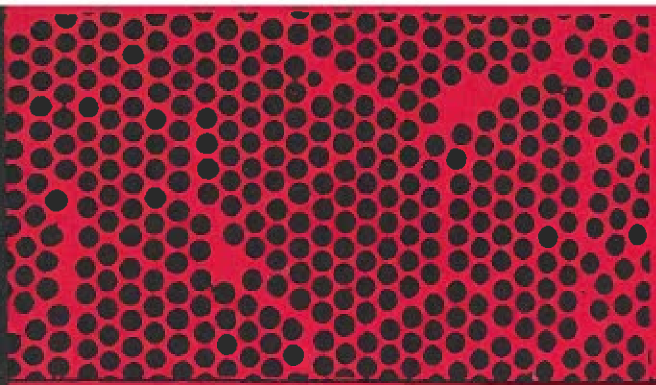

Secretary: D H Napper
School of Chemistry
University of Sydney
NSW 2006
Australia

IPCG

INTERNATIONAL POLYMER COLLOIDS GROUP

NOVEMBER 1994

VOLUME 25 NUMBER 2

NEWSLETTER

INDEX

CONTRIBUTIONS

FROM THE EDITOR'S DESK

MEMBERSHIP

Sandy Dunn has advised me that his contribution to this Newsletter will be his last as he fully retired from UMIST at the end of September. He has also expressed his wish to retire from the IPCG. So this is a very sad occasion for the Group. Sandy was the Editor of this Newsletter for several decades and its survival and good health owe much to his enthusiasm and good judgement. That contribution when coupled with Sandy's important scientific contributions to polymer colloids means that he has well merited a long and happy retirement. Sandy, we will all miss you!

I must apologise to several members whose contributions arrived after I had sent the May Newsletter to the press. These are included here.

UK POLYMER COLLOIDS FORUM

Sandy Dunn's last contribution is a report of the 2nd UK Polymer Colloids Forum organized by Peter Lovell. These forums now seem to be well established. Well done Peter *et al.*

GORDON RESEARCH CONFERENCE

Theo van de Ven reminds all members of the dates of the next Gordon Conference on Polymer Colloids: 2–7 July, at Tilton, NH.

69TH ACS COLLOID & SURFACE SCIENCE SYMPOSIUM

Details of the above conference to be held in Salt Lake City from 11–14 June, 1995 are enclosed.

THE ULTIMATE CONFERENCE

Would members please note that Polymer Colloids has been accepted as a theme for MACRO 98 which will be held on the Gold Coast, Australia from 12–17 July, 1998. Bob Gilbert and I will keep you informed as time goes by.

NEXT NEWSLETTER

Contributions for the next Newsletter should reach me at the University of Sydney by 30 April, 1995.

D H NAPPER
Editor

UMIST

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2nd Meeting of the UK Polymer Colloids Forum

Ably organised by Peter Lovell in his capacity as Chairman, this meeting was held at Keele University in September. There were 67 participants although Peter has now 170 names on the Forum's Mailing List including representitives of 28 companies. There is a much more widespread interest in polymer colloids in Britain than anyone had previously realised. Even academic interest has increased as was demonstrated by the poster session where there were 12 posters by post-graduate students, 2 from UMIST, 3 from Bristol, 4 from Keele Physics Departmnent all on aspects of the effects of ultrasonics on colloids, and one each from Nottingham Trent University (John Hearn), Bradford, and Greenwich. Also on display were Brookhaven and Malvern Particle Sizers. Although the posters were all impeccably neat, presenters could learn something by studying newspaper billboards and commercial 'special offer' displays rather than including all the small print in the poster itself. But it is a good idea to include the presenter's portrait (to facilitate identification).

Dr D.M.C.Heymans (Shell Research, Belgium) opened the lecture programme with a paper on the copolymerisation of their VeoVa monomer with butyl acrylate. The VeoVas are branched vinyl esters and are amongst the most hydrophobic monomers available: they are stable to alkaline hydrolysis and have been in use for copolymerisation with vinyl acetate for over 30 years. In that case the reactivity ratios are close to 1 and copolymerisation is straightforward. However reactivity ratios with acrylic and methacrylic esters are very unfavourable which can produce latex particles with a VeoVa rich shell even when semi-batch conditions are used. Hoy's power feed procedure can produce particles with uniform composition. Guillot's computer simulation programs have been found valuable. Applications for the copolymers include anti-corrosion primers, water-repellant coatings for concrete, emulsion paints for outdoor use, and adhesives for polypropylene.

Dr J.L.Keddie, an American post-doctoral recruit to the recently formed Polymer & Colloids Group at the Cavendish Laboratory, Cambridge spoke on the application of Environmental Scanning Electron Microscopy and Spectroscopic Ellipsometry to the kinetics of film formation from latex mixtures. Material properties can be tailored inexpensively by mixing latices but film formation from such mixtures has not been studied previously. By contrast with SEM, ESEM can be applied to wet latices and biological tissue eliminating the possibility of artefacts being formed during specimen preparation. Although the time required for a continuous film to be formed varied widely between 3 weeks for 'hard' latices (T_g ca. 13 °C) and 'soft' latices with a lower T_g for which the process could be completed within an hour, film formation was found to start at the same time irrespective of T_g (presumably depending on the time required for the water to evaporate which might be a function of particle size).

John Hearn described studies of the permeation of gases, water vapour and tritiated water, salts, nitrophenol, sucrose, and substituted anilines through latex firm formed both from soap-free latices and commercial latices It was possible to distinguish diffusion through pores (for which similar fluxes are found for the homologous series of anilines despite differences in their partition coefficients) from activated transport through the film (which depends on the solubility of the probe molecule in the film). Hydrophilic additives increase the permeation rate of hydrophobic solutes but decrease gas permeation. Leaching these additives creates pores so long as the film is kept wet but the porosity is lost on drying unless the polymer has a high T_g. These studies relate to the application of barrier coatings and controlled drug release.

Brian Brooks (Loughborough) pointed out that, despite their widespread use in industry, semi-batch reactors had attracted comparatively little study. Such reactors have an input but no output until the reaction is complete: thus the reaction volume increases continuously. The principal incentive for the use of such systems is to achieve uniformity of composition in copolymers but, conversely, they can be used to produce structured particles. Additionally they allow exotherms to be controlled and reduce the difficulties encountered in using reactants with high vapour pressures. Mathematical models applied to these systems so far have been over simplified asssuming absence of renucleation, absence of particle coalescence, no significant polymerisation in the aqueous phase, termination rate coefficients independent of conversion, a constant number of radicals per particle, and that mass transfer is not rate determining. In semi-batch reactors a distinction needs to be made between the stationary state and a steady state. Taking radical desorption and the variation of rate coefficients, radical and monomer concentrations in the particles with conversion greatly improves the fit of model calculation to experimental results. Oscillatory behaviour can be predicted at high feed rates.

Dr R.Groves (Doverstrand) reviewed the use of emulsion polymers in coated papers and board. The coatings consist primarily of clay or calcium carbonate particles: the emulsion polymer which may be styrene-butadiene, butyl acrylate-styrene, or vinyl acetate acts as a binder which control the mechanical strength of the coating which is particularly important in high speed lithography. The polymer needs to be designed so that voids remain in the coating after drying to permit the penetration of ink during printing and to control the opacity of the coating. The extent of coating consolidation also affects the orientation of the pigment particles which influences the gloss achieved on calendering.

Dr S.P.Armes (Sussex, formerly at Bristol) has been working on the polymerisation of pyrrole and aniline for the last 11 years. This is an oxidative polymerisation which produces materials which are stable in air (unlike polyacetylene) and have a conductivity similar to that of carbon black. But the polymers are unprocessable. However if the polymerisations are done in the presence of colloidal silica composite particles 100-300 nm diameter with a 'raspberry' morphology are obtained which can be stable in aqueous media. The proprtion of polymer in the composite particles can be determined by thermogravimetric analysis. Nitrogen adsorption (B.E.T.) shows the particles to be porous. X-ray photoelectron spectroscopy shows that silica is concentrated at the particle surface. The conductivity of the particles is almost as high as that of the pure polymer. The only other inorganic oxide found suitable is SnO_2. Conductive magnetic particles can be produced by the use of silica-coated Fe_3O_4. There are potential applications for the particles in medical diagnostics.

The second session was devoted to the characterisation of polymer colloids. It did not prove as controversial as it looked as though it might be from the programme.

Dr P. Macfadyen (Brookhaven Instruments) compared and contrasted Photon Correlation Spectroscopy (PCS) and Disc Centrifuge Photodensitometry (DCP) for particle sizing. (Brookhaven market instruments for both techniques!). Neither instrument needs empirical calibration. Both can be used on emulsions as well as sols. PCS is restricted to particles with diameters less than 1 μm: with sufficient laser power polymer molecules in solution can be studied and their molecular weights derived: the only additional data needed is the viscosity of the continuous phase although the optical properties of the disperse phase also need to be known if distributions are to be derived. However the resolution achievable for particle size distributions is relatively low: because small particles scatter less light than large particles a bimodal distribution with a weight ratio of small to large particles of 3:1 would appear as monomodal. The hydrodynamic diameter is measured: if the particles have a surface charge this includes part of the electrical double layer as is demonstrated when water is replaced by an electrolyte solution as the continuous phase.

DCP has excellent resolution for multimodal distributions and will resolve particles differing in diameter by 13%. However the densities of continuous and disperse phases as well as the viscosity of the continuous phase must be known if absolute values are to be derived for particle size and distribution data are enhanced by taking account of refractive indices. A homogeneous start can have advantages over the more usual line start technique particulary for small particles not much denser than water: these can be creamed by replacing water by a deser spin fluid.

Dr F.K.McNeil-Watson (Malvern Instruments) talked about the problems of studying concentrated dispersions by PCS. Multiple scattering soon becomes a problem although it can be mitigated by reducing the path length in the sample: its general effect is to reduce the average particle size reported. The fact that a sample appears clear to the eye does not guarantee that multiple scattering is eliminated: it may result from the difference in the refractive indices of the phases being small. Multiple scattering increases the apparent breadth of the distribution.

