groups are not practically dissociated. The composition of basis monomers in researched latexes includes: series I - styrene (S) - methylmethacrylate(MMA), 2-ethylhexylacrylate(2EHA)(15:15:20); series 2 - styrene - butylacrylate (BA)(32:22). The content of AA as to the sum of the basis monomers was changed within 0-8%. The PPS concentration is 0.5%. The synthesis of series I was performed under 70 and 80°C.

On Fig.1 the relation between [AA] and some physico-chemical latex parameters of the first series are presented. Fig. shows that with the increase of AA concentration up to 2% stability grows till maximum value, then remains constant. Moreover the particle charge grows and then essentially decreases and it does not affect latex stability. Herewith S_{COOH} with growing AA decreases.

On Fig.2 the same relations to latexes of series 2A and 2B are shown. A more strongly expressed relation between stability and [AA] is observed than in case of latexes series I, especially for latexes obtained under lower temperature (70°C). The stability of all latexes of these series is lower than in series I, but latexes obtained under higher temperature (80°C) are characterized by greater stability. The stability increase is accompanied by decrease of ξ-particle potential and S_{COOH}, more sharp for latexes of series 2A obtained under lower temperature.

Fig.1 and 2 show an essential decrease of σ with injecting AA due to the formation of "own" surface active substances (SAS) and the growth of their concentration in carboxyl-containing free emulsifier latexes.

The particle charge in these systems is determined by SO_4^- groups concentration on their surface, since COOH groups under conditions of polymerization are not dissociated. Its reduction with injecting of AA into polymer indicates that the concentration of surface SO_4^- groups decreases under given initiator concentration. It could be connected with the decrease of ratio $[SO_4^-] / [OH^{\bullet}]$ /1/ (which would lead to the drop of stability) or with partial expenditure of PPS on the formation of water-soluble oligomer radicals terminating in water solution with the formation of surface active substance (SAS) which is confirmed by the reduction of σ latexes.

The observed sharp increase of stability of latexes with the same decrease of ξ-potential - electrostatic factor (Fig.2) - and with increase of COOH group concentration permit to draw a conclusion about the role of hydration of a particle surface - structural factor - in the stability of carboxylcontaining free emulsifier latexes.

Thus the data obtained show a certain role of the hydration effect of particle surfaces with carboxyl groups and partially of the absorption of formed oligomer SAS upon latex stability. Probably a certain effect of "persulfate stabilization" on copolymerization with AA occurs. It is shown from a initial part of ξ - potential curve (Fig.1). However further direction of this curve and other ones (Fig.2) indicate that it has obviously no predominant importance.

The effect of basis monomer nature on the stability of carboxylcontaining free emulsifier latexes is an object of interest. In comparing the data (Fig.1 and 2) it is clear that the latexes on the base of mixture containing more polar monomer MMA (Fig.1) are considerably more stable than the latexes on the base of hydrophobic monomers (Fig.2) obtained under the same polymerization temperature. The first ones are characterized by smaller size but higher ξ-particle potential value. As free emulsifier polymerization always begins in water solution it can be connected with greater rate of SO$_4^-$ radicals capture by more water-soluble MMA and greater nucleation rate of particles in the stabilization of which fastforming radicals MnSO$_4^-$ $\bullet$ enriched MMA take part. The same reasons lie in greater stability of latexes of more hydrophobic monomers used for synthesis under increased temperature. The latter are characterized by smaller size and higher ξ-potential value: the increase of the radical formation rate and the origin of particles the surface of which rapidly captures initial and oligomer radicals (promoting the stabilization of it by end groups SO$_4^{-\bullet}$) leads to the formation of a greater number of charged particles.

I. Cheska G.W. Polym. Preprints. Am. Chem. Soc. Phyladelphia. 1975, v.16, No.1, p.161.

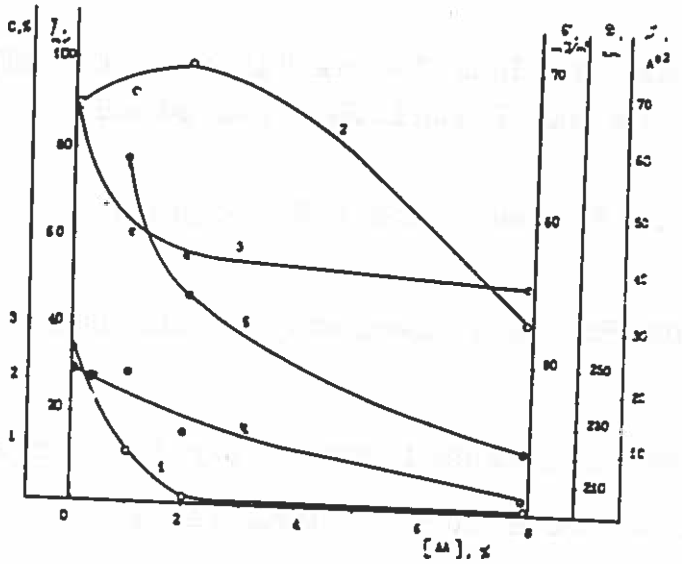

Fig.1

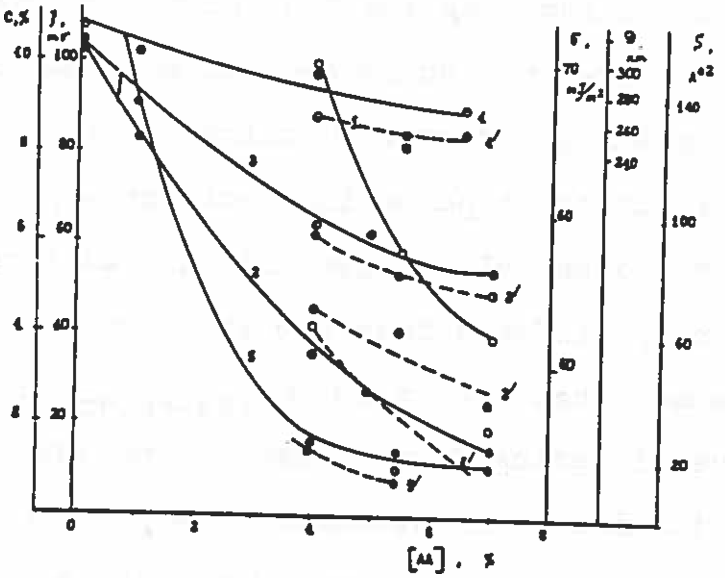

Fig.2

The relations of coagulate (C), ξ-potential, surface tension (σ), diameter of a particle (D), area per one COOH group (S) for latexes of series I and 2 and AA concentration

Fig.1 - series I; 80°C

Fig.2 - series 2; curves (I'-5')-70°C; curves (1-5) -80°C.

THE ROLE OF PHASE INTERACTIONS IN THE STRUCTURE OF LATEX PARTICLES AND FILMS

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We have established previously that in seed polymerization (SP) of chloroprene (CP) on PBMA latex the former is diffused into the volume of latex particles as a result of which the polymerization leads to phase inversion and the formation of the composition particles: core (PCP) - shell (PBMA) [I]. This phenomenon is explained by a discrepancy in polarity of monomers and lowering the free energy of system in going from interface PCP-water to PBMA-water and PBMA-PCP. In the present work such a regularity is confirmed using the quantitative characteristics of phase interactions - γ - at SP of I.I - dihydroperfluorheptylacrylate (FA) on PMA latex, whose monomer is strongly differed from the first one by its polarity. It was assumed that the ratio γ_1'(FA-water) : γ_2'(MA-water) is preserved in going from monomer to polymer (as a result of polymerization) correspondingly to $\gamma_1 : \gamma_2$.

Proceeding from paper [I] we have assumed that for a formation of "inversed" structure of particles inequality (I) should be satisfied

$$\gamma_1 < \gamma_2 + \gamma_{PMA-PFA} \qquad (I)$$

that corresponds to inequality (2)

$$\gamma_1' < \gamma_2' + \gamma_{PMA-PFA} \qquad (2)$$

It was found that $\gamma_1' = 24.5$ mJ/m^2, $\gamma_2' = 8.3$ mJ/m^2. $\gamma_{PMA-PFA}$ was taken to be equal to 2 mJ/m^2. From these data it follows that inequalities (I) and (2) are satisfied in the system investigated.

Values γ_1' and γ_2' are decreased in the systems having emulsifier (partially sulphated polyoxyethylated alkylphenol used in polymerization) and become equal to $\gamma_1'' = 10.5$ mJ/m^2 and $\gamma_2'' = 6.99$ mJ/m^2, respectively.(The adsorption energies of emulsifier are $E_1 = 27,57$ kJ./mol and $E_2 = 19,58$ kJ /mol). When substituting γ_1'' and γ_2'' into inequality (2) it is seen that the difference between the right- and left-hand sides is sufficiently decreased, i.e. the drawing force initiating phase inversion is reduced.

The figure presented below illustrates electron microphotography of the composition particles in which PFA, containing I% of isoprene is contrasted with osmium tetroxide.

It is seen that in contrast to [I] the particles are not characterized by the core-shell structure: they consist of PMA matrix with PFA domain inclusions. One of the reason of such a disrepancy may be a difference in interface energy between polymer phases: when interface energy increases the more polar phase tends to form a concentric sphere on the surface of particles [I].

As is seen from figure, at the particle coalescence in aqueous phase this structure is preserved. PMA phase, in which

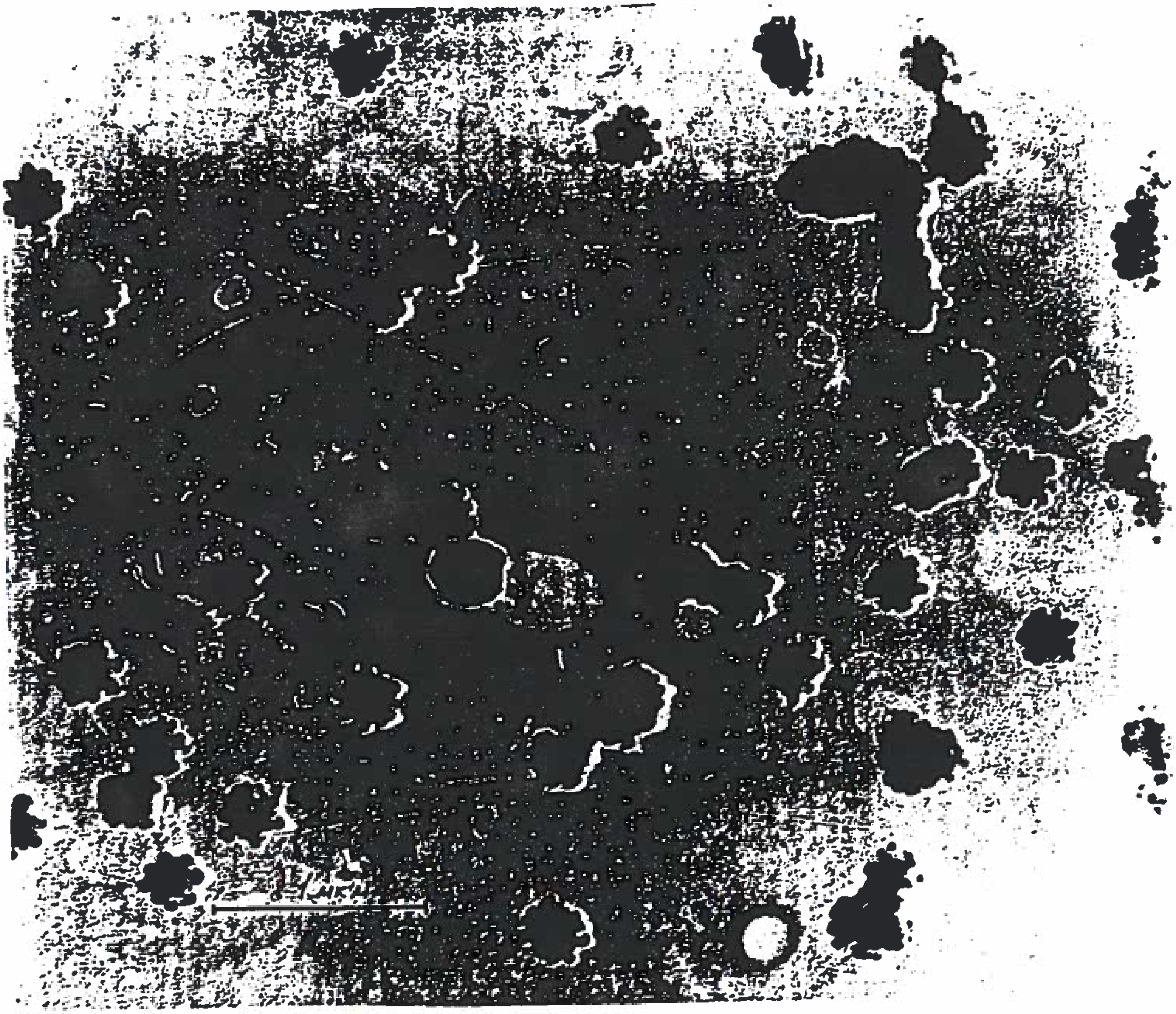

Fig.I. Electron microphotography of the contrasted composition latex particles produced by SP of FA on PMA latex.

PFA domains are distributed, remains external continuous matrix.

Under the film formation - particle coalescence in the air atmosphere, the ratio of phase interaction with medium is changed for a reverse one :

$$\gamma'''_{FA-air} = 10.9\ mJ/m^2 \quad \text{and} \quad \gamma'''_{MA-air} = 25.4\ mJ/m^2$$

This gives rise to the new morphological changes and PFA becomes external phase. We established this fact by studying the surface and volume properties of the composition films, which are mainly determined by the PFA. As T_g of both polymers is lower that the room one, and one of them (PMA) is in high-elastic and second (PFA) in viscous-flow states, the macromolecules mobility is sufficient for the realization of phase inversions, caused by decreasing the free interface energy in film.

[I] V.I.Eliseeva, N.V.Titova et al. Doklady AN SSSR, I98I, v.26I, p.402 (in Russian).

INTERNATIONAL POLYMER COLLOID GROUP

Contribution from Bob Fitch & SCJohnson Wax

Racine, Wisconsin

Two publications have recently issued [copies available on request]:

1. Tien-Teh Chen & R.M.Fitch, The Preparation and Surface Chemistry of Polystyrene Colloids Stabilized by Thiosulfate Surface Groups. J. Colloid Interface Sci. **137**, 163 (1990).

Emulsifier-free polystyrene latices could be made especially easily by the Cu(II)/thiosulfate redox system. Conductometric titration showed only strong acid surface groups are present on the particles.The surface charge densities decreased upon heating (hydrolysis) or treating with cyanide ion (nucleophilic substitution). Thiosulfate free-radical ions, $\cdot S_2O_3^-$, are believed to be the initiating species. By means of IR spectroscopy, the end groups were found to be S-alkylated rather than O -alkylated.

2. Moshe Puterman & R.M.Fitch, Latex Preparation and Stabilization by Hydrophobically Modified Hydroxyethyl Celluloses. J. Applied Polymer Sci. **40**, 333 (1990).

Because these amphiphilic, water-soluble polymer molecules are known to adsorb strongly on water-oil interfaces, they were tested as nonionic surfactants and stabilizers in emulsion polymerization. Styrene and methyl acrylate were used as water-insoluble and slightly water -soluble monomers. *In situ* nucleation, seed polymerization and post-polymerization addition of HMHEC's were examined. The main difficulty with the HMHEC materials is their bridging effect, which enhances aggregation. However, these nonionic materials impart extremely pronounced stability to latices against electrolytes. This property can be achieved also by post addition of the HMHEC to a preformed emulsion.

3. Lao-So Su, Sunil Jayasuriya [at SCJohnson Wax] & R.M.Fitch

Work on dielectric spectroscopy of model polymer colloids continues. Earlier studies showed that counterion "condensation" could be estimated quantitatively, and that specific ion effects were evident in the case of strong electrolyte surface groups. We are now investigating weak electrolytes where more complex behavior may be expected.

Contribution to the International Polymer Colloids Group Newsletter

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Polymer encapsulation of submicron inorganic particles in aqueous dispersion

Introduction:

In literature several processes have been described to obtain particles that consist of an inorganic core and a polymer shell. Polymer encapsulated particles offer interesting prospects in applications requiring a good coupling between a polymer matrix and inorganic particles, like e.g. water based paints, fillers for composites, electroconductive additives to plastics, carriers for catalysts, diagnostic materials etc. The processes described in literature to obtain such particles can be divided into two main groups: already existing polymer chains are bound to the inorganic surface [1,2], or polymerization is carried out at the particle surface [3,4].
The latter method has also been applied in "emulsion polymerization" techniques. Oligomeric chains, formed in a soapless emulsion polymerization, were adsorbed at the inorganic surface, thus creating a hydrophobic layer at the surface in which further polymerization can take place [5,6]. Hasegawa et al. [7] found that at low surfactant concentrations emulsifier molucules are adsorbed at the particle surface, thus forming a hydrophobic double layer in which an "emulsion" polymerization can be carried out. These techniques have the disadvantage that the adsorption at the particle surface strongly depends on reaction conditions like pH and ionic strength. Even after polymerization is completed these conditions remain very important, as desorption can take place when they are changed.
The goal of this investigation is to provide a method that can be used to encapsulate inorganic particles (like TiO_2 pigments) with a polymer layer.
In an emulsion-like system a physical or chemical bond is formed between the inorganic particle and the polymer layer, synthesized at its surface.

Results and Discussion

Polymerizations are carried out at the surface of pure rutile particles with a diameter of about 260 nm and a specific surface area of 8.5 m^2/g. These particles, containing acidic hydroxylic groups at their surface, are modified with titanate coupling agents, according to figure 1.

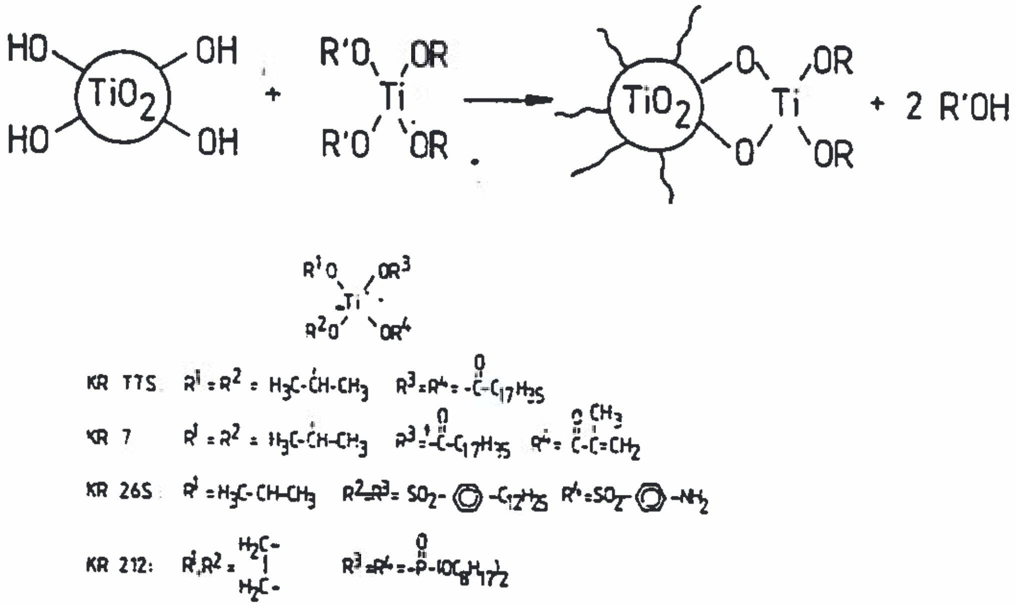


Figure 1. Modification of TiO_2 with titanate coupling agents.

The presence of titanates at the particle surface renders the hydrophilic surface hydrophobic. Upon dispersing these modified particles in an aqueous surfactant solution the emulsifier (SDS) is adsorbed at the particle surface, thus forming a hemimicelle in which monomer can be absorbed. Now polymerization can take place at the particle surface. A physical bond between polymer and titanate will be formed because of entanglements with the titanate chains. By using a titanate containing a copolymerizable group (C = C) [8] or an initiating moiety (N = N), also a chemical bond can be obtained (figure 2).

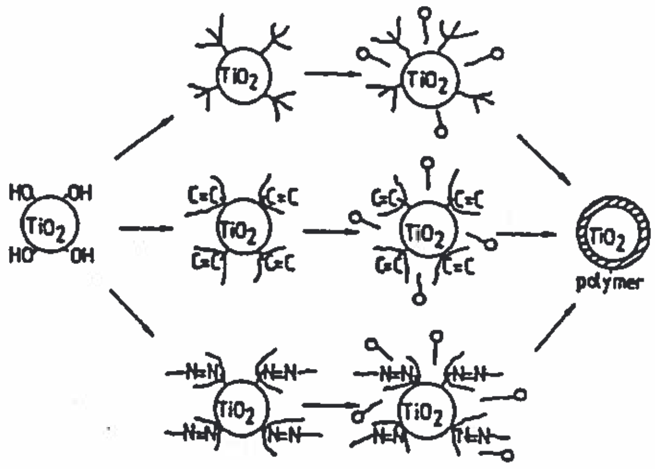


Figure 2. Polymerization at the surface of TiO_2, modified with titanates.

The effect of the presence of TiO_2 on the polymerization behaviour of MMA is demonstrated in figure 3. Unmodified TiO_2 particles do not seem to affect polymerization kinetics. However, the presence of hydrophobic TiO_2 particles during polymerization results in a temporary decrease in polymerization rate. This effect can be explained by flocculation of encapsulated TiO_2 and polymer particles at a certain moment during reaction, as was shown by means of dark field and electron microscopy [9].

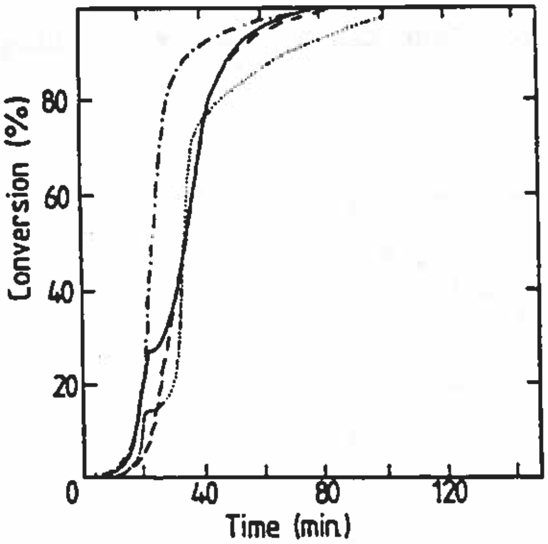


Figure 3. Effect of (modified) TiO_2 on the polymerization kinetics of methyl methacrylate; (modified) TiO_2: MMA = 1:3; -.-.- MMA; — MMA + TiO_2; MMA + TiO_2/KR TTS; .... MMA+ TiO_2/KR 26S.

In order to prevent a competitive polymerization in normal micelles reactions are carried out at a surfactant concentration just above the cmc. As the growing particles require more surfactant molecules for their stabilization, a deficiency arises resulting in some coagulation of the particles. At the same time polymer is formed at the inorganic surface, which can lead to bridging flocculation, if not all particles are fully covered with polymer. In a regular emulsion polymerization (i.e. "zero-one" system) growing particles contain only one radical at the same time, as the entrance of a second radical results in immediate termination with the first. However, as the TiO_2 core cannot be penetrated by primary or oligomeric radicals, TiO_2 particles with a thin polymer shell are likely to contain more than one radical at the same time. Thus, the average life-time of radicals at the inorganic surface will be longer than the average life-time of radicals in regular polymer particles. So, after "large" coagulates have been formed, the polymerization rate is bound to decrease, because many radicals may become trapped inside. Because we use a water soluble initiator (ACPA) in the aqueous phase new radicals will be generated, causing an increase in polymerization rate after some minutes. Thus, in the second part of the reaction polymerization will continue mainly in free polymer particles, but also in newly formed polymer particles, generated because surfactant molecules have become available as a result of the limited coagulation.

In case of a rather water soluble monomer like methyl acrylate these effects cannot be observed, as the polymerization to a larger extent takes place in the continuous phase. However, when a more hydrophobic monomer like styrene is used, the effects are even larger, as this monomer is more easily adsorbed at the particle surface, as can be concluded from figure 4.

By increasing the stirring rate mixing conditions can be improved, resulting in less flocculation.

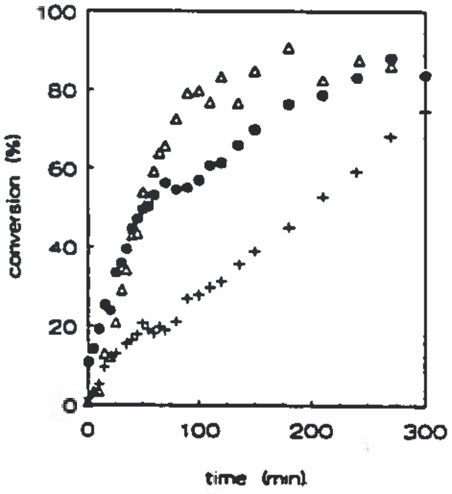
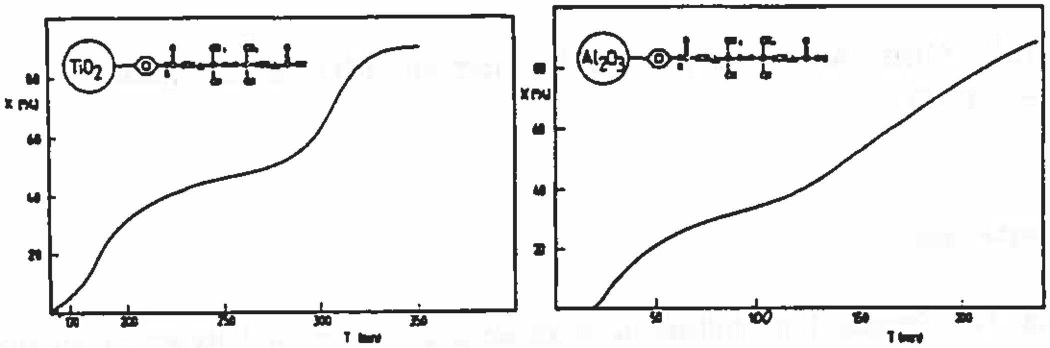


Figure 4. Effect of mixing conditions on the polymerization of styrene (33.3 g TiO_2/l, 0.32 mol styrene/l, 10.4 mmol SDS/l); Stirring rate (butterfly-type stirrer): + 230 rpm; o 250 rpm; Δ 350 rpm.

The place where initiation takes place also plays a very important role in the polymerization behaviour. The azo initiator (ACPA) was bound to the aromatic amine group of KR26S at the particle surface [10]. A typical conversion-time curve for the polymerization of MMA is shown in figure 5. Apparently the induction period is quite long. This is probably due to the photochemical activity of pure rutile particles: radicals formed at the surface can be terminated by radicals formed in the TiO_2 lattice by UV irradiation. α-Al_2O_3 modified with KR26S and ACPA does not show this effect. As the surface of most commercially available TiO_2 pigments consists of Al_2O_3 and/or SiO_2 there won't be a problem in technical applications.

At a conversion of about 30% the reaction rate decreases, but now it takes a relatively long time before it increases again. Like in the case of TiO_2 modified with KRTTS, this temporary slow-down is caused by flocculation of the particles. However, in this case new radicals can only be generated inside the agglomerates, and initiation in free polymer particles and micelles will therefore be hindered by a slower radical diffusion, which accounts for the long period of low reaction rate.

The presence of a radical initiator at the particle surface instead of dissolved in the aqueous phase results in a much higher polymer content of the TiO_2 particles [9,10]. Flocculation of the encapsulated particles can be prevented by using low monomer concentrations. Polymerizations under starving conditions seem to result in a higher stability of the dispersions and the formation of a rather large amount of polymer at the inorganic surface.



(A) (B)

Figure 5. Initiation at the particle surface

A) Polymerization of MMA, initiated by TiO_2/KR26S/ACPA (10.40 mmol/l SDS, 1.00 mol/l MMA, 33 g/l TiO_2);

B) Polymerization of MMA, initiated by Al_2O_3/KR26S/ACPA (10.40 mmol/l SDS, 1.00 mol/l MMA, 33 g/l Al_2O_3).

References

1. L.A. Pririen, J.A. Stolp, R. Zgol; J. Colloid Int. Sci., 28 (1968), 466-474

2. R. Laible, K. Hamann; Adv. Colloid Int. Sci., 13 (1980), 65-99

3. F. Fukano, E. Kageyama; J. Polm. Sci.: Polym. Chem. Ed., 13 (1975), 1309-1338

4. R. Laible, K. Hamann; Angew. Makromol. Chem., 48 (1975), 97-133

5. T. Yamaguchi, H. Tanaka, T. Ono, M. Endo, H. Ito, O. Habashi; Kobunshi Ronbunshu, Eng. Ed.; 4 (1975), 150-157

6. W. d. Hergeth, K. Schmutzler; Acta Polym., 36 (1985), 472-474

7. M. Hasegawa, K. Arai, S. Saito; J. Polym. Sci, Part A: Polym. Chem, 25 (1987) 3231-3239

8. C.H.M. Caris, L.P.M. van Elven, A.M. van Herk, A.L. German; Brit. Polym. J., 21 (1989), 133-140

9. C.H.M. Caris; Polymer Encapsulation of Inorganic Submicron Particles in Aqueous Dispersion; Ph. D. thesis, Eindhoven University of Technology (1990)

10. C.M.H. Caris, A.M. van Herk, A.L. German; Materialen (March 1990), 19-22

Recent dissertations

1. K.H. van Streun, Immobilization of cationic polymers and its effect on the cobaltphthalocyanine-catalyzed thiol oxidation, Ph.D.Thesis, Eindhoven University of Technology, 1990

2. G.F.M. Hoedemakers, Continuous emulsion polymerization in a pulsed packed column, Ph.D.Thesis, Eindhoven University of Technology, 1990

3. P.A. Weerts, Emulsion polymerization of butadiene; a kinetic study, Ph.D.Thesis, Eindhoven University of Technology, 1990

4. C.H.M. Caris, Polymer encapsulation of inorganic submicron particles in aqueous dispersion, Ph.D.Thesis, Eindhoven University of Technology, 1990

CONTRIBUTION TO POLYMER COLLOID GROUP NEWSLETTER FALL 1990

from

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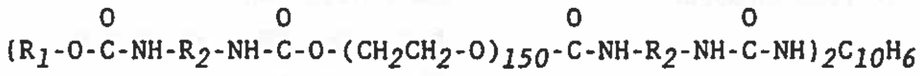
COMPETITIVE ADSORPTION AND PHASE FORMATION OF ASSOCIATIVE THICKENERS

At the UoO we are starting slowly to build the research group. I have one new research assistant who will be working mainly on our associative thickeners project. Last year I had an NTH (Trondheim) student (mr. K.Larsen) at Dyno who started work on competitive adsorption of associative thickeners and emulsifiers on model polystyrene latex particles. For this purpose dr. Fonnum synthesized a special thickener with a naphthyl group in the middle. This has the structure,



$$(R_1\text{-}O\text{-}\overset{O}{C}\text{-}NH\text{-}R_2\text{-}NH\text{-}\overset{O}{C}\text{-}O\text{-}(CH_2CH_2\text{-}O)_{150}\text{-}\overset{O}{C}\text{-}NH\text{-}R_2\text{-}NH\text{-}\overset{O}{C}\text{-}NH)_2C_{10}H_6$$

where R_1 is a straight hydrocarbon chain C_6H_{13} to $C_{13}H_{27}$, R_2 is methylene bis(cyclohexyl) and $C_{10}H_6$ is the naphthyl group. This naphthyl group facilitates analysis of the serum by UV adsorption. In a mixture with nonionic emulsifiers on nonyl phenyl basis, both emulsifier and thickener may be detected simultaneously because of the difference in the adsorption band. Adsorption was measured on 0.5 µm PS particles by filtration or centrifugation of the latex, and UV analysis of the serum.