The use of fibre optic techniques can help to overcome difficulties caused by multiple scattering and have been used to study concentrated dispersions up to a concentration of 40% by volume but in such concentrated dispersions long range interactions prevent particles diffusing freely: this requires measurements at a series of dilutions until a valid operational concentration is found: this may be about 10% but is generally lower for emulsions.

A new heterodyne optical configuration was described which has the advantage of greatly reducing distortion by dust particles and enabling the first order correlation function to be measured directly rather than after taking a square root as in the normal homodyne PCS procedure.

Dr A. Doroszkowski (Paint Research Association) considered that Transmission Electron Microscopy had a lot to be said for it. It might be necessary to measure 4000 particles in a polydisperse sample but appropriate statistical techniques could reduce the labour. Provided representitive areas are selected and all particles in them counted it was only necessary to continue until 10 particles had been counted in each size group: in this way counting 79 particles could be equivalent to a straight count of 325. He recommended Irani & Challis 'Particle Size' (1963) for relations which allow the various average determinable by different techniques to be interconverted enabling the average you need to be calculated from the average you have determined (though possibly only if a log normal distribution can be assumed).

Professor R.E.Challis (Keele) indicated the potential of ultrasound measurements. Practical colloidal dispersion are too concentrated for photometric measurements to be possible on-line. Although X-ray and neutron scattering can be applied to concentrated dispersion they are not suitable for use in industrial situations. Measurement of ultasound absorption and phase velocity at a series of wide bandwidths should allow the volume fraction and particle size to be determined but further work to take the effect of interparticle interactions is needed.

Dr J. Castle (Bradford) comes from a rheology group interested in concentrated suspensions which was interested in using latex particles as models for practical systems of irregularly shaped particles. Particles produced using a combination of an electrostatic and a polymeric stabiliser were however proved by argon adsorption to have rough surfaces.

It had been possible to produce samples of the same size, all monodisperse, but varying in surface roughness so that the effect of surface roughness on flow could be studied and compared with computer simulations of monodisperse hard spheres.

In the final session four industrial research managers gave their assessments of the potential for industry-university collaboration.

Dr Stephen Downing (ICI Paints Division) noted that current wisdom in industry was to concentrate on core business whilst seeking to add value to the product. This had resulted in a severe reduction of long-term corporate research in the hope that universities might undertake more pre-competitive, speculative research in areas of industrial interest. He felt that there was overemphasis in trying to understand well-known systems. Environmental considerations were increasing the importance of water-borne systems. There was scope for work on associative thickeners to achieve the application properties which customers require, on reactive surfactants, on the preparation of core/shell particles, on the dispersion of preformed polymers, and to solving the problems encountered when processes were scaled-up from the laboratory to the plant.

Mr John Cruden (Harco), by contrast, thought it vital to discover what was really happening in known processes because this was the only way by which they could be improved. He instanced the effect of oxygen in PVC suspension polymerisation. To get the best results a measured amount has to be added after the sample has been completely degassed. This is known to work but why?

Dr Paul Reynolds (Bristol but formerly Courtaulds Coatings) emphasised the need for interdisciplinary teams and agreed with Dr Downing that there was need for better integration across departments, between British universities, and between European universities and industries.

Dr John Padget (Zeneca Resins) listed the dispersion of pre-formed step-growth polymers in water and highly carboxylated aqueous dispersion as two areas of great industrial importance in which there was little or no academic activity. There was a lot of academic activity on the mechanism of emulsion polymerisation which was also very important industrially but very little of this activity was in the UK. There was a great need for academics to take some interest in the relevant patent literature which was generally much in advance of the scientific literature. More could be done on sequential emulsion polymerisation, on the study of the elimination of monomer remaining in the last stage of emulsion polymerisation, on the determination of reliable kinetic coefficients and partition coefficients required for computer simulation and for more critical comparisons of simulations with experimental results.

A. S. Dunn

International Conference on

Multi-Phase Materials

prepared by

Emulsion Polymerisation

Synthesis, Characterisation and Properties

4 - 7 April 1995, Lancaster University, England

Topics:

Thermodynamics & synthesis of multi-phase particles
Encapsulation of inorganic particles
Synthesis of functionalised particles
Characterisation of multi-phase particles
Properties of coatings and bulk materials from multi-phase particles
Biomedical applications of multi-phase and functionalised particles
Latex rheology

Organisers:

Professor Doug Hourston	Dr. Peter Lovell
IPTME	Manchester Materials Science Centre
Loughborough University	University of Manchester and UMIST

Call for papers:

Oral and poster papers are invited on topics within the theme of the conference. A 200 – 300 word synopsis of the paper should be submitted with the name and address of the presenting author and the names of co-authors. The deadline for submission of papers for consideration by the organising committee is 30 November, 1994.

All correspondence and enquiries for further information should be sent to:

Miss L Edwards, Conference Office, Bowland College, Bailrigg, Lancaster, LA1 4YT, United Kingdom

Tel. +44 (0)524 65201 Ext. 2177 Fax. +44 (0)524 843695

McGill

Paprican

Pulp and Paper Research Centre
3420 University Street, Montreal, Quebec, Canada H3A 2A7
Telephone (514) 398-6180 • Fax (514) 398-8254

October 17, 1994

Professor D.H. Napper,
School of Chemistry,
University of Sydney,
Sydney, N.S.W. 2006,
Australia.

Dear Don:

Please find enclosed my contribution to the next newsletter.

Could you also mention the next Gordon Conference on Polymer Colloids:

GORDON RESEARCH CONFERENCE ON POLYMER COLLOIDS
Tilton, New Hampshire, U.S.A.
July 2-7, 1995

Chairman: T.G.M. van de Ven
Pulp and Paper Research Centre
McGill University
3420 University Street
Montreal, Canada, H3A 2A7
Phone: (514) 398-6177
Fax: (514) 398-6256

Sincerely yours,

Theo

T.G.M. van de Ven

69TH ACS COLLOID AND SURFACE SCIENCE SYMPOSIUM

University of Utah
Salt Lake City, Utah 84112 USA
June 11-14, 1995

This is a General Call for Papers and a listing of Specific Sessions. For more information regarding session format and topics, please contact the particular session organizers listed in the enclosed document. Meeting information and pre-registration materials will be mailed early in 1995.

69th ACS Colloid & Surface Science Symposium
Conferences & Institutes
2174 Annex Building
University of Utah
Salt Lake City, UT 84112
USA

Non-Profit Organization
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Salt Lake City, Utah
Permit Number 4034

69th Annual
COLLOID AND SURFACE SCIENCE SYMPOSIUM
Supported by a grant from Henkel Corporation

University of Utah, Salt Lake City, Utah
June 11-14, 1995

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Technical Sessions	Organizers
Symposium in Honor of Sydney Ross	Craig Herb, Ian Morrison
Colloidal Dispersions	John Berg, David Devore, Theo. Tadros
Micellar Systems	Ben Chu, Björn Lindman, Natalya Rapoport
Controlled Colloid Synthesis	John Garside, Ronald Sapieszko
Electrochemistry of Organized Monolayers	Richard Crooks, Henry White
Colloids in Gene, Drug, and Antigen Delivery	Daan Crommelin, Jindrich Kopecek
Catalysis and Solid State Gas Sensors	Thomas Beebe, Wayne Goodman, Masatake Haruta
Modelling of Interfacial Phenomena	Daniel Klingenberg, Jay Magda
Scanning Probe Microscopies and Surface Spectroscopy	Joel Harris, Vladimir Hlady, Clayton Williams
Wetting and Interfacial Phenomena	Milind Deo, Jan Miller, Wilhelm Neumann
Biopolymers and Cells at Interfaces	Joseph Andrade, Allan Hoffman, Sung-Wan Kim
Instrumentation in Colloid and Surface Analysis	Calvin Giddings, Theodore Provder, Bruce Weiner
General Papers	Eric Nuttall, Jr., Edward Trujillo

For specific information, see the following pages

ROYAL SOCIETY OF CHEMISTRY - FARADAY DIVISION

x

COLLOID & INTERFACE SCIENCE GROUP

CONFERENCE ANNOUNCEMENT and CALL FOR POSTERS

CONCENTRATED DISPERSIONS - BRISTOL - 29th-31st March 1995

The Colloid and Interface Science Group of the Faraday Division of the RSC plans to hold a three-day meeting on the subject of "Concentrated Dispersions" at Bristol in March 1995.
The meeting will cover a wide range of aspects of the subject, including dynamics and rheology, scattering, aggregation, mesophases and the colloidal aspects of materials science.
The meeting will comprise both talks and posters.
One feature of the meeting will be the presentation and discussion of new work emerging from research groups supported by the Department of Trade and Industry Project in "Colloid Technology". It is anticipated that about half of the posters and talks will come from groups involved in this initiative. The university departments participating in the Project include Physics, Chemical Engineering and DAMPT at Cambridge, Chemical Engineering and Chemical Technology at Imperial College, Physical chemistry at Bristol and Physics at Edinburgh.
Prof. Sir Sam Edwards has been invited to give an introductory lecture and there will a number of distinguished speakers from overseas, including, S.J. Candau (Strasbourg), M. Doi (Nagoya), T.W. Healy (Melbourne), R. Klein (Konstanz), A. Philipse (Utrecht), W.B. Russel (Princeton), H. Wennerstrom (Lund).
It is anticipated that the total cost attending the meeting, including accomodation and all meals, will be between £120 and £180 (depending upon status and type of accomodation elected for). Further details will be sent to members of the Group in late January. Others wishing to be put on the mailing list should complete the slip below.

OFFERS OF POSTERS ARE INVITED NOW with a closing date of 30th December 1994

To: Dr. J.W. Goodwin, School of Chemistry, University of Bristol, Bristol BS8 1TS (England).