The results are most interesting (some of them were presented by dr.Fonnum at Lehigh this summer). The thickener adsorbs in a "normal" manner when added alone. Adsorption isotherms may be measured, and are approximately of the Langmuir-like type. However, when emulsifier is added, the thickener desorbes and emulsifier adsorbs as may be expected, but after some time (several hours) the emulsifier partly desorbes again. The same phenomenon takes place when the emulsifier is added first; the thickener adsorbs, and then desorbes again, leading to partly reabsorption of the emulsifier. The adsorption isotherms taken at equilibrium (more then 15 hours) shows a typical low affinity (S-type cooperative) form. The starting point of the adsorption is proportional to the amount of emulsifier in the system.

We believe these results indicate a type of phase equilibrium in the water, a gel or mixed micellar phase that are thermodynamically more favored than adsorption on a PS surface. The phase formation takes a long time to reach equilibrium. This phase seem to have a fixed ratio between emulsifier and thickener molecules of 20-30, dependent on the hydrophobicity of both thickener and surfactant. We naturally find these results very interesting, and are now going to investigate such mixed systems with several techniques, in particular NMR and light scattering techniques where we will be cooperating with groups here i Oslo and in Sweden. Presently, we have promising results on NMR diffusion measurements where we show that diffusion in such mixed systems changes dramatically with composition.

MAXIMUM ENTROPY INVERSION OF ELASTIC LIGHT SCATTERING DATA FOR THE PARTICLE SIZE DISTRIBUTION BY NUMBER AND VOLUME

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ABSTRACT

The application of Maximum Entropy analysis of elastic light scattering data for the evaluation of particle size distributions by number and by volume in the submicron size range is reported. The practical performances for homogeneous spheres are illustrated with simulated data and experiments on unimodal, bimodal and trimodal distributios of monodisperse latices. Accurate reconstructions by number are observed. The reconstructions by volume lead to somewhat broadened distributions. The method also allows the resolution of closely spaced distributions of particle sizes.

PHYSICAL REVIEW A VOLUME 42, NUMBER 4 15 AUGUST 1990

Dynamic light scattering by nonergodic media: Brownian particles trapped in polyacrylamide gels

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(Received 12 March 1990)

Dynamic light scattering (DLS) is used to study the diffusional behavior of polystyrene latex spheres incorporated in polyacrylamide gels. It is shown that the gel systems exhibit nonergodic features, implying that the time-averaged intensity correlation function (ICF), the quantity obtained from a single DLS experiment, is not equal to the ensemble-averaged ICF. It is demonstrated that the theory of Pusey and van Megen [P. N. Pusey and W. van Megen, Physica A 157, 705 (1989)] on DLS by nonergodic media can be used to extract dynamic structure factors from single DLS experiments. It appears from this analysis that large values of the diffusion coefficient of the tracer particles, which would have been obtained in a classical analysis, do not imply rapid particle motions but result simply from an incorrect analysis of the data. The initial decay of the dynamic structure factor gives a short-time diffusion coefficient of the particles that hardly depends on the degree of cross-linking. We also show that a proper analysis of the data results in a dynamic structure factor that develops a nondecaying component. This component is a measure for the fraction of frozen-in fluctuations resulting from constrained diffusion of the tracer particles. From the nondecaying component in the dynamic structure factor, a distribution of root-mean-square displacements of the particles is calculated that appears to be an exponential distribution of which the decay length decreases with increasing degree of cross-linking. Although the scattering from the systems with probes is much higher than that of the matrix, we cannot neglect the gel scattering completely. We present theoretical expressions allowing corrections for gel scattering.

BASF Aktiengesellschaft

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Dispersionen

Contribution to Polymer Colloid Group Newsletter

The following paper has been presented at the 64th Colloid and Surface Science Symposium at Lehigh University and is published now in Makromol. Chem.

Makromol. Chem., Macromol. Symp. 35/36, 423–446 (1990)

INFLUENCE OF CHEMICAL HETEROGENEITY ON STRUCTURE AND PROPERTIES OF EMULSION COPOLYMERS

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Abstract: Wher comonomers of different hydrophilicity are copolymerized in emulsion polymerization, a heterogeneous distribution of the polar groups in the resulting latex can occur which is mainly caused by differences in the solubilities of the monomers as well as the polymerization products in the water and the polymer phase. By a combination of various methods, analytical ultracentrifugation of the latices, mechanical spectroscopy, tensile tests and electron microscopy of the latex films, the distribution of the polar groups in the latex, the structure of the latex particles, and the morphology and mechanical behaviour of the latex films have been studied. Films of emulsion copolymers in many cases show a very pronounced two-phase morphology consisting of the main polymer within the particles and a second hard phase which is concentrated in the interfaces and wedges between the original particles, forming a honeycomb-like continuous structure throughout the film which has a strong influence on the mechanical properties of the films. When emulsion copolymers are cross-linked via reactive monomers with a higher degree of hydrophilicity than the main monomers, structurized networks may result with a spatially inhomogeneous distribution of cross-links. Structure and properties of films from emulsion copolymers are determined by the polymer bulk properties as well as the multiphase structure.

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Single Particle Optical Sizing (SPOS)

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I. Design of an Improved SPOS Instrument and Application to Stable Dispersions

We describe an instrument for single particle optical sizing, based upon small angle light scattering by individual particles. A colloidal dispersion is hydrodynamically focused into a narrow stream of 5 μm width, which is illuminated over a length of 30 μm by a perpendicular laser beam with a constant intensity across this detection volume, using a specially designed elliptical optical focus. As the particles pass one-by-one through the detection volume. the light pulses are detected under a scattering angle of 5°. The signals are stored in a multichannel analyzer and electronically processed. This set-up enables one to measure accurately the particle size and particle size distribution of both stable and aggregating colloidal dispersions. In this paper, we give some illustrative results for stable systems.

II. Hydrodynamic Forces and Application to Aggregating Dispersions

The shear and extension forces occurring during the hydrodynamic focusing in our SPOS instrument which is described in the preceding paper (E. G. M. Pelssers, M. A. Cohen Stuart, and G. J. Fleer. *J. Colloid Interface Sci.* 137, 350 (1990)), are analyzed and compared with estimates for the binding forces between particles in salt coagulation and polymer flocculation. It is found that the hydrodynamic forces are several orders of magnitude smaller than these binding forces, so that the aggregate size distribution is not changed during the measurement. Also the additional orthokinetic aggregation in the apparatus is shown to be negligible. The aggregate size distribution of a coagulating dispersion could be monitored very accurately up to heptaplets. The intensity scattered under 5° by aggregates of latex particles of 350 nm radius is found to scale as $V^{1.70}$, where V is the (coalesced) volume of the aggregates. The coagulation of latex by salt follows the overall bimolecular kinetics as predicted by M. Von Smoluchowski (*Phys. Z.* 17, 557, 585 (1916) and *Z. Phys. Chem.* 92, 129 (1917)).

Sept 28, 1990

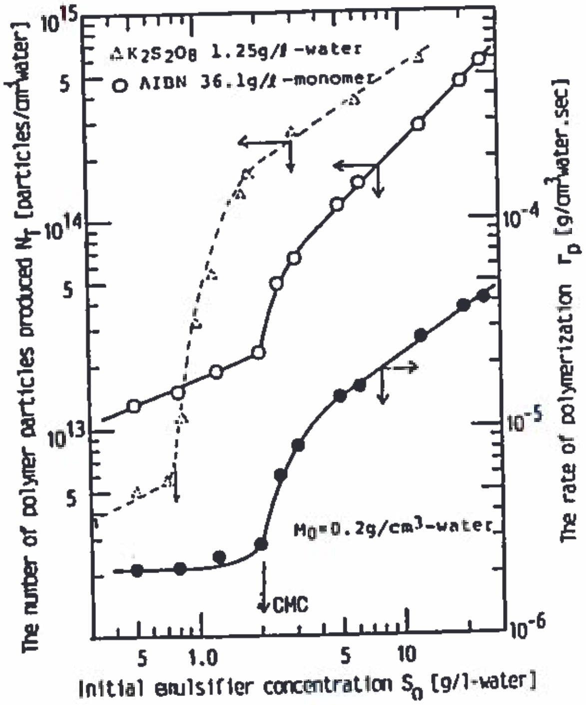
Contribution to Polymer Colloids Group Newsletter

by
Mamoru Nomura

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

As have been already announced, "International Symposium on Polymeric Microspheres" will be held in Fukui in Oct. 23(wed)-26(sat), 1991 under the auspices of the Ministry of Education, Japan and in cooperation with Lehigh University(EPI), McMaster University(MIPPT) and CNRS(LMO). First circular will be sent soon to all the members of the IPCG(International Polymer Colloids Group). We hope that many of the IPCG members will participate in this symposium. Those who are interested in attending this symposium, please contact the symposium secretariat, Mamoru Nomura.

A paper entitled "Kinetics and mechanism of emulsion polymerization initiated by oil-soluble initiators. 2. Kinetic behavior of styrene emulsion polymerization initiated by 2,2'-azoisobutyronitrile." was submitted for publication in J. Polymer Sci. Chem Ed. The aim of this paper is to clarify the general kinetic behavior of emulsion polymerization initiated by oil-soluble initiator. As a typical example, styrene emulsion polymerization initiated by AIBN was investigated thoroughly, examining the changes in the rate of polymerization and the number of polymer particles formed with changes in emulsifier(NaLS), initiator and monomer concentrations initially charged and the reaction temperature. It was shown from these experimental results that the kinetic behavior of this emulsion polymerization system is quite similar to that of styrene emulsion polymerization initiated by water-soluble initiator such as $K_2S_2O_8$. Fig. 1 shows the effect of initial emulsifier concentration on the rate of polymerization (o) and the number of polymer particles produced(o). Triangles( ) indicate the number of polymer particles produced when $K_2S_2O_8$ initiator is used in place of AIBN. In both cases, the number of polymer particles produced abruptly increase in the vicinity of the CMC. The literature value of the CMC of NaLS in the absence of electrolyte is 2.3 g/l-water(8mM). This can be taken as a good evidence that emulsifier micelles are important in particle formation.



KINETICS OF POLY(N-ISOPROPYLACRYLAMIDE) MICROGEL FORMATION

X.Wu, R.Pelton, D.Woods, A.Hamielec

Department of Chemical Engineering
McMaster University, Ont., Canada

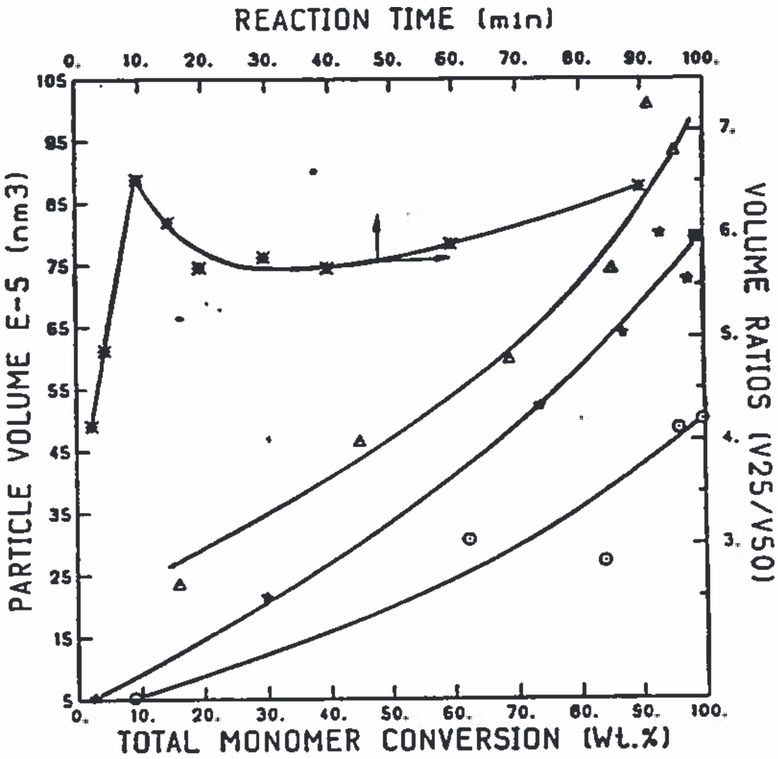
The heterogeneous polymerization of N-isopropylacrylamide (NIPAM) with or without N,N'-methylene bisacrylamide (BAM) were conducted in aqueous medium at the temperature above the LSCT of NIPAM polymers to find out the formation mechanism and the growth rate of the microgel particles and to investigate the kinetics of the polymerization. In the reaction, 10^{-3} M $K_2S_2O_8$ was used as initiator and 10^{-4} M sodium dodecyl sulfate as surfactant. The total monomer concentration was 10^{-1} M.

The monomer conversion was determined by high performance liquid chromatography and the particle size was measured by dynamic light scattering.

The total monomer conversion increasing with reaction time has a normal trend. No gel effect has been observed. The quicker consumption of BAM (monomer 2) implies its higher reactivity comparing with NIPAM (monomer 1).

The top curve of Fig.1 shows the change of particle volume ratio, the volume measured at 25 ^{0}C divided by that at 50 ^{0}C, with the reaction time. In the beginning, the ratio increases to a maximum. This may infer that BAM content in the polymer reduces due to the decrease of BAM monomer fraction. Thereafter, the decrease of the volume ratio may imply the formation of tighter cross-linking structure by consumption of the pendant double bonds. In the final stage, the increasing ratio may be caused by the connection of NIPAM only polymer chains on the particles since at this stage no BAM monomer has been left.