Concentrated Dispersions - I should like to offer a poster entitled:-

and I enclose a brief abstract.

I should like to receive further details of the meeting .....

Name and address:

CALL FOR PAPERS

Please, submit titles for your intended presentation to the appropriate session organizer by November 30, 1994. Pending acceptance, ACS standard abstract forms will be forwarded to each speaker during the month of December. Deadline for receipt of Abstracts is January 31, 1995.

SYDNEY ROSS SYMPOSIUM

To honor Professor Sydney Ross on the occasion of his 80th birthday

Submissions are solicited for oral presentations devoted to the areas of research and interests of Professor Ross. Former students and colleagues are especially urged to contribute.

Organizers:

Ian D. Morrison
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(716-422-4797 (FAX)
morrison.wbst102a@xerox.com

Craig Herb
Helene Curtis Inc
4401 West North Avenue
Chicago Il 60639-4769
(312)292-7093
(312 384-3539 (FAX)

COLLOIDAL DISPERSIONS

Submissions are solicited for oral presentations devoted to experimental and/or theoretical investigations of the behavior of colloidal dispersions. Topics of interest might include, but are not limited to:

- aggregation stability (electrostatic, steric, electro-steric)
- kinetic properties
- colloids at or near macro-interfaces
- depletion effects
- dispersion rheology
- phase segregation phenomena
- concentrated dispersions
- statistical mechanics of colloids
- electrokinetic properties
- new experimental techniques
- stabilization of block-copolymers

Organizers:

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Bracknell Berkshire RG12 6EY
United Kingdom
44-344-42470 (telephone)
44-344-55629 (FAX)

MICELLAR SYSTEMS

Submissions are solicited for oral presentations of experimental and theoretical work related to micellar systems. Topics of special interest include, but are not limited to:

- Polymeric Micellar Systems;
- Surfactants;
- Mixed Micellar Systems, including polymer-surfactant-surfactant and polymer-polymer mixtures;
- Molecular architecture;
- Dynamics;
- Simulation.

Organizers:

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CONTROLLED COLLOID SYNTHESIS

Control of particle morphology, size, and surface characteristics to meet product specifications is the overall objective of controlled colloid synthesis. To improve the scientific understanding in this area, the fundamentals of particle synthesis must be understood and manipulated. These fundamentals include:

- Mixing effects on the competition for solute used in particle nucleation and growth
- Discontinuous particle growth phenomena
- Primary particle aggregation and deaggregation
- Particle interactions as they are relevant to particle formation

Papers that provide insights into these aspects of particle synthesis are sought for this symposium.

Organizers:

Dr. Ronald Sapieszko
3M Center, Building 201-3N06
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(612) 733-9612
(612) 737-4682 FAX

Professor John Garside
Dept. of Chemical Engineering
UMIST
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Manchester, M60 IQ
United Kingdom
44-61-2004360

CATALYSIS AND SOLID STATE GAS SENSORS

Submissions are solicited for oral presentations to be made in a symposium about fundamental and applied aspects of heterogeneous catalysis and/or solid state gas sensors. Some examples of topics of interest include, but are not limited to:

- chemistry on oxide surfaces
- structure-reactivity relationships in catalysis
- theory and modeling of molecule-surface interactions
- nanocharacterization of model catalyst/sensor surfaces
- optical probes of sensor and catalyst surfaces
- chemical modifications for intelligent gas sensors

Please note that the 14th North American Meeting of the Catalysis Society will also be held independently during the time of this meeting, at the Snowbird Conference Center. We hope that you will include both meetings on your schedule while in Salt Lake City.

Organizers:

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Osaka, 563 Japan
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MODELING OF INTERFACIAL PHENOMENA

Molecular length scale interfacial regions can be effectively studied using statistical mechanics, molecular modeling, and molecular-based computer simulations. These techniques often provide results and insights which complement experimental measurements. We invite papers on this subject, covering topics such as colloids, micelles, and polymeric interfaces.

Organizers:

Prof. Jules J. Magda
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SCANNING PROBE MICROSCOPY AND SURFACE SPECTROSCOPY

Submissions are solicited for oral presentations devoted to experimental or theoretical investigations of surfaces by Scanning Probe Microscopy and/or Surface Spectroscopic techniques. Topics of interest include, but are not limited to:

- Cells/Membranes
- Bio-macromolecules
- LB/ Self assembled films
- Small molecule adsorption
- Particle/Surface interactions
- Novel techniques

Organizers:

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WETTING AND INTERFACIAL PHENOMENA

Submissions are solicited for oral presentations of work related to wetting and intefacial phenomena. Topics of special interest include, but are not limited to:

- Oil recovery, production and remediation
- Fundamental aspects of interfacial phenomena
- Flotation and detergency
- Advanced materials; new surfactant structures
- Thin film interfaces

Organizers:

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BIOPOLYMERS AND CELLS AT INTERFACES

Submissions are solicited for oral presentations of work regarding all aspects of the interfacial behavior of proteins and cells. Contributions in the following areas are particularly solicited:

- Role of Adsorbed Proteins in Cell Motility
- Modification of Protein Thin Films by Cells
- Theory of Multicomponent Protein Adsorption
- Protein Repulsive Surfaces: Mechanisms, Models and Optimization, and Stability

Organizers:

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joe.andrade@m.cc.utah.edu

INSTRUMENTATION IN COLLOID AND SURFACE ANALYSIS

Submissions are solicited for oral presentations of work related to instrumentation and techniques for colloid and surface analysis. Topics of special interest include, but are not limited to:

- Instrumentation and Methods for Characterizing Particle Size and Distribution
- Techniques and Applications Relating to the Characterization of Electrical Surface, and Rheological Properties of Particle Systems
- Characterization of Particle Shape and Structure
- Novel Instrumentation and Methods for Characterizing Surfaces and Interfaces.

Organizers:

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(216) 826-5233 FAX

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CATALYSIS AND SOLID STATE GAS SENSORS

Submissions are solicited for oral presentations to be made in a symposium about fundamental and applied aspects of heterogeneous catalysis and/or solid state gas sensors. Some examples of topics of interest include, but are not limited to:

- chemistry on oxide surfaces
- structure-reactivity relationships in catalysis
- theory and modeling of molecule-surface interactions
- nanocharacterization of model catalyst/sensor surfaces
- optical probes of sensor and catalyst surfaces
- chemical modifications for intelligent gas sensors

Please note that the 14th North American Meeting of the Catalysis Society will also be held independently during the time of this meeting, at the Snowbird Conference Center. We hope that you will include both meetings on your schedule while in Salt Lake City.

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MODELING OF INTERFACIAL PHENOMENA

Molecular length scale interfacial regions can be effectively studied using statistical mechanics, molecular modeling, and molecular-based computer simulations. These techniques often provide results and insights which complement experimental measurements. We invite papers on this subject, covering topics such as colloids, micelles, and polymeric interfaces.

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GENERAL PAPERS

Submissions are solicited for oral presentations devoted to experimental or theoretical investigations of colloids and surface interactions of a general nature. Topics of particular interest include:

- colloid deposition in porous media
- colloid remediation in groundwater
- biosorption of metals
- colloidal transport phenomena
- bacterially produced metal colloids
- competitive adsorption of heavy metals
- in-situ mobilization of nonaqueous phased liquid
- environmental colloids

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CONFERENCES

CONFERENCE	LOCATION	DATE/CONTACT
	1995	
20th Australian Polymer Symposium	Adelaide	5-8 February
209th ACS National Meeting	Anaheim	2-7 April
Multiphase Materials Prepared by Emulsion Polymrization	Lancaster	4-7 April (Lovell)
69th ACS Colloid and Surface Science	Salt Lake City	11-14 June
International Symposium on Associating Polymers	Loen, Norway	25-30 June (Hansen)
Gordon Conference on Polymer Colloids	Tilton, NH	2-7 July (van de Ven)
210 ACS National Meeting	Chicago	20-25 August
4th Pacific Polymer Conference	Kauai, Hawaii	12-16 December

THE ROLE OF STRUCTURAL FORCES OF PARTICLES INTERACTION IN STABILIZATION OF CARBOXYLCONTAINING LATEXES.

Aslamazova T.R., Bogdanova S.V.

The definite role of structural forces of particles interaction has been established in the stabilization of emulsifier free latexes (EFL) obtained by copolymerization of methylmethacrylate, MMA, and butylacrylate, BA, at their different relation in the presence of persulphate as an initiator ("Newletters", 1993, v.24, N2, p.1). The stability is shown to increase at increasing the content of MMA in comonomers composition and decreasing herewith the particles surface hydrophobicity estimated by water contact angle for films of the corresponding latexes. In these experiments the values of zeta-potential of particles surface of PMMA and PBA are practically equal that permits to simplify the equation used in the calculation of coefficient of structural forces of their interaction, K_a.

In this report the effect of structural factor on the stability of carboxylcontaining EF latexes based on hydrophobic copolymer of styrene-BA (St:BA=3:2) has been studied. POlymer hydrophobicity is changed by varying the concentration of acrylic acid, AA, from 0 to 7 mas.% per (St+BA).

On Fig.1a the dependence of coagulum, m, upon concentration of acrylic acid, C_{AA} (curve 1) and surface area per one carboxyl group, S_{COOH} (curve 2) is given. As seen, the stability of EFL increases with increasing of C_{AA} and decreasing of S_{COOH}. Herewith the carboxyl groups are in nondissolved form at the observed value of latex pHs equal 2,1-2,3, and do not to participate in electrostatic stabilization of particle surface.