In contrast to the classical emulsion polymerization, the dependence of particle volumes on the monomer conversion was cubic rather than linear (See Fig.1, the bottom three curves). This along with the volume ratio results, suggest that particle density is a function of conversion. Experiments with a disk centrifuge will be used to test this.



DEPENDENCE OF VOLUME RATIOS OF POLYNIPAM GEL AT 25 °C TO 50 °C ON THE REACTION TIME

PARTICLE VOLUME VS MONOMER CONVERSION FOR POLYNIPAM GEL

⊙ = NL4 F20=0.0 POLYMERIZED AT 70 °C
△ = NL2 F20=0.068 POLYMERIZED AT 50 °C
✳,★ = NL1 F20=0.068 POLYMERIZED AT 70 °C

Contribution to Polymer Colloid Newsletter
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Minimum Stabilizer Chain Length For Steric Stabilization

Silicone-stabilized poly(methyl methacrylate), PMMA, latexes dispersed in heptane were reacted with acidified montmorillonite that randomly decomposed the steric barrier to the point of flocculation. The flocculated latex particles were isolated and the amount of silicone remaining in the steric barrier was determined by NMR. From these data the molecular weight distribution of the steric layer at the flocculation point was computed assuming that random silicone equilibration occurs for the poly(dimethyl siloxane) on the latex particle surfaces.

Three types of latexes were studied: 1) latex with silicone chains attached to the PMMA surface at one end; 2) latex with silicone chains attached at both ends; and, 3) latex with attachment points at one or more positions along the silicone chain.

The average silicone chain length at the point of flocculation, DP^{crit}, agreed with estimates based on Napper's "pragmatic expressions" for the potential energy of sterically stabilized particles. DP^{crit} was dependant upon two independent parameters - the number of silicone chains per unit surface area and the Flory Chi value. As expected, DP^{crit} decreased with increasing solvent quality (for silicone) and with increasing number of silicone chains per unit surface area.

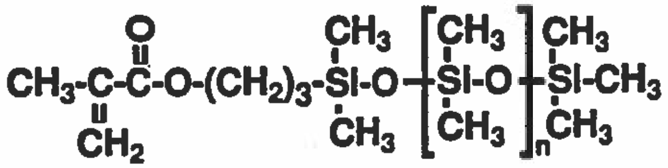
Typical results are shown for latex 81 on the following page. Figure 1 shows the silicone stabilizer precursor structure and Figure 2 shows the amount of silicone on the latex particles as a function of equilibration time. Particle size was monitored during these experiments with a Horbita sizer and the onset of flocculation was obvious and occurred between 72 and 74 hours of equilibration.

Approximately 2/3 of the silicone could not be removed from the latex after very long equilibration times. This, we believe, is a result of buried silicone which complicates our interpretation. Assuming that only surface silicone is attacked by the dispersed montmorillonite catalyst then the amount silicone on the surface at the flocculation point, DP^{crit}, was computed from the experimental data in Figure 2 and is shown in Figure 3 (squares) as a function of the assumed initial fraction of silicone on the particle surface (i.e. not buried).

The other curve in Figure 3 was computed from Napper's constant segment density equations (12.44 to 12.46 in his book) assuming a secondary minimum of > 10 kT leads to flocculation. The computed curve in Figure 3 is a weak function of the fraction of surface silicone because the greater this parameter, the more silicone chains per unit surface area.

Figure 1

Stabilizer:



$$CH_3\text{-}\underset{\underset{CH_2}{\parallel}}{C}\text{-}\overset{\overset{O}{\parallel}}{C}\text{-}O\text{-}(CH_2)_3\text{-}\underset{CH_3}{\overset{CH_3}{Si}}\text{-}O\text{-}\left[\underset{CH_3}{\overset{CH_3}{Si}}\text{-}O\right]_n\text{-}\underset{CH_3}{\overset{CH_3}{Si}}\text{-}CH_3$$

MW 38,000

Latex: diameter 1.13mm, SD 0.4mm

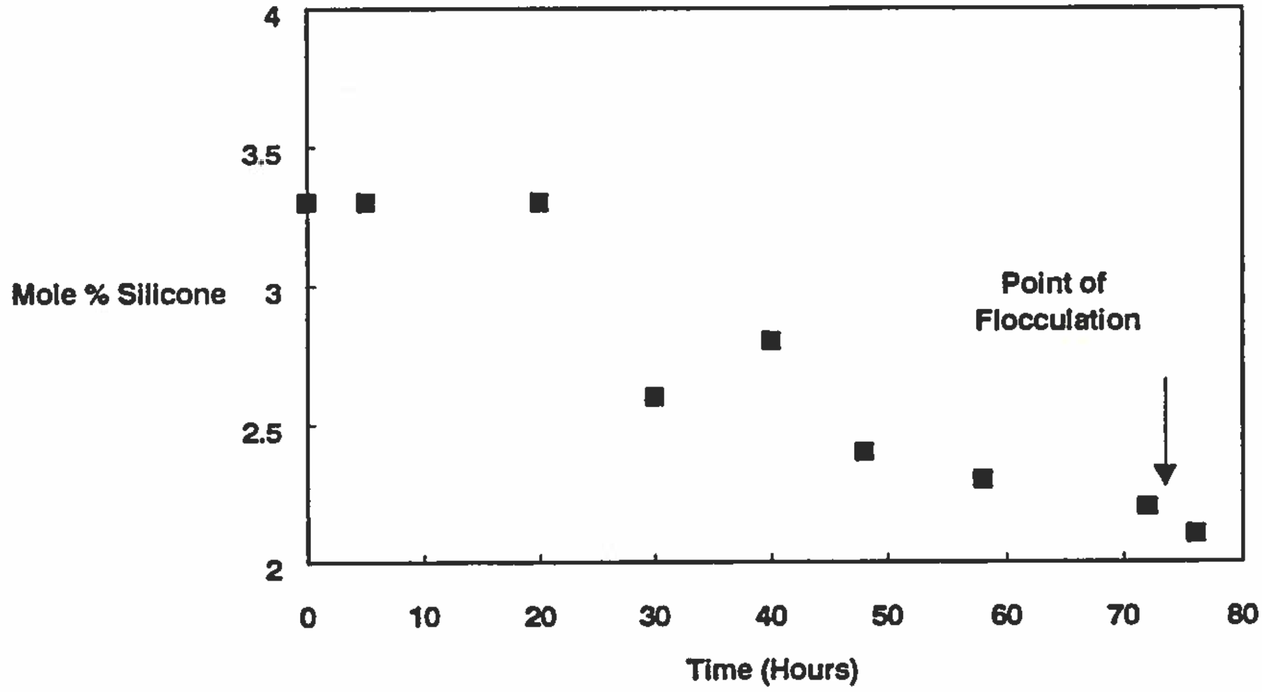


Figure 2

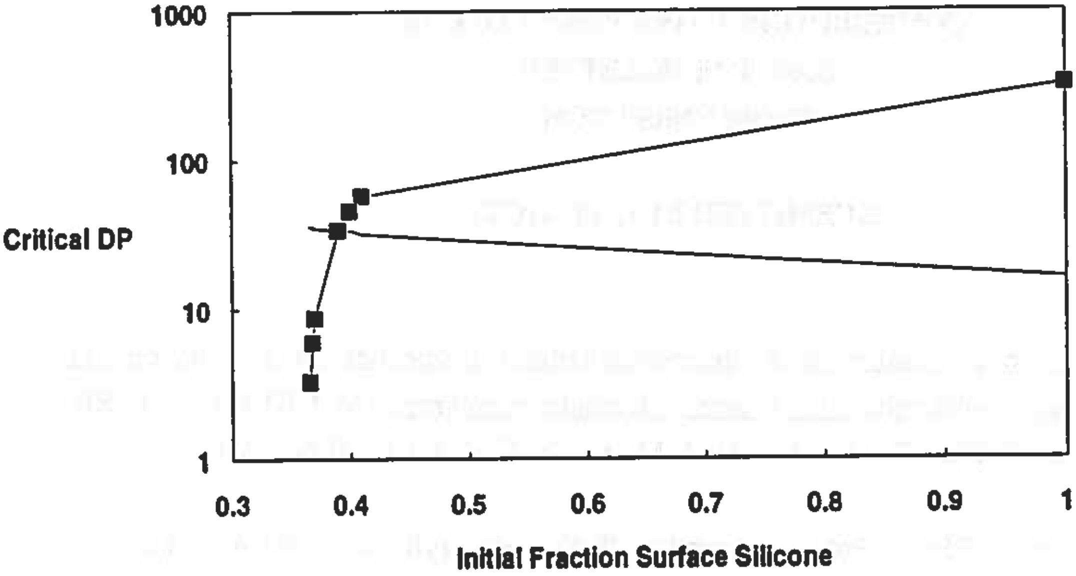

1000
100
10
1
Critical DP
0.3
0.4
0.5
0.6
0.7
0.8
0.9
1
Initial Fraction Surface Silicone

Figure 3

CONTRIBUTION TO POLYMER COLLOID
GROUP NEWSLETTER
FROM CNRS/LYON

(SUBMITTED BY C. PICHOT)

* Studies on the preparation and thermomechanical properties of polystyrene (1) / polybutylacrylate-methacrylic acid (2) core-shell emulsion polymers (M. HIDALGO - L. RIOS - C. PICHOT - J. GUILLOT - A. GUYOT (L.M.O.) J.Y. CAVAILLE (I.N.S.A.)

Polystyrene (PS) (1)/Poly(butylacrylate (BA)-methacrylic acid (MAA) (2) composite latexes have been prepared through a two-stage emulsion polymerization process using monodisperse polystyrene latex seed (118 nm) and different BA/MAA ratios. The amount of MAA in the shell copolymer was found to be the main factor controlling the particle shape and morphology. The shape of the structured particles was generally non sphrerical and the shape irregularities increased as a function of reaction time. At the beginning of the second stage reaction, new small particles were observed, which coalesced onto the PS seed as the polymerization proceeded. The distribution of the MAA groups in the latex particles and in the serum was analysed by alkali-back-acid titration using ionic exchanged latexes. No MAA groups were detected in the latex serum. Due to the low Tg of the BA-MAA copolymers, alkali conductimetric titrations accounted for all the MAA groups on and within the polymer particles.

Further study was then investigated on the thermomechanical behavior of films cast from these latexes, using differential thermal analysis and dynamic mechanical spectrometry working in the temperature range from 100°K to 700°K, and comparison was made with analogous unfunctionalized PS/PBA systems. It was found a strong effect of MAA upon the phase arrangement in the film, the evolution of which as a result of annealing being dependent on the heat treatment conditions (see figure). The thermomechanical behavior of films was related to the structural features of the corresponding latexes and simulation techniques were used in order to provide a mechanistic support to these relations.

(two papers to be submitted)

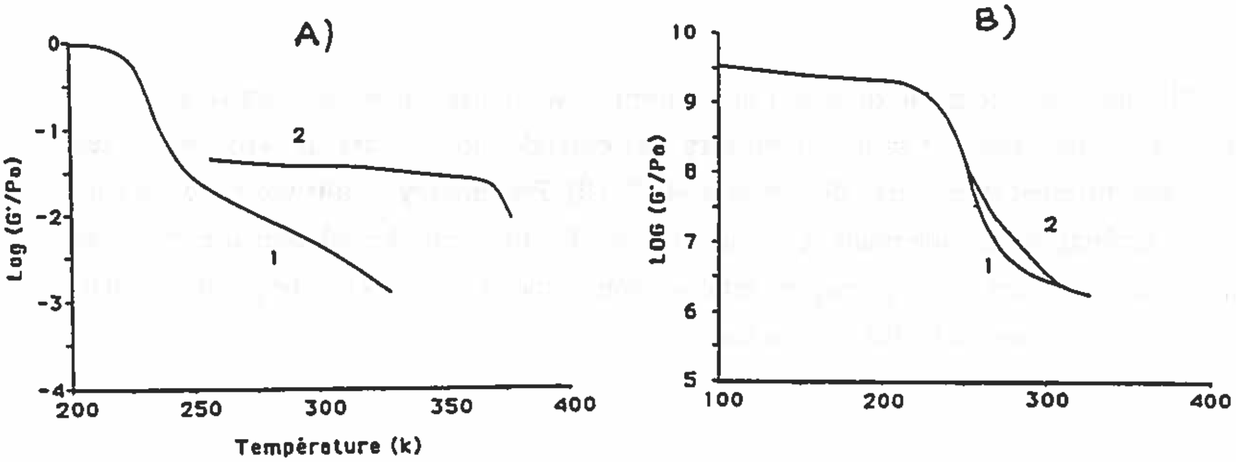


Figure : Effect of methacrylic acid (MAA) on the storage shear moldulus (G') of core-shall styrene (1) - butyl acrylate copolymers (2) latex films.

A) without MAA ; B) with MAA (5 wt %) ;

1) Curve 1 : befor annealing ; 2) curve 2 : after annealing (140°C/3H.)

* Kinetic and colloidal studies in emulsion (Co)polymerization of 2-ethyl hexyl acrylate (T. DESROCHES-LMO).

More data have been collected on the emulsion polymerization kinetic behavior of 2-ethyl hexyl acrylate (EHA) for which, the propagation rate constant (kp) has been found lower than for acrylates having lower alkyl group. Owing to a UV method allowing to harden the low-Tg polymer particles transmission electron microscopy could have been applied on the latexes, in order to examine the particle size distribution as a function of conversion : results clearly evidence that coagulative nucleation mechanism is operative with this monomer under the selected conditions. However in some cases, the presence of a second population of small particles is observed even at high conversion, what indicates a complex process of particle formation and growth.

* Studies on the stabilizing properties of zwitterionic emulsifiers (M.F. LLAURO - H. ESSADDAM - LMO).

More work has been developed mainly with the purpose to explain the strong adsorption energy displayed by two sulfobetaines(having different intercharge distance and structure) at the polymer particle interface. A ^{13}C.NMR study is being curently investigated on micellar solutions of these surfactants in the presence of compounds having or not an aromatic group.

The study on the mode of action of zwitterions when used as surface active agents in emulsion polymerization or as poststabilizers was extended to the case of carboxybetaïnes having three different intercharge distances (n=1, 3, 10). Preliminary results seem to indicate that these surfactants provide much less colloidal stabilization than the sulfobetaïne, however when used under moderate or high concentrations, monodisperse particles can be produced up to 35 nm (as already reported by KATO for n=1).

* Preparation and characterization of polystyrene latex particles having surface aldehyde groups (B. CHARLEUX - Unité mixte CNRS/BioMérieux).

Monodisperse polymer latexes bearing surface-CHO-groups have been prepared through a two -step process, comprising first a soap-free emulsion polymerization of styrene using potassium persulfate as an initiator, secondly a surface functionalization by copolymerization of various amounts of para-formylstyrene either by a "shot" process or by post polymerization on the polystyrene seed particles.

A preliminary study was investigated on the kinetics of solution copolymerization of the binary system styrene(1)/para-formylstyrene(2) so as to determine the reactivity ratios (r1=0.2;r2=2.9) and the copolymer microstructure.Moreover soap-free polymerization of p-formylstyrene has been found more rapid than for styrene then ensuring efficient surface polymerization when using two-step processes .