As known, the electrostatic stabilization of EFL particles in the case of PSP initiation is achieved by surface ionized sulphate groups of macromolecules as well as surface-active oligomers formed in the course of polymerization and adsorbed on particle surface. On Fig.2 (curve 1) the decrease of surface tension, σ, of film-forming EF latexes of MMA-BA (the increase of concentration of SA-oligomers or their surface activity) is

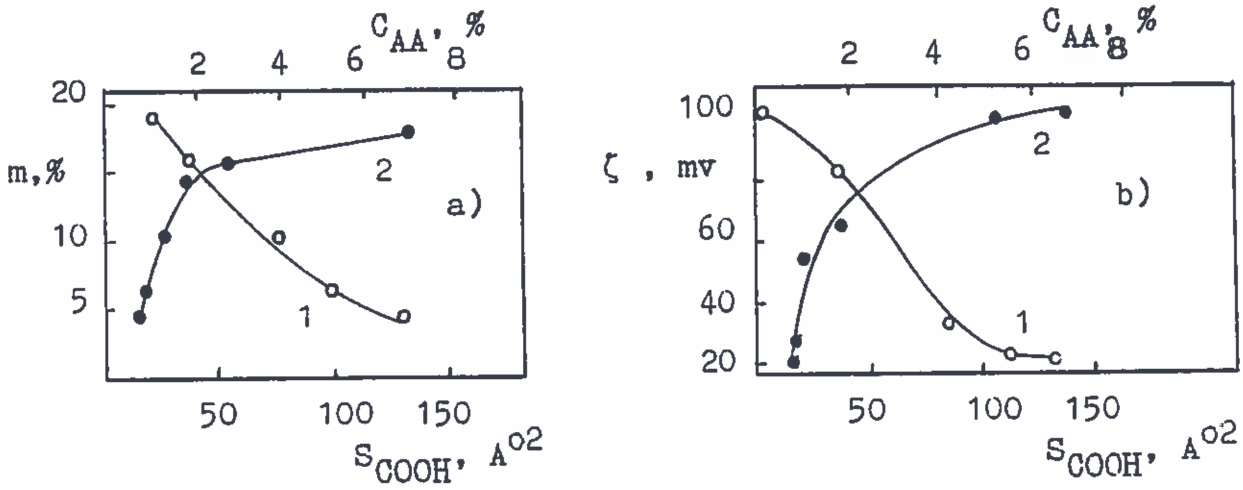
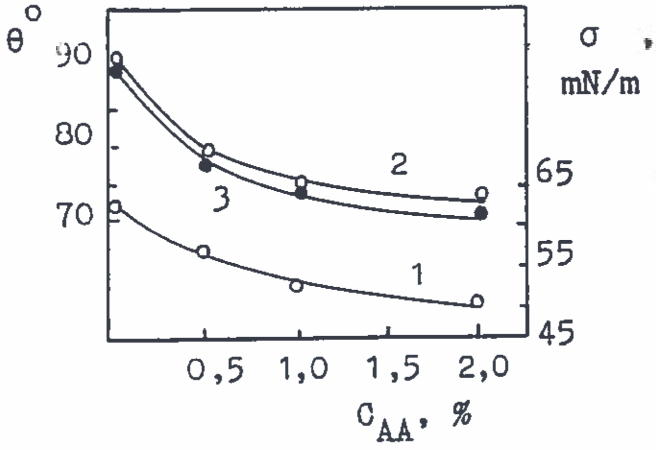


Fig.1. Dependences of coagulum (a) of 25% latexes St-BA formed at EF polymerization (initiator-persulphate potassium, T = 353K) and zeta-potential of particles surface (b) upon AA concentration (curves 1) and surface area per 1 COOH group (curves 2).

shown at increasing of AA concentration. The decrease of zeta-potential of surface and simultaneously the increase of SA-oligomer concentration testify that the role of the latter in particles stabilization is rather lower than of sulphate groups of macromolecules located on the surface.



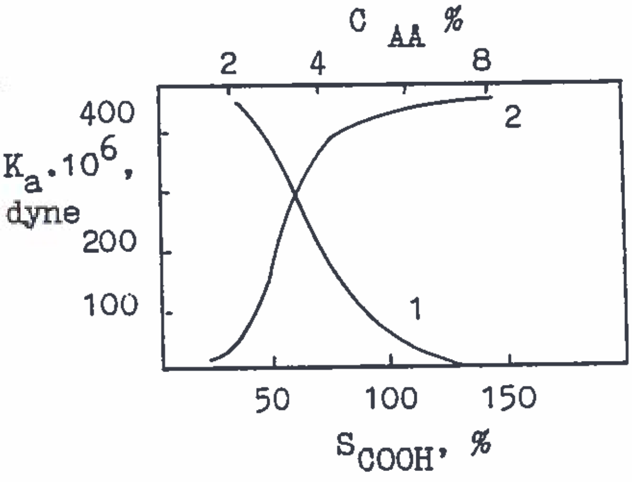


Fig.2. Dependences of surface tension, σ, of MMA-BA latexes (curve 1), contact angle θ for their films by water (curve 2) and latex (curve 3).

Fig.3. Dependences of coefficient of structural forces of interaction of St-BA latex particles (curve 1) and surface area per 1 COOH group (curve 2).

Taking into account the increase of latex stability (Fig.1a) and herewith the decrease of zeta-potential of particles surface (Fig.1b), the effect of structural forces of their interaction in stabilization process is estimated. According to the literature and the data on contact angle θ (Fig.2, curves 2,3) higher 70^o, the polymer surface is considered as hydrophobic. Herewith coefficient of structural forces, K_a, is connected with attraction energy ($K_a>0$). In the connection with the observed change of surface zeta-potential (Fig.1b), the estimation of K_a is carried out with using the equation added by the term ΔV_{el} – change of electrostatic component of potential energy of particles interaction in two experiments: x and y.

$$K_{ay}=K_{ax}\cdot\frac{r_y}{r_x} + \frac{kT[\ \ln(m_y/m_x)-2\ln(C_y/C_x)-3\ln(r_y/r_x)] + \Delta V_{el}}{r_x \exp(-H^{max} / H_s)},$$

where $K_{ax,y}$, $m_{x,y}$, $r_{x,y}$, $C_{x,y}$ – respectively, coeficient of structural forces, coagulum, radius of particles , their concentration in two experiments: x and y; k – Bolzmann constant, T – absolute temperature; H^{max}, H_s – distance between particles, respectively, at maximal energy of interaction and when it decreases at e times.

As shown on Fig.3, the coefficient K_a significantly decraeses at increasing C_{AA} and decreasing S_{COOH}. The comparison of the data of Fig.1a and Fig.3 shows the correlation between latex stability and structural forces of hydrophobic particles attraction: in the case of low values of the latters (when C_{AA}= 7 mas.%), the EF latexes are characterized by larger stability. The direct relationship of coefficient K_a and polymer surface hydrophobicity is observed at comparing the results of Fig.2 and Fig.3. As followed from these figures, the increase of polymer hydrophobicity (contact angle for film) corresponds the increase of coefficient of structural component of potential energy of particles interaction.

Thus the results obtained show the possibility of theoretical and experimental estimation of emulsifier free latexes stability in view of electrostatic and structural factors of their stabilization.

EFFECT OF PARTICLE SWELLING IN MONOMER ON THE STABILITY OF EMULSIFIER-FREE ACRYLATE LATEXES

Aslamazova T.R., Bogdanova S.V.

According to the work / 1 / thermodynamic interaction of hydrophobic polymer - solvent and interfacial energy on the boundar of polymer-solvent can detect the swelling particles and their coalescence during polymerization. They showed that the interaction parameter μ can be estimated graphically as an intercept on the $/-(\ln \Phi_1 + \Phi_2)/$ axis of linear dependence of this axis upo value of $1/r \cdot \Phi_2^2$, where Φ_1, Φ_2 - molar fraction of solvent and polymer in the swollen particle, r - radius of polymer-solvent particle at the equilibrium conditions.

In our work the stability of emulsifier-free latexes (EFL) of hydrophobic monomers (styrene, St, and butylacrylate, BA) modified by high hydrophilic comonomers - acrylic acid (AA), methylacrylate (MA), MA and methacrylic acid (MAA) is studied. Concentration of AA is changed from 0 to 7%, MA - from 0 to 100%, MA and MAA - from 4 to 90%. Parameters Φ_1 and Φ_2 is calculated with account of the monomers composition and Gerens´ ratio of $\Phi_1/\ \Phi$ for St, BA and MA / 2 /. The radius of latex particles formed is used at the calculation as the close values of size of latex particle and polymer-monomer particle at the equilibrium condit ons are found for EF polymerization of methylmethacrylate / 3 /

The values of interaction parameter μ found are given in Ta

Table. Effect of monomer composition on parameter μ and latex stability K .

Monomer composition	Comonomer(s) concentration,%	μ	K,
St-BA- AA	0	0,635±0,005	20
-"-	7	-"-	7
BA - MA	0	0,590	14
-"-	10	0,565	8
-"-	50	0,525	4
-"-	100	0,450	50
BA - MA - MAA	4	0,550	
-"-	14	0,545	
-"-	52	0,455	
-"-	90	0,450	

As followed from Table: 1) there is the correlation of polymer-monomer interaction and polymer polarity (water solubility of monomer). Water solubility is 0,025(St); 0,16 (BA); 5,6%(MA) unlimited mixing (AA, MAA). The increase of polymer polarity corresponds to the decrease of parameter μ and increase of polymer-monomer interaction and polymer swelling in monomer; 2) there is the correlation of polymer-monomer interaction and latex stability (coagulum concentration, K) at the high concentration of hydrophilic comonomer (MA, MA and MAA). The increase of polymer-monomer interaction can be accompanied with increasi the polymer swelling in monomer, possibility of the swollen particles coalescence and particles destabilization; 3) there is not correlation between parameters μ and K: a) at the hydrophilic comonomer concentration from 0 to 50%, and b) for BA-MA and BA-MA-MAA latexes.

The results obtained testify that the contribution of polymer-monomer interaction in the particles destabilization is observed only at the high content of hydrophilic monomer. The consideration of the other factors responsible for emulsifier-free latex stability is of necessity. These factors will be discussing in our following report.

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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

DEVELOPMENT OF PARTICLE MORPHOLOGY IN EMULSION POLYMERIZATION. I. CLUSTER MIGRATION.

Luis J. González-Ortiz and José M. Asua

The formation of a structured latex particle occurs through several series-parallel processes including: i) Formation of polymer chains in given positions in the polymer particle; ii) Phase separation to form clusters; and iii) Cluster migration towards the equilibrium morphology. During the migration the size of the cluster may increase by polymerization of monomer inside the cluster, difusion of polymer chains into the cluster, and coagulation with other clusters.

The theoretical approaches for the prediction of the particle morphology fall into two limiting situations: i) the polymer chains do not move from the locus where they are formed (1,2), and ii) the polymer chains are completely mobile and the equilibrium morphology is reached (3,4,5). Although experimental examples of these limiting situations have been reported (6,7), intermediate morphologies found by several authors (8,9,10) show that kinetic factors such as the polymer difusion and the cluster migration can determine the morphology of the polymer particles.

In order to develop a mathematical model including all the kinetic and thermodynamics factors controlling the latex particle morphology, adecuate models for each process should be developed. In this work, a model for cluster migration without polymerization is presented.

A composite latex particle in wich clusters of polymer 1 are dispersed in a matrix of polymer 2 was considered to be the initial state. This situation is similar to that ocurring during the aging of composite latex particles (10,11). This system is in a metastable state and will evolve towards the equilibrium morphology. The motion of the clusters is due to the balance between the Van der Waals forces and the viscous forces. The model includes the calculation of the forces of the interaction of one cluster with each other cluster and with the aqueous phase. Several illustrative simulations have been carried out including systems for which the final equilibrium morphology were: i) core-shell; ii) inverted core-shell; and iii) occluded morphology. The dynamics of the cluster migration depends heavily on the viscosity of the polymer matrix. A good agreement betwen the predictions of the model and previously published experimental results was obtained.

Figures 1 and 2 present an example of the evolution of the particle morphology for occluded equilibrium morphology. It can seen that at the initial state, there are clusters embedded in the surface of the polymer particle and inside of the polymer particle. The shape of the clusters at the surface of the particle is given by the minimization of the interfacial energy, the equilibrium morphology is not a sphere as depicted in figures 1 and 2, but they have an occluded morphology. Although the program calculates the actual shape, the graphic implementation is much more difficult, and hence, in figures 1 and 2, the clusters at the particle surfaces are represented as spheres. Figures 1 and 2 show that in addition to the mutual coagulation of the clusters, they migrate towards the surface of the polymer particle where they also attract each other until the equilibrium morphology is reached. The evolution of the particle morphology given in figures 1 and 2 agrees well with the aging experiments reported by Min et al. (11).

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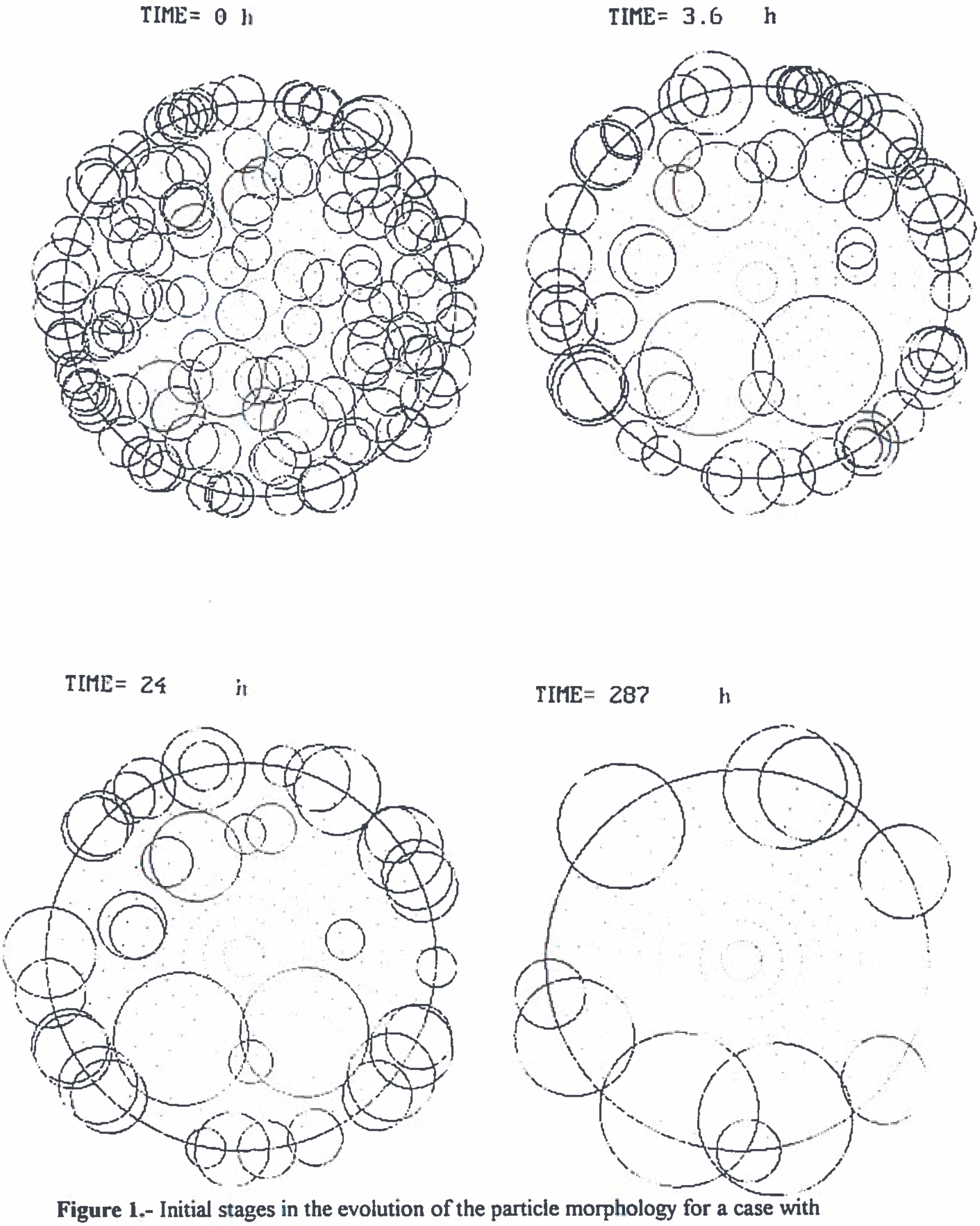

Figure 1.- Initial stages in the evolution of the particle morphology for a case with occluded equilibrium morphology. $\mu=10^8$ Pa.s

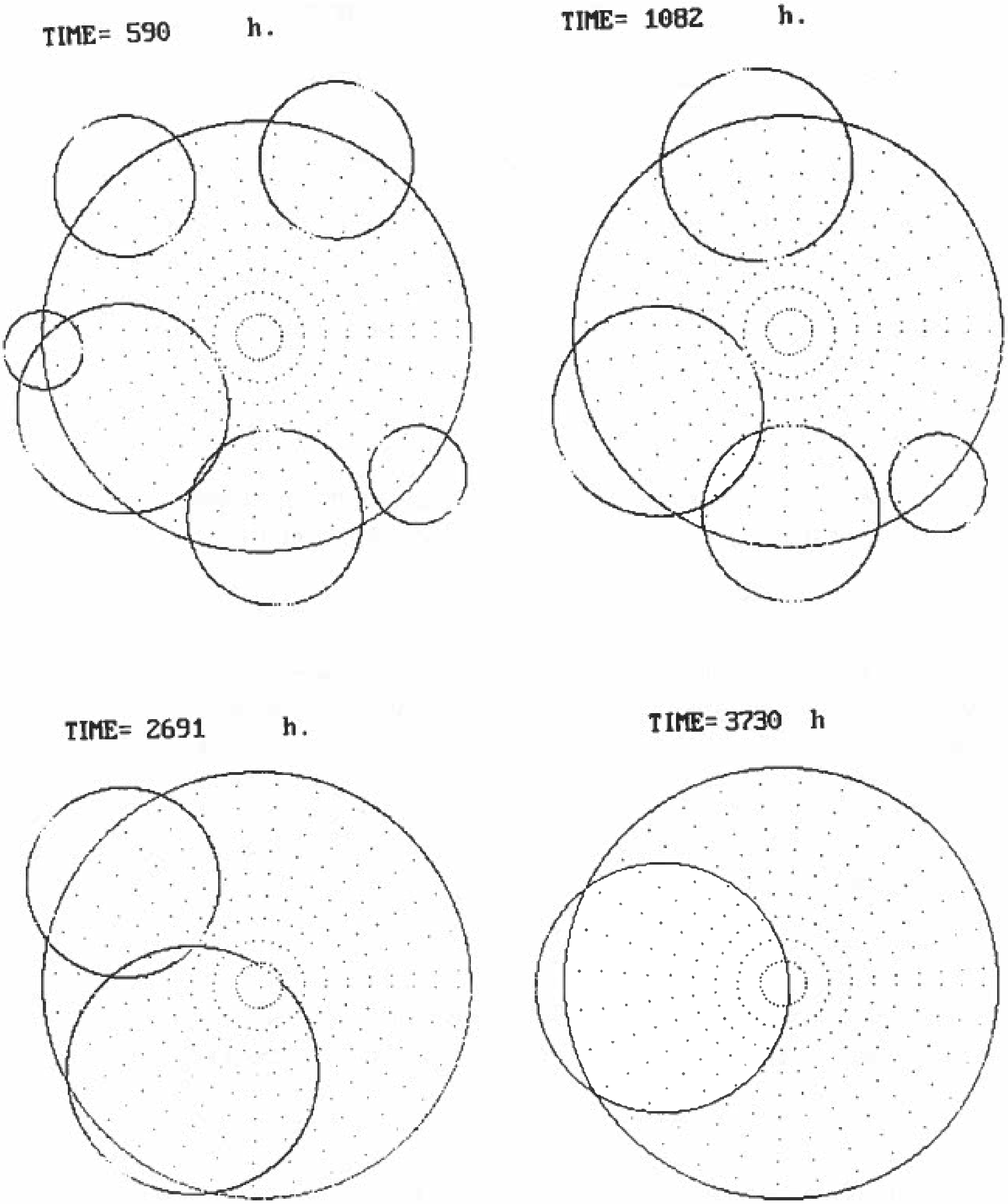

Figure 2.- Final stages in the evolution of the particle morphology for a case with occluded equilibrium morphology. $\mu = 10^8$ Pa.s

CHOICE OF THE MONOMER PARTITION MODEL IN MATHEMATICAL MODELING OF EMULSION COPOLYMERIZATION SYSTEMS

Luis M. Gugliotta, Gurutze Arzamendi and José M. Asua

A criterion for the choice of the monomer partition model in mathematical modeling of emulsion copolymerization systems is presented. In order to develop this criterion, seeded emulsion copolymerizations of several monomer systems with a wide variety of reactivity ratios and water solubilities were simulated using monomer partition models of different complexity. The simulations included different processes, solids contents and amounts of seed. The criterion for the choice of the monomer partition model was made on the basis of using the simplest but sufficiently accurate model.