Final latexes were characterized with respect to conversion, composition and particles size and distribution using Transmission Electron Microscopy and Quasi Elastic Light Scattering methods. Particular attention was paid to the surface characterization of the polymer particles, especially to evaluate the amount of aldehyde groups covalently bound the surface in comparison with a poly-p-formylstyrene latex prepared under the same soap-free conditions used as a model. Various analytical methods were investigated such as ESCA, aldehyde reduction by labelled sodium borohydride followed by radioactivity measurements or reaction of the aldehyde groups with a labelled amine compound.

(Two papers to be submitted).

RECENT PAPERS

Emulsifier-free emulsion copolymerization of styrene and butyl acrylate, I. Kinetic study in the absence of emulsifier. J.L. GUILLAUME - C. PICHOT - J. GUILLOT - J. Polym. Sci., Part A, 28 (1), 110 (1990).

Emulsifier-free emulsion copolymerization of styrene and butyl acrylate. I. Kinetic study in the presence of a surface active comonomer acrylamidoundecanoic acid. J.L. GUILLAUME - C. PICHOT - J. GUILLOT - J. Polym. Sci., **Part A**, 28 (1), 137 (1990).

Ordering of latex particles during film formation . M. JOANICOT - K. WONG - J. MAQUET - Y. CHEVALIER - C. PICHOT - C. GRAILLAT - P. LINDNER - L. RIOS - C. CABANE - Prog. Colloid. Polymer. Sci., 81, 195 (1990).

Papers in Die Makromol. Chem. Macromol. Symp., Second International Symposium on Copolymerization and copolymers in dispersed media, Lyon, Vol 35/36, (1990) :

- Modelling and simulation of emulsion copolymerization of monomers of different polarities. Relationships kinetics - microstrucure - properties. J. GUILLOT - p 269.

- Recent developments in the functionalization of latex particles - C. PICHOT, p. 327.

- Synthesis of reactive latexes by copolymerization of methyl acrylamidoglycolate methyl ether (MAGME) with styrene and butyl acrylate. J GUILLOT - S. MAGNET, p. 367.

- Dielectric characterization of latex suspensions by microwave spectroscopy using mixture laws. R. DAVID - F. HENRY - C. PICHOT, p. 381

- Batch emulsion copolymers of styrene with ethyl acrylate : microstructure and glass transition temperature. S. DJEKHABA - J. GUILLOT. Europ. Polym. J., **26**, 9, p . 1017 (1990)

THESIS :

- Kinetic study of emulsion polymerization of 2-ethyl hexyl acrylate. Copolymerization with styrene and methyl methacrylate.
(T. DESROCHES). Universiy of LYON - Oct. 1990.

- Thermodynamic and kinetic study of styrene-acrylonitrile copolymerization onto polybutadiene latexes.
(P. MATHEY-MULLER). University of LYON. Oct. 1990.

Newsletter Contribution from The University of Akron

by I. Piirma
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Copolymerization of Butadiene and Acrylonitrile

Report from Sam Laferty

A study was carried out to evaluate what effect the butadiene-acrylonitrile seed latex properties have on the subsequent grafting of acrylonitrile-methyl acrylate to the copolymer in the seed particle. It was found that the most important factor was the gel content of the seed latex. This finding, in turn, led to experiments which would pinpoint the variables affecting the gel formation. A polymerization recipe with AIBN as the initiator at 50°C and t-dodecyl mercaptan at concentration of 0.77g/100g of monomers resulted in latices which at approximately 90% conversion contained only 2% gel. This gel content was found to increase rapidly with aging unless hydroquinone was added to stop further free radical processes which led to crosslinking. Since the presence of hydroquinone in the seed latex would completely hinder any further polymerization, the grafting reactions had to be carried out without the inhibitor, which in turn created great variations in the gel content of the latex due to its unavoidable exposure to traces of oxygen and other, yet unknown, factors.

A preliminary study of the grafting reaction with latices with two different crosslink densities, one latex carelessly exposed to air and the other with 2% gel was carried out. Acrylonitrile and methyl acrylate were added to the seed latex and polymerized. The morphology of the resulting latex particles was studied with transmission electron microscopy. It was observed that the gel content and crosslink density greatly affected the morphology of the new particles. With the high crosslink density latices very definite phase boundaries were apparent in the osmium tetroxide stained acorn shaped particles. The dark colored seed particles being the core with the poly(acrylonitrile-co-methyl acrylate) cap. When a seed latex with much lower crosslink density was used, the particles had hardly any visible exposed dark seed core, the particles were almost completely covered with the new copolymer.

Polymerization of Single Phase Microemulsions

H. Michael Cheung*, Mohan Sasthav, and Raj Wallajapet

We are investigating polymerization of several single phase microemulsions for the purpose of producing microstructured polymer solids (as opposed to latex). The systems we are currently studying utilize methyl methacrylate and acrylic acid as the polymerizable elements in combination with an aqueous phase. Single phase microemulsions can be formed over a fairly wide composition range both with and without surfactant (we're using sodium dodecyl sulfate at present). The microemulsions have been characterized using conductivity, thermal, and viscosity measurements. Both the conventional and surfactantless systems show evidence of bicontinuity. We have begun utilizing QELS and static scattering to further characterize the precursor microemulsions. Ultraviolet polymerization is performed in a temperature controlled photoreactor to produce both thin films (200 micron thickness) and "bulk" solid polymer. SEM examination shows evidence of microstructuring on a submicron to few micron length scale. The method of drying (removing the aqueous phase after polymerization) appears to have a significant effect on the final microstructure of the polymer. Supercritical carbon dioxide drying and freeze vacuum drying produce a more open microstructure than conventional low temperature (50 deg. Centigrade) oven drying. Efforts are underway to quantify this difference using BET surface area and flow porosity measurements. It is our hope to eventually be able to correlate the precursor microemulsion structure and the final polymer microstructure.

*Associate Professor Chemical Engineering

Recent Publications

"Synthesis of Poly(methyl methacrylate)-graft-polyoxyethylene for Use as a Polymeric Surfactant in the Emulsion Polymerization of Methyl Methacrylate", Polymer Latex III Conference publication by P.R.I. London 1989, G. Jialanella and I. Piirma

"Colloids", Encyclopedia of Polym. Sci. and Eng., Supplement Volume, 2nd Ed., page 123-129, 1989, Wiley & Sons, Inc., I. Piirma

"Preparation of a Water Soluble Polyester Surfactant and its Use in the Emulsion Polymerization of Styrene", Polym., Bulletin 23, 367-371 (1990) T. McCartney and I. Piirma

"Polymeric Surfactants in Emulsion Polymerization", Macromol. Chem., Macromol. Symp. 35/36, 467-475 (1990) I. Piirma

Faxed and sent by Airmail 9/26/90

Contribution to the Polymer Colloids Group Newsletter
Autumn 1990

Magic-Angle Carbon-13 Nuclear Magnetic Resonance Analysis of Polybutadiene - Poly(methyl methacrylate) Core-Shell Latex

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High resolution solid state NMR has been developped during the last years as a powerful tool for the structural analysis of polymer blends, including compatible systems, as well as two-phase materials (1 - 11). Especially as shown by SCHAEFER et all (12), ^{13}C high resolution NMR can be used to determine the spin-lattice relaxation times $T_1\ \rho\ (H)$ of the protons in the rotating frame, which leads to interesting conclusions regarding the microscopic structures and dynamics in polymer blends.

These NMR techniques have not yet been applied, to our knowledge, in order to study polymer latex particles, such as a core-shell latex.

In this paper we report the application of the cross polarization technique in order to characterize polybutadiene (PBut) - poly(methyl methacrylate) PMMA, having a PBut core and a shell with different amounts of PMMA. Such a latex with an elastomer core and a thermoplastic shell is of practical importance as "impact improver" for various thermoplastics (13, 14).

The determination of the spin-lattice relaxation times $T_1\ \rho\ (H)$, determined at various contact times, could therefore be useful to determine the two-phase characterics and the interphase of two incompatible polymers, e.g. PBut and PMMA, in a core-shell latex.

Experimental

The PBut latex, as starting material, has kindly been supplied by ROHM-HAAS. It has an average particle size of 55.5 nm. A latex of PMMA homopolymer, with an average particle size of 63.2 nm, is obtained by emulsion polymerization in a batch process at 60°C.

The different samples of core-shell latex are prepared either in a batch or in a semicontinuous process at 60°C, by adding MMA monomer to the PBut seed latex. $K_2S_2O_8$ was used in all cases as initiator.

The size of the latex particles determined by photon correlation spectroscopy (Coulter N4) is given in Table 1 as a function of the PMMA content. Therefore all samples have the same PBut core and different thicknesses for the PMMA shell.

weight percent of PMMA	0	15	30	40	57	57 (batch)	75	100
particle size (nm)	55.5±3.0	55.7±2.9	64.4±1.0	65.1±2.5	74.3±0.8	71.4±0.3	87.9±1.0	63.2±0.5

table 1. particle size (weight average) of P(But)-PMMA latex samples

The latex samples are then precipitated with a solution of concentrated sodium chloride, filtered, washed with distilled water and finally dried under vacuum at room temperature. The blend of PBut and PMMA is obtained in a similar way by coprecipitation of both types of latex.

About 200 mg of powder were packed in 7 mm Zirconia spinners with Kel-F caps and were spun at the magic angle at 3.7 kHz. Solid-state ^{13}C-NMR cross polarization, proton dipolar decoupling and magic-angle spinning (CP/DD/MAS). NMR experiments were performed at 75.47 MHz on a BRUKER MSL 300 spectrometer. Depending upon sample composition, 200-400 scans were necessary per contact time value for a satisfactory signal-to-noise ratio. All spectra were obtained at a temperature of 20°C.

The cross polarization pulse sequence used in the experiments is shown in Figure 1. The matched spin-lock cross polarization transfers employed ^{13}C and ^{1}H magnetic field strengths of 34 kHz. Contact times from 2 ms to 24 ms were used and delays between scans (recycle time) were 2.5 s.

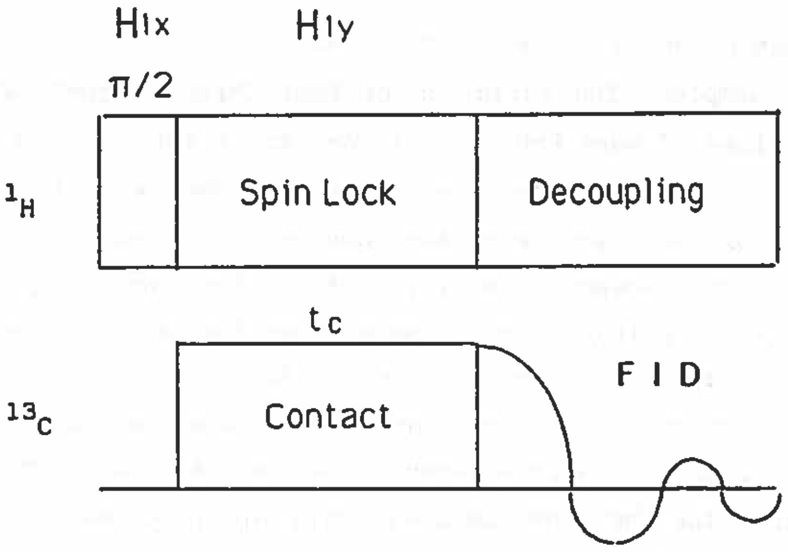

fig 1: The cross polarization pulse sequence used in the experiments

Results and discussion

The solid-state ^{13}C NMR spectra of PMMA is shown in Figure 2. The main features are the peaks due to the α-methyl carbon (C_9) at 15-27 ppm, the quaternary carbon (C_6) at 48 ppm, the methoxy (C_5) at 55 ppm, and the carbonyl (C_1) at 172 ppm. The methylene carbon peak is a broad underlying peak at 45-60 ppm.

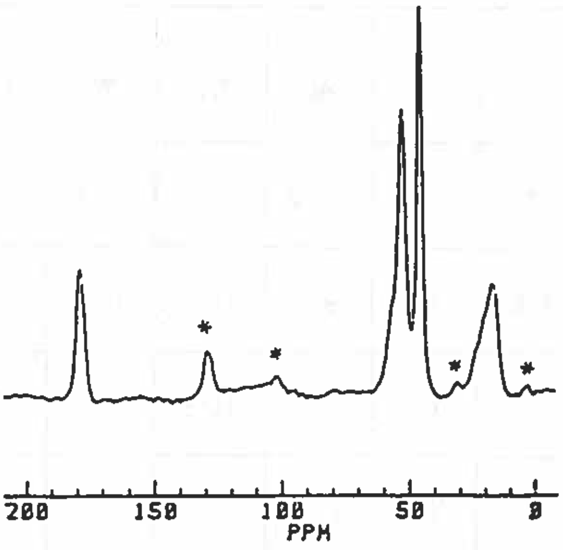

Fig 2:Solid-state 13C NMR spectrum of poly(methyl methacrylate).
The asterisks indicate peaks due to spinning sidebands

Cross polarization experiments with various contact times were made on the differents samples. The variation of PMMA Carbon magnetisation as a function of the contact time of pure PMMA and of core-shell latex samples of various composition is shown in Figure 3 for the carbon C_6. The relaxation time T_1 ρ (H) is obtained by taking the negative of the inverse of the slope (-1/slope). Duplicate experiments have shown reproducibility of ± 1 % for carbons C_5, C_6 and C_1 and ± 10 % for carbon C_9. T_1 ρ (H) values so determined for the different protons attached to chemically different carbons are listed in Table 2. Because of the spin-diffusion phenomena, this parameters are averaged and differences in the values obtained from the various carbon lines of the pure PMMA is lower than 5 % (2). This is true for the other samples. This in an extreme case where the protons are closely coupled by rapid spin-spin exchange through dipole-dipole interactions. If the different protons are not in contact on a sufficient distance, each of them would have its own characteristic relaxation times.