ESTIMATION OF CONVERSION AND COPOLYMER COMPOSITION SEMICONTINUOUS EMULSION POLYMERIZATION USING CALORIMETRIC DATA

L.M. Gugliotta, M. Arotçarena, J.R. Leiza and J.M. Asua

A new approach to estimate conversion and copolymer composition in semicontinuous emulsion copolymerization systems based on calorimetric measurements was developed. The proposed approach was checked for two different monomer systems: butyl acrylate-styrene and vinyl acetate-butyl acrylate. The estimated values of conversion and copolymer composition obtained from calorimetric data were compared with measurements of conversion and cumulative copolymer composition by gravimetry, gas chromatography and ^{1}H NMR. A good agreement was achieved.

EMULSION COPOLYMERIZATION OF VINYL ESTERS IN CONTINUOUS REACTORS: COMPARISON BETWEEN LOOP AND CONTINUOUS STIRRRED TANK REACTORS

Carlos Abad, José C. de la Cal, and José M. Asua

The high solids emulsion copolymerization of vinyl acetate and veova 10 was studied in a continuous loop reactor and in a CSTR in an attempt to elucidate the similarities and differences between these reactors. Reactions were carried out under comparable conditions, namely, similar macromixing and the same feed composition and space time. The behavior of both reactors was almost the same when the heat generation rate was low, but otherwise thermal runaway occurred in the CSTR whereas the loop reactor temperature was easily controlled.

PARAMETER ESTIMATION IN EMULSION COPOLYMERIZATION USING REACTION CALORIMETER DATA

María J. Barandiaran, Lourdes López de Arbina, José C. de la Cal,
Luis M. Gugliotta and José M. Asua

The feasibility fo estimating the kinetic parameters of emulsion copolymerization using only calorimetric measurements was investigated by simulation. It was found that for the case in which the average number of radicals per particle exceeds 0.5 only two of the three estimable parameters (k_I, k_a, and k_t) could be estimated together provided that an accurate value for the third parameter is available from independent measurements. For systems with n<0.5, the three unknown parameters k_I, k_d and k_a were accurately estimated.

International Polymer Colloid Group Newsletter

Contribution from the Department of Polymerization Reactions, Polymer Institute SAS,
842 36 Bratislava, Slovak Republic

Reporter: J.Barton

Polymerization of Acrylamide in Inverse Microemulsions Under Special Conditions

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The kinetics of free-radical polymerization of water soluble monomers in inverse microemulsion is governed not only by parameters such as reactivity and concentration of reactants but also by factors which are characteristic for a given dispersion system. Thus , for example, percolating behaviour of polymerizable inverse microemulsion Acrylamide/ Water/ Toluene/ AOT (AOT: sodium bis(2- ethyl hexyl) sulfosuccinate) influences the relationship expressing the rate of polymerization and of polymer molecular mass as a function of acrylamide concentration in aqueous phase of the dispersion system. The values of exponents x and y for acrylamide concentration are given in Table together with some other data characterizing the inverse microemulsion prior to polymerization.

TABLE Characteristics of inverse microemulsion

	A	B
[W]/[AOT]	10.3	10.3
[T]/[AOT]	20.1	20.1
ϕ / % 1)	7.2 - 8.3	8.7 - 9.6
[AAm] 2)	0.9 - 3.8	4.7 - 7.5
AAm/W 3)	0.1 - 0.3	0.3 - 0.5
x	1.8	1.4
y	1.1	0.4

1) Volume fraction of aqueous phase.
2) Related to water content of inverse microemulsion.
3) Mass ratio of water and AAm.

The percolating behaviour of the inverse microemulsion influences also the number of polymer chains Np in polymer particle. The average number of Np found for non-percolating (A) system is about 1.5, the percolating (B) system shows the tendency to increase Np (Np ~ 3.5) . Most papers so far published were devoted to polymerization studies in inverse microemulsion systems limited to relatively low aqueous phase volume fraction (Fig., area X). Under suitable conditions polymerization in one-phase system, characterized by higher volume fractions of aqueous phase (ϕ up to 60 % or more) can also be studied (Fig., area Y) . Such systems are easily obtained by adding water solution of AAm to toluene solution of AOT (along the line crossing area Y on Fig.). The dilution of the inverse microemulsion system leads to transformation of W/O dispersion into O/W one. The transformation process is accompanied by strong increase in viscosity (up to 100 mPa s for ϕ ~50 %) and it is characterized by a decrease of reduced rate of AAm polymerization (Rp/[AAm]). Thus, for example, the reduced AAm polymerization rate at ϕ ~ 40 % has a value of 1/5 of that found for ϕ= 10 %.

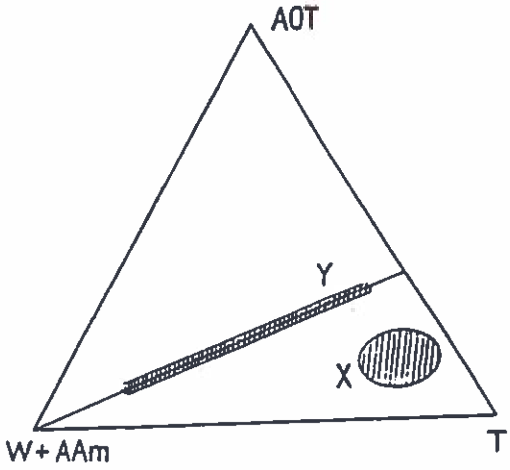

FIG. Pseudoternary diagram of inverse microemulsion toluene T, AOT, water W, acrylamide AAm.

(1 page abstract of invited lecture for 5th SPSJ International Polymer Conference (IPC 94) - Challenges in Polymer Science and Technology- Osaka Japan, November 28th -December 2nd, 1994).

On the Kinetics of Free Radical Microemulsion Colymerization of Butyl Acrylate and Acrylonitrile

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Summary

The o/w microemulsion copolymerizations of butyl acrylate and acrylonitrile initiated by a water (ammonium peroxodisulfate, APS) - and/or oil (dibenzoyl peroxide, DBP) - soluble radical initiator at various initiator concentrations were investigated. The polymerization rate vs. time curve shows a two - interval behavior; initiation (≤ 10% converion) and long termination (≥ 10% conversion) intervals, but no constant interval. The microemulsion copolymerization of butyl acrylate and acrylonitrile is much slower than the microemulsion polymerization of butyl acrylate. The polymerization or the rate per particle is found to be proportional to the 1.06th and 0.96th power or the 0.8th and 0.55th power of the APS and DBP concentration, respectively. The rate of polymerization increases with increasing the particle concentration and the number of particles with increasing initiator concentration.

Introduction

Generally, microemulsions are transparent or translucent "solution" which contain ordinarily immiscible liquids (water, monomer), emulsifier, coemulsifier and additives. Oil-in-water-type (o/w) microemulsion polymerizations of styrene were mostly investigated [1]. There are also several studies on the microemulsion polymerizations of acrylates and methacrylates [2].

A little has been done, however, on the kinetics of o/w microemulsion copolymerizations of unsaturated monomers. Besides, experience shows that the monomer distribution between the continuous phase and the micellar phase plays dominant role on the kinetic and molecular weight parameters and the microstructure of copolymers, as well. Copolymerization systems are more complex than the homopolymerization ones but can give more valuable information about the reaction loci.

The emulsion polymerization or copolymerization that uses oil-soluble initiators was characterized with lower rates, limiting conversions and lower latex stability [3]. Two mechanisms for the production of radicals are proposed: 1) in the monomer - swollen polymer particles formed radicals desorb to the continuous phase and 2) in the continuous phase formed radicals are generated from the fraction of the oil-soluble initiator dissolved in water. Besides, the kinetics of suspension polymerization is also discussed.

mol.dm^{-3}, [BA] = 0.39 mol.dm^{-3} and [AN] = 0.94 mol.dm^{-3}):

1.7 (4% conversion) < 2.9 (7%) < 3.74 (10%) > 3.5 (14%) > 3.0 (17%) > 2.2 (40%) > 1.0 (60%) > 0.2 (80%).

The rate of microemulsion polymerization of butyl acrylate (under the same reaction conditions ([APS] = 0.001 mol.dm^{-3} and [BA] = 0.78 mol.dm^{-3}) is ca. by one order in magnitude larger:

32 (5% conversion) < 48 (10%) < 56 (15%) < 60 (20%) < 64 (30%) > 60 (40%) > 52 (50%) > 44 (60%) > 16 (80%)

The first value denotes the rate of polymerization (in mol.$dm^{-3}.s^{-1}$ x 10^{-4}).