For all the other samples, the carbons C_1, C_5, C_6 and C_9 of PMMA show identical trends in their relaxation time dependance on composition ratio. In fact the decreasing T_1 ρ (H) values with decrease of weight fraction PMMA in the core-shell latex samples is due to the increasing amount of PMMA at the interface with respect to the total amount of PMMA. The main reason of this decreasing in T_1 ρ (H) or increasing mobility of PMMA in the core-shell samples is that PMMA protons have either direct dipole interactions with P(But) nuclei or have sufficient P(But) near-neighbours to alter the molecular motion of PMMA (2).

weight percent of PMMA	15	30	40	57	75	100	57 (batch)	57 (blend)
C1 (172 ppm)	*	8.7	10.2	11.5	13.5	14.3	12.6	15.0
C5 (55 ppm)	6.6	7.9	9.1	10.4	12.1	13.8	11.4	13.8
C6 (48 ppm)	5.9	7.7	9.1	10.4	11.8	13.6	11.2	13.2
C9 (15-27 ppm)	*	9.6	11.4	12.0	13.1	14.4	12.3	15.0

table 2. relaxation times $T_1\rho$(H) (ms) of differents samples with variable composition of PMMA
* no quantitative signal intensity

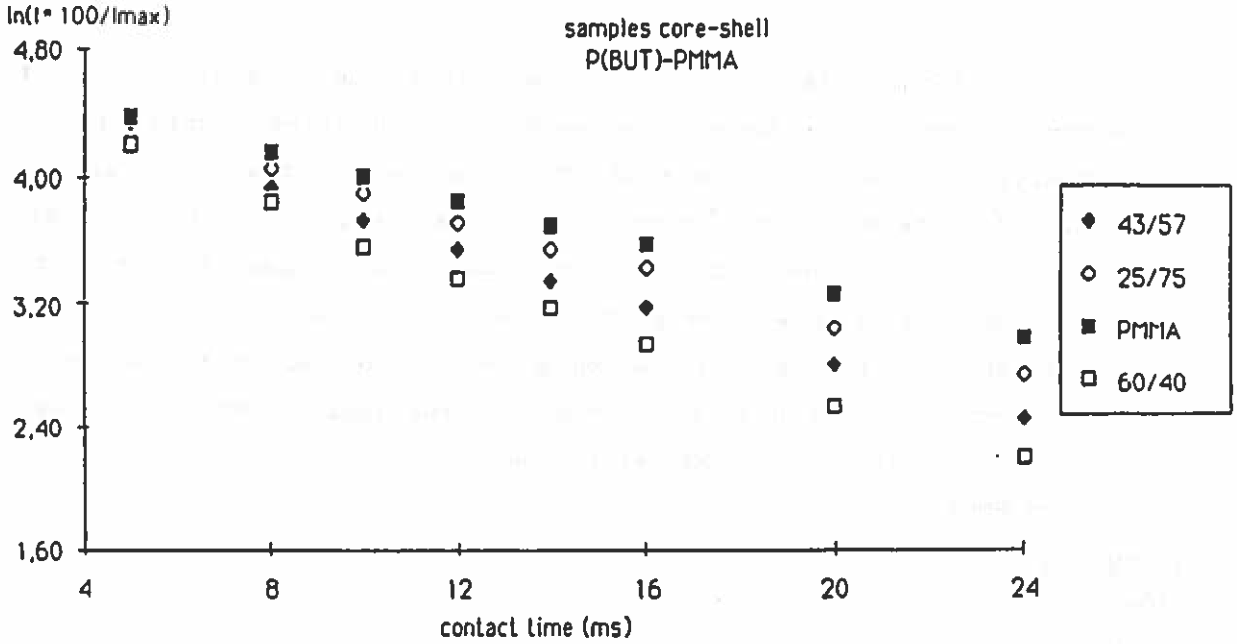

Fig. 3 :Natural logarithm of peak intensities of the carbon resonances of PMMA scaled to the maximum intensity versus cross polarization contact time for various compositions of samples core-shell

It is interesting to note that a straight line is obtained with correlation coefficient of 0.9974 for PMMA content between 15 and 100 % Figure 4.

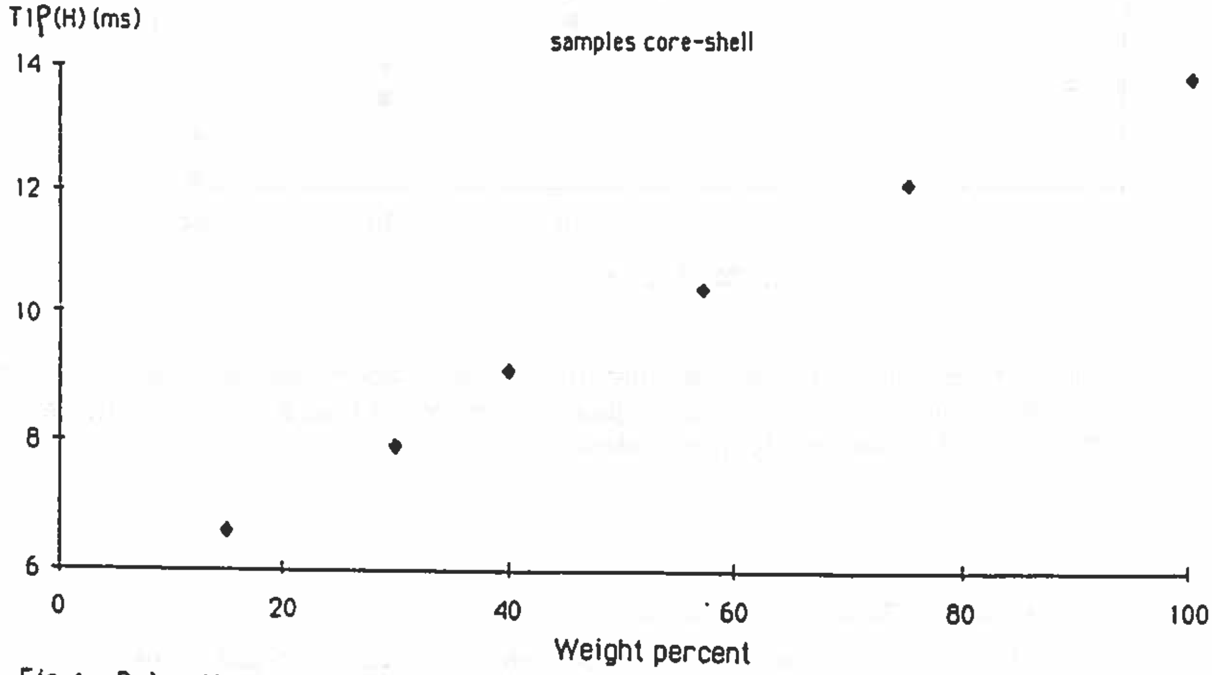

Fig. 4 : Relaxation time T1ρ(H) of the quaternary carbon (C6) versus weight fraction of PMMA

From Table 2 it also appears that the relaxation time for a given carbon depends on the preparation method of the latex sample. Thus, for a same composition (57 weight percent of PMMA), we notice that the relaxation time is highest for the blend and lowest for the sample prepared by the semi-continuous procedure. For the sample prepared by a batch technique, the relaxation time has an intermediate value with respect to the two previous ones. This behaviour which is also shown in Figure 5 can be explained by the fact that the fraction of PMMA in the interphase seems to be highest for the latex "semi-continuous" and lowest for the latex blend. The PMMA relaxation times for the blend are the same as those of pure PMMA.

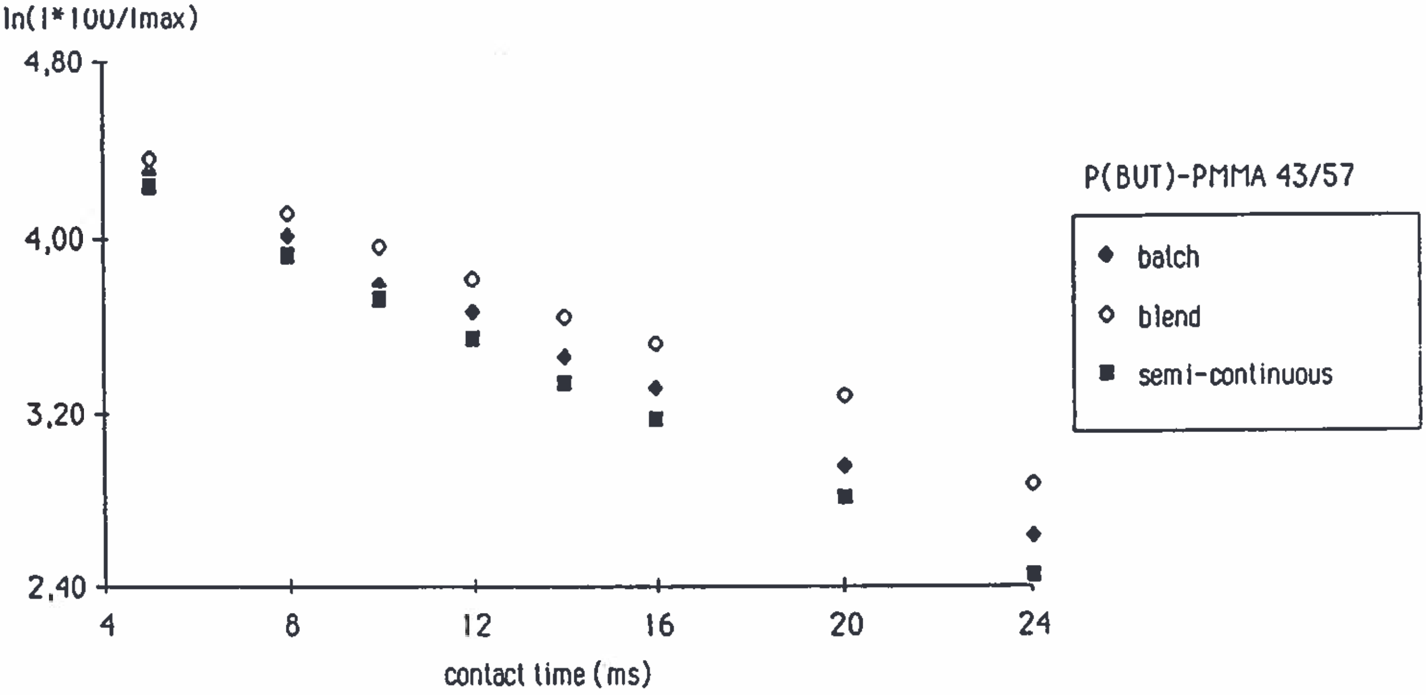

Fig. 5 : Natural logarithm of peak intensities of the carbon resonances of PMMA scaled to the maximum intensity versus cross polarization contact time according to different methods of the latex samples preparation

References

1) R.A. GRINSTED and J.L. KOENIG
J. Polymer Sci., Part B : Polymer Physics, 28, 177-188 (1990)

2) P. TEKELY, F. LAUPRETRE and L. MONNERIE
Polymer, 26, 1081 (1985)

3) D.C. DOUGLASS and V.J. Mc BRIERTY
Macromolecules, 11, 766 (1978)

4) T.C. WARD and T.S. LIN
Adv. Chem. Ser., 206, 59 (1984)

5) F.A. BOVEY, F.C. SCHILLING, T.K. KWEI and H.L. FRISCH
Macromolecules, 10, 599 (1977)

6) E.O. STEJSKAL, J. SCHAEFER, M.D. SEFCIK and R.A. Mc KAY
Macromolecules, 14, 275 (1981)

7) T. NISHI, T.T. WANG and T.K. KWEI
Macromolecules, 8, 227 (1975)

8) V.J. Mc BRIERTY, D.C. DOUGLASS, T.K. KWEI and H.L. FRISCH
Macromolecules, 11, 1265 (1978)

9) L. C. DICKINSON, HSINJIN YANG, C.W. CHU, R.S. STEIN and J.C.W. CHEIN
Macromolecules, 20, 1757-1760 (1987)

10) D.G. CORY, F.C. de BOERAND and W.S. VEEMAN
Macromolecules, 22, 1618-1621 (1989)

11) J. SCHAEFER, M.D. SEFCIK, E.O. STEJSKAL and R.A. Mc KAY
Macromolecules, 14, 188-192 (1981)

12) J. SCHAEFER, E.O. STEJSKAL and R. BRUCHDAHL
Macromolecules, 10, 384 (1977)

13) W.H. GIFT
U.S. Patent, 4.341.883 (1982)

14) G.H. HOFMANN
U.S. Patent, 4.180.529 (1979)

IPCG Newsletter Contribution
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University of New Hampshire
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Donald C. Sundberg
September, 1990

Morphology Development in Emulsion Polymers

We have continued to apply our equilibrium, interfacial free energy concepts to the subject of morphology control of emulsion polymer particles by extending our previous analyses to take into consideration the influence of monomer (or solvent). Although the equations which allow the computation of the interfacial energies of the various morphologies remain unchanged from our previous analysis, all of the interfacial tensions are markedly affected by the presence of monomer or solvent. Beyond that, the volumes of the two phases within the particle change throughout the process and the equilibrium compositions of those phases charge as well. We have submitted for publication a series of papers on this subject which addresses the impact of the monomer (in synthetic latices) and solvent (in artificial latices) on the conversion dependent morphology of emulsion polymers. Specific attention is given to the prediction of phase equilibria, interfacial tensions between the polymer (solution) phases and water (with surfactant), and interfacial tensions between the two polymer (solution) phases themselves. It has been found that the presence of monomer (or solvent) can dramatically change the interfacial tensions (as compared to those for monomer-free polymers) and that such changes often lead to the condition that the interfacial free energies of two or more morphologies are quite close in value during a portion of the process (polymerization reaction or solvent removal). This gives rise to the thought that two or more morphologies may be found at the same time during the early part of the process, or that there may be a change in the morphology of the particles during this period. More likely, however, our calculations suggest that the possibility of finding occluded structures (incompletely phase separated core-shell, hemisphere, etc., morphologies) should be reasonably high, especially in synthetic latices.

Another of our projects of possible interest to the IPCG is that concerned with three component emulsion polymer particles. We have extended our morphology predictions and experiments to this area and find, as expected, that a new variety of morphologies must be considered. These would include core-shell-shell (six possibilities), sandwiches (3 possibilities), tri-sectional (three lobed, semi-spherical particles), "hemi-shell" (a single core surrounded by a two phase hemisphere-3 possibilities) and "hemi-core" (a two phase hemisphere surrounded by a single shell-3 possibilities). Via the artificial latex route we have produced tri-sectional and hemi-core particles while working with a couple of different systems. As previously seen in our work on two component emulsion particles, the effect of the surfactant can be important in determining the ultimate morphology of the three component particles as well.

Graft Copolymerization Studies

In collaboration with Gary Poehlein at Georgia Tech, the UNH group is involved in a fundamental study of free radical grafting in solution, bulk and emulsion polymerization systems. Current activities involve the production of well characterized, low molecular weight backbone polymers via solution polymerization to be used in graft solution polymerization. These graft copolymers are being used to investigate new analytical methods of measuring graft site frequency along the backbone polymer chain. Kinetic modeling and experimentation in solution polymerization will be used to develop reliable values for the rate constants involved in the grafting reactions and these subsequently used in the emulsion polymerization studies.

Microencapsulation for Sustained Release Coatings

The UNH Polymer Research Group is involved with a marine biosurfaces research effort to develop new, antifouling coatings. Among other techniques, microencapsulation of potential fouling inhibitors is being pursued within our group. The encapsulation process is done in a water emulsion and the control of the microcapsule structure has many parallels to morphology control in emulsion polymers. Sustained release of certain inhibitors from the microcapsule depends to a large extent upon the morphology of the particle and the specific microphase characteristics of the polymer(s) surrounding the inhibitor. Release rates are determined from the microcapsules themselves and also as they are incorporated within a polymer matrix to form a coating. Release rates of the order of magnitude of $25 \mu g/day, cm^2$ of coating are required for marine applications.

CONTRIBUTIONS TO THE
INTERNATIONAL POLYMER COLLOIDS GROUP NEWSLETTER
IPOC Polymer Colloid Research:

"Modeling particle coalescence phenomena during the emulsion polymerization of vinyl chloride"

Klaus Tauer

After the particles have been formed their further fate depends on the polymerization conditions. The classical case that, after particle formation, their number remains unchanged during further polymerization, does not apply in general.In order to prove the validity of the HANSEN-UGELSTAD model for the very first stage of the vinyl chloride emulsion polymerization experimental investigations have been performed. Unexpectedly, we observed a rapid decrease in the number of particles from the very beginning of the reaction in batch reactors on laboratory scale [1]. Figure 1 shows a particle number/time curve for polymerization measured under our standard condition, e.g. at an initial emulsifier concentration being sufficiently above the critical micelle concentration.
Although we investigated a wide variety of polymerization conditions a particle number maximum has never been observed. It could only be detected by combining experimental data for the rate of polymerization and the increasing particle diameter with model assumptions [2]. The decrease in the number of particles in experiments was observed both below and above the critical micelle concentration. Further on the experimental results [1] clearly show that the drop in the particle number only takes place in a polymerizing (living) system. If the polymerization stops the decrease in the particle number stops, too. In view of the possible importance of these findings a quantitative treatment together with a theoretical explanation will be tried. We interpret the observed decrease in the particle concentration as a coalescence process. This means that two particles flow together to form a new spherical particle. A quantitative treatment of the experimental data is possible in the following manner.

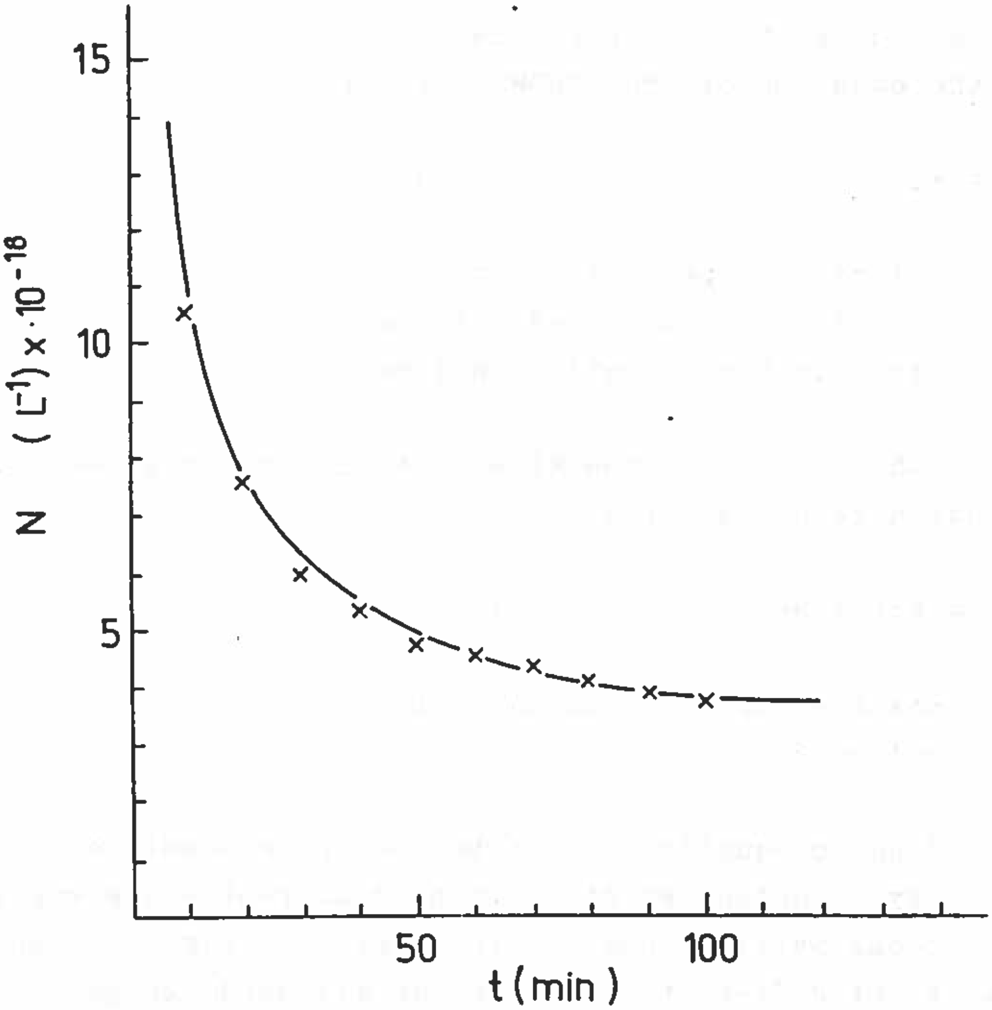

Fig. 1 Particle/number time curve for a discontinuous emulsion polymerization of vinyl chloride under standard conditions

The velocity of a two-particle contact is calculated according to the equation of SMOLUCHOWSKI (1) [3].

$$r_c = k_c N^2 \qquad (1)$$

r_c - velocity of particle contact, mol cm^{-3} s^{-1}
k_c - velocity constant, cm^3 mol^{-1} s^{-1}
N - particle concentration, mol cm^{-3}

From this equation the kinetic time law for a second order reaction is derived (2).

$$N^{-1} = k_c t + N_0^{-1} \qquad (2)$$

N_0 - maximum particle concentration
mol cm^{-3}

According to equation (2) it is therefore possible to obtain the velocity constant kc directly by differentiating experimental reciprocal particle number/time curves . Figure 2 shows the result of differentiation for our standard recipe. It can be clearly seen that the value for kc is not constant from the beginning. For reaction times longer than 100 minutes nearly constant values have been obtained. This result shows that the mere number of particle contacts alone is not sufficient for the description of the particle decrease. It is obviously that beside the closest possible distance between the particles under reaction conditions there must be another process initiating the coalescence. In agreement with the experimental results that the decrease in the particle number only occurs in a polymerizing system we are assuming that the radical desorption out of a particle is the coalescence initiating process. The quantitative treatment of the desorption-initiated coalescence goes on in the following manner.

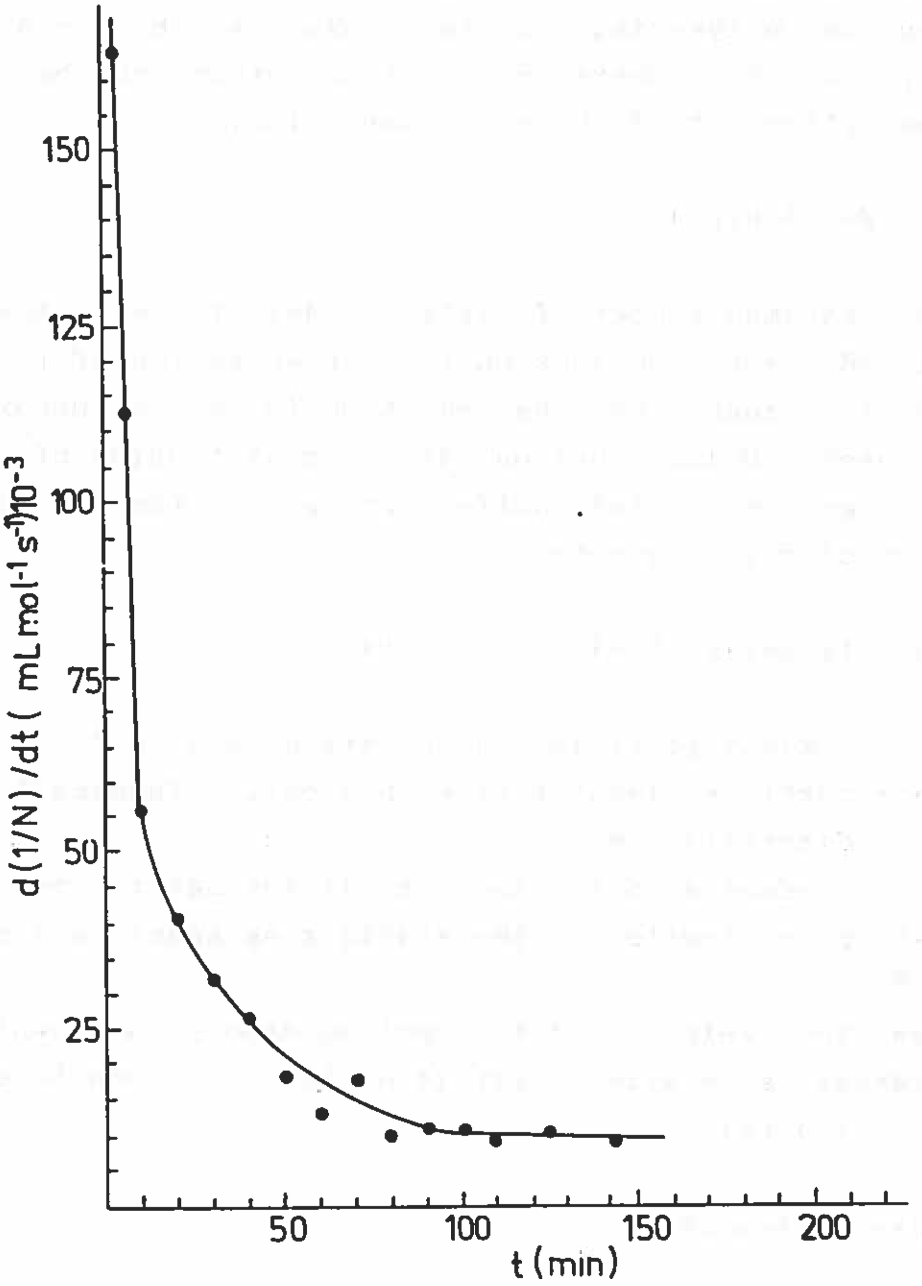

Fig. 2 Differentiated reciprocal particle/number time curve according to Figure 1

The mean number of radicals at the very beginning of a VC emulsion polymerization can be expressed by a reduced UGELSTAD formula (3), where $\bar{n}$ is mainly determined by the radical desorption out of the small particles.

$$\bar{n} = N^{-0.5}(k_2 D^2)^{0.5} \qquad (3)$$

The maximum number of particles detectable in the above mentioned manner depends on the concentration of the stabilizing agent in such a way that equation (4) as an approximation can be used. Using equation (4) the contribution of the initiator end groups (mainly sulfate groups) to the stabilization of particles is neglected.

$$N_o = (a_s S_M)/(\ \ D_o^2) \qquad (4)$$

N_o - maximum particle concentration, mol cm^{-3}
D_o - particle diameter after nucleation (nucleation diameter), cm
a_s - surface area for the stabilizing agent, cm^2
S_M - concentration of the stabilizing agent, mol cm^{-3}

Now the velocity of the radical desorption, which has the highest value after particle nucleation, can be expressed by equation (5).

$$r_{des} = k_{des} \bar{n}_o N_o \qquad (5)$$

r_{des} - desorption rate, mol cm^{-3} s^{-1}
k_{des} - desorption rate constant, s^{-1}
$\bar{n}_o$ - mean number of radicals per particle after nucleation

The drop in desorption velocity according to our model assumption is caused by the increasing particle diameter, which brings about a decrease in radical desorption. Thus, the velocity constant of radical desorption out of a particle is described by equation (6).

$k_{des} = (6/\pi)^{2/3} D_R\ D^{-2}$ (6)

D_R - diffusion constant of a desorbing radical within the particle, $cm^2\ s^{-1}$

Combining the equations (5) and (6), equation (7) stands for the radical desorption velocity out of a particle with a given diameter.

$r_D = (6/\pi)^{2/3}\ D_R\ n_o\ N_o\ D^{-2}$ (7)

If there is no change in the reaction conditions, such as emulsifier and initiator concentration, the change of desorption velocity is mainly caused by the change of the particle diameter. Assuming that the desorption of a radical is the rate-determining step of particle coalescence, the combination of equations (1), (5) and (7) leads to an equation (8) for the calculation of the coalescence rate constant.

$k_C = k_{C1}\ D^{-2}$ (8)

The real coalescence rate constant under the conditions of emulsion polymerization of VC can be calculated according to the above assumptions using equation (9).

$k_{C1} = (6/\pi)^{2/3}\ D_R\ n_o\ N_o^{-1}$ (9)

Substituting n_o and N_o in equation (9) by the expressions (3) and (4), affords equation (10), which makes it possible to calculate k_{C1} from initial polymerization parameters.

$k_{C1} = 1.729\ ((D_R\ \rho_{io}\ D_o^8)/(a_s\ S_M)^3)^{0,5}$ (10)

ρ_{io} - initial initiation rate, $cm^{-3}\ s^{-1}$

Hence, the following equation (11) results for the coalescence rate.

$r_C = k_{C1}\ D^{-2}\ N^2$ (11)

The rate of the particle coalescence during emulsion polymerization of VC is thus determined by the change of particle diameter and particle concentration.

The value of the coalescence velocity constant k_{c1} can be calculated from the experimentally determined particle number-/time curves by equation (12).

$$k_{c1} = (d(1/N)/dt)\ D^2 \qquad (12)$$

k_{c1} - coalescence velocity constant, $cm^5\ mol^{-1}\ s^{-1}$
N - particle concentration, experimental values, $mol\ cm^{-3}$
D - mean particle diameter, experimental values, cm
t - time, s

Table 1 shows the comparison between experimental values of k_{c1} and values calculated according to equation (10) for discontinuous emulsion polymerizations of VC with different emulsifier and monomer concentrations.

For the calculation of $k_{c1,c}$ according to equation (10) the following values were used: $D_R = 7\ 10^{-10}\ cm^2\ s^{-1}$, $\rho_{io} = 2.722\ 10^{-11}\ mol\ cm^{-3}\ s^{-1}$ and $a_s = 5\ 10^{-10}\ cm^2$.

The values compared in Table 1 show a surprisingly good accordance. However, we have to realize that values for D_o and D_R are affected with a relatively high uncertainty. In particular, k_{c1} changes with the fourth power of D_o.

Table 1: Comparison between experimental (e) and calculated (c) values of k_{c1}

S_M $mol\ cm^{-3}$	ϕ_M	D_o $cm\ 10^7$	$k_{c1,c}$ $cm^5mol^{-1}s^{-1}$	$k_{c1,e}$ $cm^5mol^{-1}s^{-1}$
$1.17\ 10^{-5}$	0.35	3.5	$1.62\ 10^{-7}$	$2.53\ 10^{-7}$
$1.17\ 10^{-5}$	0.30	2.3	$1.10\ 10^{-8}$	$4.72\ 10^{-8}$
$1.17\ 10^{-5}$	0.27	1.8	$2.66\ 10^{-9}$	$1.77\ 10^{-8}$
$2.56\ 10^{-5}$	0.30	1.8	$1.91\ 10^{-9}$	$5.47\ 10^{-9}$
$1.17\ 10^{-5}$	0.30	2.3	$1.10\ 10^{-9}$	$4.72\ 10^{-8}$
$8.23\ 10^{-6}$	0.30	2.3	$1.85\ 10^{-8}$	$8.00\ 10^{-8}$

References

[1] K.-H. Goebel, H.-J. Schneider, W. Jaeger and G. Reinisch, Acta Polymerica, 32, 117 (1981)

[2] K. Tauer, B.-R. Paulke, I. Müller, W. Jaeger and G. Reinisch, Acta Polymerica, 33, 287 (1982)

[3] M. Smoluchowski, Physik. Zeitschr., 17, 557 (1916)

This is a part of a publication which we have submitted to the Journal of Macromolecular Science. In this publication the influence of the particle coalescence for modeling the emulsion polymerization of vinyl chloride is discussed in more detail and examples are given in which cases the paticle coalescence has necessarily to take into account.