Table 2. Variation of kinetic and colloidal parameters in the microemulsion copolymerization of butyl acrylate and acrylonitrile with DBP concentration.

$[DBP].10^3$ ($mol.dm^{-3}$)	$R_{p,max}.10^4$ 1) ($mol.dm^{-3}.s^{-1}$)	$R_{pp}.10^{22}$ 2) ($mol.s^{-1}.particle^{-1}$)	D 3) (nm)	$N.10^{18}$ 4) /dm^3	[η] 5) ($dl.g^{-1}$)	Conv. 6) (%)
0.5	0.577	0.34	40	1.7		50
1.25	1.443	0.633	39	2.28	4.18	75
2.5	2.62	1.05	39	2.5		85
5.0	3.33	1.15	37	2.9	2.27	85

1-5) see the legend to Table 1. 6) Final conversion at 300 min.

The maximum rate of polymerization is observed at ca. 10% conversion in the AN/BA systems and at ca. 20% in the BA system. The decrease of the rate beyond certain conversion (10% or 20%) is due to the depletion of free monomer phase. The high-water solubility of AN favors the homonucleation of particles which leads to the formation of larger number of primary particles, increased aggregation of primary particles and reaching the monomer- starved conditions at lower conversion range. Besides, the contribution of water-phase polymerization and the growth of particles by agglomeration lead to lower rates of polymerization. Indeed, the polymerization of BA is faster than its copolymerization with AN. In other case, the copolymerization would be faster because the rate constant for propagation for AN is by one order larger in magnitude than that for BA [7].

The rate of polymerization (R_p) was found to increase with increasing the initiator (APS or DBP) concentration (see Table 1 and 2). The reaction order x from the dependence $R_p \propto [APS]^x$ or $[DBP]^x$ was found to be 1.06 or 0.96 for APS or DBP. This reaction order is twice or three-times that for the BA system (0.46 and 0.26 for AP and DBP, respectively). The reaction order x > 0.5 indicates that the unimolecular termination (the first - order radical loss process) of growing radicals is operative.

The reaction order (y) 0.8 or 0.55 estimated from the dependence $R_{pp} \propto [APS]^y$ or $[DBP]^y$ also deviates from the classical emulsion model ($y \leq 0.1$) and the microemulsion polymerization of

BA, as well and favors the unimolecular termination mechanism.

The strong deviation from the micellar model also showed the dependence R_p α N. Here the reaction order was estimated to be as large as 4.

The size of polymer particles was found to decrease and the number of particles to increase with increasing [APS] or [DBP]. The increase in N with [initiator] was relatively slight (the reaction order (z) from the dependence N α [initiatior]^z was as small as 0.2).

Conclusion

Copolymerizations of transparent o/w microemulsions of SDS/water/BA/AN initiated by APS and DBP produce stable and bluish-translucent microlatexes. These latexes contain spherical polybutylacrylate/acrylonitrile particles with diameter ranging from 30 to 40 nm.

A common feature of these microemulsion copolymerizations is the relatively short rise to a maximum rate and the two - interval (nucleation and monomer-starved) process. Monomer - swollen micelles and the monomer-saturated aqueous phase are considered as monomer and emulsifier reservoirs.

The presence of monomer (AN) with a high water-solubility favors both the polymerization in water and the homogeneous nucleation of particles. The polymerization of BA was faster than the copolymerization of BA and AN. This was discussed in terms the homogeneous nucleation, the water phase polymerization and the growth of particles by agglomeration. Thus, the formation of primary particles rich in acrylonitrile by the homogeneous nucleation may favor the growth of particles by agglomeration and occludation of growing radicals. Besides, the polymerization initiated by AP is faster than that initiated by DBP.

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ZINC DESTABILISATION OF CARBOXYLATE-STABILISED LATICES (CONCLUDED)

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This contribution completes the summary of some of the work we have carried out in previous years on the colloidal destabilisation of carboxylate-stabilised latices by sparingly-soluble zinc compounds, in particular, by zinc oxide. The reasons for interest in this topic are given in the first of our contributions on this subject to the Polymer Colloids Group Newsletter. Reference was made there to the detailed investigation into the colloidal destabilisation of well-characterised model polystyrene latices by zinc ammine ions which has been carried out by Nithi-Uthai. These polystyrene latices were used as models for natural rubber latex, the intention being to gain deeper understanding of the colloidal destabilisation of ammonia-preserved natural rubber latex. The polystyrene latices were prepared by seeded emulsion polymerisation, and were essentially monodisperse with particle diameters ranging from *ca.* 90 nm to *ca.* 830 nm. In most cases, the latices were stabilised by adsorbed laurate anions, the effective surface potential in alkaline medium being *typically ca.* −20 mV. The results were interpreted using a value of $4{\cdot}3\times10^{-21}$ J for the effective Hamaker constant for polystyrene particles in water. The zinc ammine ions used to destabilise the latices colloidally were pre-formed in aqueous solution by dissolving precipitated and washed zinc hydroxide in ammonium hydroxide solution.

A particularly interesting observation, to which attention has been drawn in a previous contribution, is that the variation of the effective surface potential of the polymer particles with overall concentration of added zinc ions is consistent with the reduction in effective surface potential being attributable to adsorption of zinc-containing ions in accordance with a Langmuir adsorption isotherm. The particular latex which was used to obtain this result had an average particle diameter of *ca.* 170 nm; the ratio of weight- to number-average particle diameter was 1·052. The latex was stabilised with potassium laurate, the extent of the surface coverage being *ca.* 50%. The rate second-order coefficient, k_{11}, for the reduction of particle number by binary encounters between primary particles was determined by measurement of turbidity as a function of time. Values of the Stern potential, ψ_δ, at the interface between the particles and the aqueous phase were estimated from the variation of k_{11} with pH. The range of pH variation was such that it was reasonable to assume the decrease of k_{11} observed as pH was reduced to be solely a consequence of increase in the concentration of ammonium ions in the latex aqueous phase. Addition of zinc ammine ions brought about progressive reduction in ψ_δ, the variation with concentration of added zinc ammine ions, Z, being well represented by an equation of the Langmuir adsorption isotherm type. The results for ψ_δ as a function of Z gave a very good straight line when plotted as $Z/\Delta\psi_\delta$ against Z, where $\Delta\psi_\delta$ is the reduction in ψ_δ brought about by the addition of the zinc ammine ions. The slope was $0{\cdot}116\ \mathrm{mV}^{-1}$ and the intercept $5{\cdot}25\times10^{-4}\ \mathrm{mol\ dm}^{-3}\ \mathrm{mV}^{-1}$. Using the appropriate parameters derived from these values, the results for $\Delta\psi_\delta$ as a function of Z could be well represented by a curve of the Langmuir adsorption isotherm type.

Assuming that the reduction of ψ_δ was a consequence of interaction between zinc-containing ions and adsorbed laurate anions, and that there was a relationship of direct proportionality between the reduction $\Delta\psi_\delta$ and the concentration of added zinc ions, it follows that the relationship between the concentration of adsorbed zinc ions and the concentration in the aqueous phase was of the Langmuir type. This in turn is consistent with the establishment of a dynamic equilibrium adsorption condition in which zinc ions adsorb on to the particle surface at a rate which is proportional to the number of unreacted laurate sites, and in which zinc ions return to the aqueous phase from the particle surface at a rate which is proportional to the number of zinc-containing laurate sites.

The value of ψ_δ for the latex before addition of zinc ammine ions was $-18{\cdot}9$ mV. The particular isotherm which represents the data for this latex indicates that the maximum attainable value of $\Delta\psi_\delta$ was $8{\cdot}6$ mV (*i.e.*, $(0{\cdot}116\ \mathrm{mV}^{-1})^{-1}$), no matter how high was the concentration of added zinc ammine ions. This implies that the minimum value to which $-\psi_\delta$ could be reduced by addition of zinc ammine ions was $10{\cdot}7$ mV. This is presumably the value of ψ_δ which corresponds to adsorption saturation. That the effective surface potential of a laurate-stabilised polystyrene latex apparently cannot be reduced to near zero by interaction with zinc-containing ions is perhaps surprising. It may be indicative of the facility with which zinc ions can transfer back to the aqueous phase from zinc-carboxylate complexes adsorbed at the particle surface. This is contrary to the usual assumption that the reaction between polyvalent metal ions and surface-active carboxylate anions at latex particle surfaces is essentially irreversible. A second possible explanation for the non-zero limiting value of ψ_δ is that other anions were present at the particle surface besides adsorbed laurate anions. Obvious candidates are sulphate ions derived from the persulphate initiator used to prepare the latices. However, it seems doubtful that the surface concentration of sulphate anions originating in this way would be sufficient to give rise to a Stern potential of $-10{\cdot}7$ mV: this would imply that adsorption of laurate anions to the extent of 50% saturation increases $-\psi_\delta$ by a further $8{\cdot}6$ mV only.