IPOC Polymer Colloid Research

Emulsion Polymerization of Styrene Initiated by AIBN

Karl- Heinz Goebel; Katrin Stähler

The kinetics of the emulsion polymerization of styrene started by AIBN was investigated using the following recipe:

water : 1000g
styrene : 200g
[SDS] : 14.3 mMol/l water
[AIBN] : 47.9 mMol/l styrene

Changing the emulsifier concentration there is a break in the surface- tension- curve (Figure 1) in the range of the cmc of sodium dodecyl sulfate (cmc = 8.3 mMol/l). Corresponding to this result only the double logarithmic plot of the particle concentration versus the micellar emulsifier concentration gives a straight line with a slope of 0.50 + 0.03 (Figure 2). That means, the condition for the particle formation is changing by micelles (either by solubilization of AIBN alone and / or by micellar particle nucleation).
We need the change of the average radical number

$$\bar{n} = \frac{R_p \; N_A}{k_p \, C_M \, N}$$

in the course of polymerization for understanding the kinetics and the mechanism of the process.
The results given in Figure 4 were calculated using the experimental values in Figure 3 and k_p = 3551/ mol s /ref.1/. Despite of the fact that we didn't find any region with a constant polymerization rate (obtained by numerical differentiation of the conversion- time- curve) we got $\bar{n}$ = 0.5 for a broad range of conversion (28% to 53 %). Divergent from the results with water soluble initiators we found a minimum of $\bar{n}$ at higher conversions due to the formation of new particles. The reproducibility of this result was proved. A further difference to water soluble initiators consists in the initially permanent increasing of $\bar{n}$ even though the particle concentration is constant. The model of NOMURA /ref.2/ gives only correct results if it is assumed that the desorption constant and / or the initiator efficiency changes in the first period.
The further work will be concerned with the rate of initiation and with the properties of the polymer molecules.

/1/ Buback ,M. ; et al.
J. Polym. Sci. , Polymer Letters 26 (1988) 293-297
/2/ Nomura ,M.
Macromol. Chem. Rap. Comm. 10 (1989) 581-587

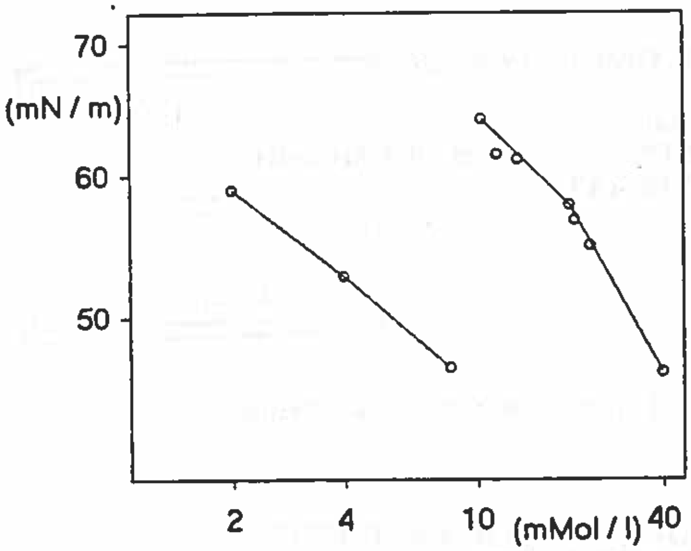

Figure 1: Surface tension of final latices versus the SDS-concentration

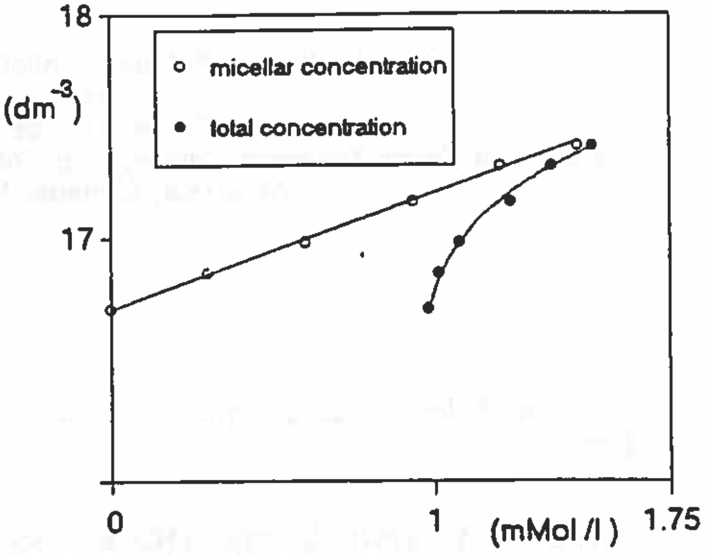

Figure 2: Double logarithmic plot of the particle concentration versus the SDS-concentration

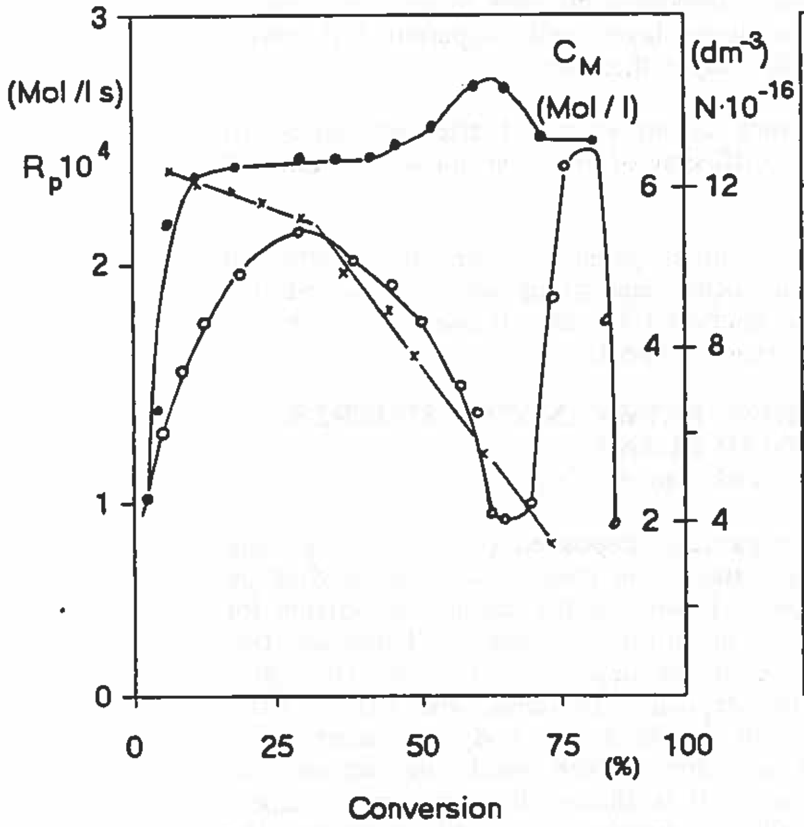

Figure 3: Rate of polymerization (R_p) ○ ,
Particle concentration (N) ● ,
Monomer concentration (C_M) ×
versus conversion

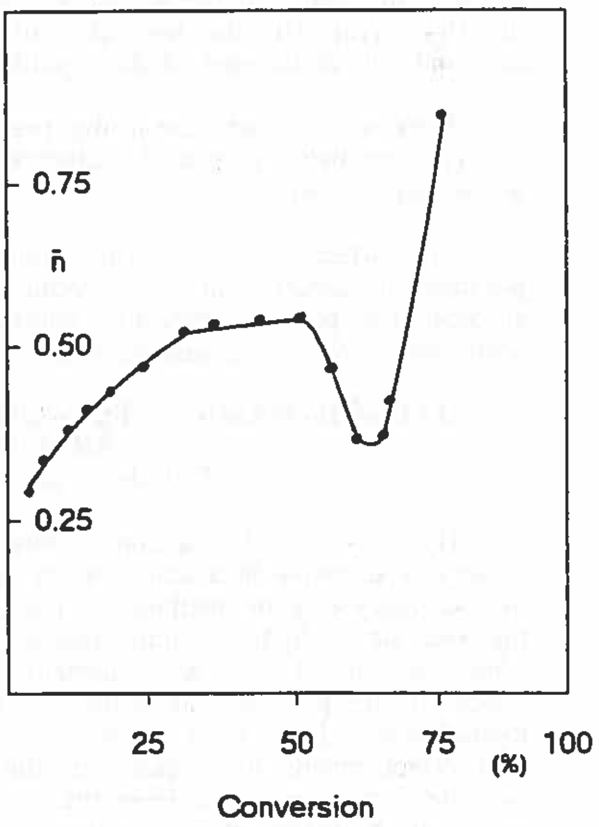

Figure 4: Average radical number per particle versus conversion

Contribution to Polymer Colloid Group Newsletter
from
T.G.M. van de Ven

Pulp and Paper Research Centre, Dept. of Chemistry, McGill University
Montreal, Canada, H3A 2A7

The following is a series of abstracts of papers submitted to various journals.

HYDRODYNAMIC LAYER THICKNESS OF POLYETHYLENE OXIDE ADSORBED ON POLYSTYRENE LATEX

L. Couture and T.G.M. van de Ven

The adsorption of polyethylene oxide onto polystyrene latex particles is investigated by means of dynamic light scattering. The data suggest that the polymer adsorption process consists of three main stages: (i) diffusion of polymer molecules to the bar surface and subsequent changes in configuration of the first layer, (ii) the formation of a dense layer until apparent full coverage, and (iii) attainment of the equilibrium layer thickness.

Data on kinetics reveal the presence of an energy barrier in stages (ii) and (iii), probably due to the hindered diffusion of polymer molecules through the adsorption layer.

The effect of tail configurations is investigated by comparing adsorbed polymer molecules with and without an anchor end group and it is found that adsorption of polymer molecules without anchors leads to a thicker hydrodynamic adsorption layer, in agreement with theoretical expectations.

HYDRODYNAMIC INTERACTIONS BETWEEN TWO SPHERES NEAR A SOLID PLANE

T. Dabros and T.G.M. van de Ven

Hydrodynamic interactions between particles deposited on a solid wall and those free to move in a simple shear or a stagnation point flow, were studied by the boundary element method. It has been shown that the method is suitable for the analysis of hydrodynamic interactions in colloidal systems. There are two effects which can play an important role during deposition, namely: (i) disturbance of the particle trajectories by the deposited particles, and (ii) an extra hydrodynamic force on a deposited particle during a two body encounter. The first effect results in blocking of the collector surface, while the second can increase particle removal from the surface. It is shown that one cannot expect extensive blocking effects without colloidal interactions. Nevertheless, the force exerted on a deposited particle can be considerably changed by the purely hydrodynamic interaction with a freely flowing one. This effect is likely to be responsible for removal of weakly-bound particles.

PHOTON CORRELATION SPECTROSCOPIC STUDIES OF BIMODAL COLLOIDAL DISPERSIONS

G.A. Schumacher and T.G.M. van de Ven

The validity of the theoretical bimodal homodyne autocorrelation function was experimentally studied for a wide range of size ratios a_A/a_B and scattered light intensity ratios I_B/I_A of the component fractions A and B making up the bimodal dispersion. The effect of varying the scattering angle θ_s on these measurements was also studied. In both studies, experimental results were in excellent agreement with theoretical predictions. A quasi-heterodyne autocorrelation function was measured using a bimodal dispersion, where $a_B >> a_A$ and $I_B >> I_A$, results of which were equivalent to that expected for a classical heterodyne experiment. Finally, a preliminary study of PCS measurements on polydisperse samples was carried out using a partially coagulated gold sol and latexes containing small amounts of doublets. It was found that the percentage of doublets in the dispersion can be estimated from both static and dynamic light scattering experiments.

BROWNIAN MOTION OF ROD SHAPED COLLOIDAL PARTICLES SURROUNDED BY ELECTRICAL DOUBLE LAYERS

G.A. Schumacher and T.G.M. van de Ven

Using photon correlation spectroscopy, translational diffusion constants of electrostatically stabilized rod shaped colloidal particles (tobacco mosaic virus) have been determined. The diffusion constant equals the value of a neutral rod at high and low electrolyte concentrations, but is reduced by a few percent when the electrical double layer is comparable to the radius of an equivalent sphere. The reduction in diffusion constant depends both on the charge on the rod and the sizes of the ions in the double layer. The experimental findings are in qualitative agreement with a theory of Vizcarra-Rendon et al., indicating that at the salt concentrations used, tobacco mosaic virus behaves like a model colloidal particle. The effective charge on the individual tobacco mosaic virus particles is obtained as a fitted parameter, and an estimate of the zeta potential on the tobacco mosaic virus particles is also made.

EVANESCENT WAVE SCATTERING STUDIES ON LATEX-GLASS INTERACTIONS

G.A. Schumacher and T.G.M. van de Ven

The intensity of light scattered by polystyrene latex particles (average radius of 46.2 nm from electron microscopy) was measured as a function of the penetration depth of the evanescent wave and then compared to the predicted values based on the distribution of particles near the glass surface, which were calculated from the appropriate DLVO theory. This was done for κa values ranging from 0.34 to 9.7. The agreement between theory and experiment was excellent. A photon correlation spectroscopic optical constant b was also measured as a function of the penetration depth. For all values of κa, except $\kappa a = 9.7$, b scaled with the scattered light intensity. The deviation at the highest κa value was tentatively attributed to the slowing down of the diffusion, which is expected at small sphere-wall separations. The feasibility of monitoring the deposition of sub-microscopic latex particles using this technique was also investigated, with promising results.

Contribution to the Polymer Colloid Group Newsletter
from the van 't Hoff-Laboratorium, Universiteit Utrecht, the Netherlands.
communicated by A.Vrij, group member

RECEIVED
24 SEP 1990

A TURBIDITY STUDY ON COLLOIDAL SILICA PARTICLES IN CONCENTRATED SUSPENSIONS USING THE POLYDISPERSE ADHESIVE HARD SPHERE MODEL.

M.H.G.M.Penders and A.Vrij.

Van 't Hoff Laboratorium voor Fysische en Colloidchemie,
Padualaan 8, 3584 CH, Utrecht.The Netherlands.

ABSTRACT.

A new type of analysis of turbidimetric measurements is proposed for concentrated sterically stabilized colloidal dispersions. It is applied to dispersions of silica spheres, coated with stearylalcohol in aromatic solvents up to high volume fractions of 0.30 – 0.40. Baxter 's polydisperse adhesive hard sphere model is used to explain the results. Influence of diameter, stickiness and polydispersity in diameter on turbidity will be discussed. Model calculations fit the experimental curves very well up to high volume fractions and from the data it can be concluded that there exists a small attraction between the particles.

SMALL-ANGLE NEUTRON SCATTERING ON CONCENTRATED ADHESIVE HARD SPHERE DISPERSIONS

M.H.G. Duits[1], R.P. May[2], A. Vrij[1] and C.G. de Kruif[1]

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2) Institut Laue Langevin, BP156X, F-3804 Grenoble Cedex, France

ABSTRACT

Small-angle neutron scattering experiments were performed on concentrated dispersions of sterically stabilized silica particles dispersed in benzene, where the particles show an effective attraction on lowering the temperature. In this study, the system was cooled down from 52 °C, where almost hard sphere behaviour is observed, to just above the phase transition temperature at 33 °C in seven steps. At each temperature, scattered intensities were measured at four volume fractions up to 0.28.

The constancy of the particle form factor allowed data analysis at the level of structure factors. Experimental data were fitted with model calculations using the Percus-Yevick solution for Baxter's adhesive hard-sphere potential, taking the particle size polydispersity into account.

A quite satisfactory model description of the experimental structure factors could be obtained. At lower temperatures and higher volume fractions, the fits are even quantitative. The obtained stickiness parameter is directly related to sample temperature, whereas it does not depend on volume fraction. These observations confirm the model of a short-ranged attraction between the particles, with a well depth governed by enthalpic and entropic contributions to the chain-chain and chain-solvent interactions.