POLYMER COLLOID GROUP NEWSLETTER

Contribution from the Institut Charles Sadron (CRM-EAHP)
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by
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MECHANISM OF THE COPOLYMERIZATION OF ACRYLAMIDE WITH A POLYMERIZABLE SURFACTANT (with V. Vaskova, D. Renoux, M. Bernard and J. Selb)

An important parameter to determine in heterogeneous radical polymerizations is the locus of initiation, as it provides useful information on the kinetic features of particle formation and growth. A possible way to estimate the locus of initiation is to study the polymerization in the presence of paramagnetic nitroxyl inhibitors of various solubilities. The interaction of the inhibitor with the radicals formed from the initiator leads to a decay of the inhibitor radicals which can be monitored by electron spin resonance (ESR). We have attempted to extend this method to a special type of microheterogeneous polymerization system. In this process, a water-soluble monomer (acrylamide, AM) is copolymerized in an aqueous medium with a cationic micelle-forming polymerizable surfactant (hexadecyldimethylvinylbenzyl ammonium chloride, N16), the former being in large excess with respect to the latter (AM content > 95 mol.%). The resulting ion-containing hydrophobically modified polyacrylamides were shown to present some interesting rheological behavior in aqueous solution due to the competition between attractive hydrophobic interactions and repulsive electrostatic interactions.(1)

In this study, three different azo initiators of varying solubility in water have been considered. One is water-soluble, ACVA (2,2'-azobis (2-cyanovaleric acid)), the two others are water-insoluble, AIBN (2,2'-azobis isobutyronitrile) and AVBN (2,2'-azobis (2,4-dimethylvaleronitrile)), the latter being more hydrophobic than the former. Three inhibitors of various solubilities have been used : the water-soluble Fremy's salt (Potassium nitrosodisulfonate, FS), the predominantly water-soluble HTPO (4-hydroxy-2,26,6-tetramethyl-piperidinyloxy) and the predominantly oil-soluble STPO (4-stearoyl-2,2,6,6-tetramethyl-piperidinyloxy). In addition to ESR measurements, the inhibition period and the subseqent monomer to polymer conversion have been determined by monitoring either the consumption of the monomers (UV spectroscopy) or the formation of the polymer (gravimetry). An example of the decay of the inhibitor and of the subsequent polymerization is given in Figure 1 for the system AM + N16 + (ACVA/HTPO)

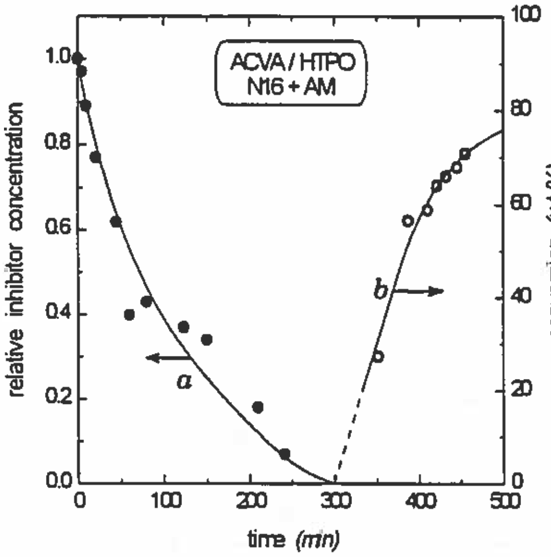

Figure 1. : ACVA/HTPO pair
a) HTPO decay with time
b) conversion-time data

The results relative to the overall data show that no general rules can be drawn out from simple considerations based on the initiator solubility (oil-soluble or water-soluble). For the hydrophilic ACVA initiator, the polymerization starts in the aqueous continuous phase as expected. For the hydrophobic AIBN initiator mainly localized within the micelles, it is the small fraction of AIBN radicals dissolved in water which initiate the copolymerization. On the other hand, the cage-effect responsible for the lowering in the factor efficiency of the oil-soluble initiators trapped within the micelles, is more or less operative, depending on the chemical nature of the azo initiators. While the cage-effect is important in AIBN system, it does not seem to be operative in ABVN systems, likely due to the larger size and lower diffusion rate of the latter radicals. Polymerization initiation within the micellar phase is therefore possible in this case.

Further studies will aim at showing how the different loci of initiation affect the characteristics and therefore the behavior of the copolymers formed in this process.

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METHOD FOR THE SCALE-UP OF POLYMERIZATION PROCESSES USING THE METTLER RC-1 CALORIMETER

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ABSTRACT

A method is described to scale-up polymerization processes using the Mettler RC-1 reaction calorimeter. The method consists in combining a series of specific polymerizations in the Mettler RC-1 reaction calorimeter with a simple mathematical treatment. The kinetic behavior is thus quickly predicted without the need of elaborate mechanistic details. The combination of experimentation and the mathematical treatment allows one ultimately to predict the thermal response of different size reactors. The method is demonstrated for a suspension and an emulsion polymerization process.

INTRODUCTION

One of the limitations in the scale-up of chemical processes is the need for a kinetic model to predict the thermal response of the process in a large reactor. Even though the kinetics of free radical polymerization are in general well understood, the values for the rate constants of the different physical events that determine the rate of polymerization and thus the rate of heat generation are difficult to obtain. As a result, a large scattering of values for propagation and termination rate constants is found in the literature for any particular monomer system [1]. In cases like emulsion polymerization the kind of physical events that determine the kinetics of the systems such as particle generation, particle disappearance, radical entry, radical desorption and chain termination may change as the temperature changes, making the development of mathematical models to predict all these events complicated [2]. This paper presents an approach to circumvent some of these difficulties by combining a protocol of experiments in a calorimeter such as the Mettler RC-1, a mathematical treatment of the data and the solution of the heat balance equation for the reactor under consideration. The process is illustrated for two polymerization processes with substantial differences in kinetics: suspension polymerization and emulsion polymerization.

EXPERIMENTAL

All polymerizations were carried out in a Mettler RC-1 reaction calorimeter. The reactor used in the calorimeter was Mettler's MP-10 reactor equipped with metal inserts.

DESCRIPTION OF THE METHOD

In order to predict the behavior of a particular reactor the following heat balance equation needs to be solved

$$-dQr/dt + UA\,(Tr-Tj) + m\,Cp\,dTr/dt + Qloss = 0 \qquad (1)$$

where dQr/dt is the rate of heat generation during the polymerization, U is the overall heat transfer coefficient, A is the area over which heat transfer takes place between the jacket and the reactor, m is the mass in the reactor, Cp is the heat capacity of the mass in the reactor, Tr is the temperature of the reactor, Tj is the temperature of the jacket of the reactor and Qloss is the rate of heat losses in the system.

The change of dQr/dt as a function of time and temperature is the key parameter that needs to be predicted to solve equation (1).

The method proposed here consists of carrying out a series of isothermal reactions in the RC-1 at different temperatures that cover the range of temperatures expected during the exotherm in the reactor under consideration for scale-up. With these reactions, curves of the rate of heat generation due to polymerization (dQr/dt) versus the calorimetric conversion are constructed for each temperature. Calorimetric conversion is defined as

$$x = \int_0^t (dQr/dt)\,dt / \int_0^{tf} (dQr/dt)\,dt \quad \text{or} \quad x = \int_0^t (dQr/dt)dt \,/\, (M \;\; \Delta Hp) \qquad (2)$$

where x is the conversion, M is the monomer mass and ΔHp is the enthalpy of polymerization.

The curves of dQr/dt versus conversion are fit to a mathematical equation. The same mathematical function is used for all temperatures. In this manner, the values of the coefficients of the equation are generated as a function of the polymerization temperature (reactor temperature) and a general equation expressing the value of dQr/dt as a function of conversion and reactor temperature (Tr) is obtained. This function will be called dQr/dt(x,Tr).

Once dQr/dt(x,Tr) is known, the heat balance (equation 1) is solved for the RC-1 calorimeter using a constant value of Tj and the evolution of Tr as a function of time in the RC-1 calorimeter is predicted. The algorithm used to solve the heat balance equation with the function dQr/dt(x,Tr) will be explained in the next section. The model prediction is compared with the experimental values obtained in an actual run in the RC-1 when the temperature of the jacket is held constant at a given Tj value. Comparing the predicted values and the experimental values for the constant Tj run, one can assess the accuracy of the empirical model and do adjustments to dQr/dt(x,Tr). This step allows the validation of the model without the need of using a different size reactor. When reasonable agreement is obtained, the value of the parameters for the large reactor (mass, overall heat transfer coefficient, transfer area, and temperature control algorithm) can be inserted in equation (1) and predictions of the feasibility of the scale-up in the reactor under consideration can be obtained. For a different size reactor the heat generated due to polymerization will be given by the expression:

$$dQr/dt = (Mr/Mrc1)\, dQr/dt(x,Tr) \qquad (3)$$

where Mr is the monomer mass in the reactor under consideration and Mrc1 is the monomer mass used in the experiments in the Mettler RC-1 calorimeter.

Mathematical Algorithm

It is important to explain why to use curves of dQr/dt versus conversion to generate a function dQr/dt(x, Tr), instead of using curves of dQr/dt versus time to generate a function dQr/dt(t, Tr), which depends on time and reactor temperature. At a first glance it seems more obvious to use dQr/dt(t,Tr) to solve the differential equation, since the ultimate goal is to determine the evolution of the reactor temperature as a function of time and not conversion.

The heat produced during the polymerization is the result of the conversion of monomer to polymer. Regardless of the thermal history followed to convert the monomer to polymer, the mass and energy conservation principles have to be satisfied. The total amount of energy released is given by the enthalpy of polymerization multiplied by the amount of mass converted from monomer to polymer. The total amount of energy produced during the polymerization is thus independent of the thermal path taken to convert the monomer to the polymer.

Mathematically, the polymerization process in a non-isothermal reactor can be visualized as a continuum of curves of dQr/dt versus time for each polymerization temperature. As the temperature of the reactor changes we move from one curve to another. Let us consider using absolute time continuum as the only criteria to switch from curve to curve. As time increases and the temperature of the reactor increases, we would move to points in curves where the polymerization rate would correspond to a conversion higher than the true conversion. On the other hand, as time continues and the temperature of the reactor decreases we would move to curves corresponding to lower temperatures, but because the criteria used to move from curve to curve was a time continuum criteria only, we would move to points in curves with values of dQr/dt that would correspond to points where the conversion is lower than that in the time interval before. Thus, the mass conservation principle would not hold. Another consequence is that the value of the integral of dQr/dt over the time that the polymerization takes place would have different values depending on the thermal path taken.

A boundary condition to take into account the mass balance must be used. This condition states that for each time interval under consideration, the value of dQr/dt at the beginning of that interval is given by the curve of dQr/dt corresponding to the particular value of Tr at the point where the conversion has a value similar to the conversion at the end of the previous time interval.

There are two ways to mathematically apply this boundary condition. In the first approach, for each integration step used to solve the differential equation, the function dQr/dt(t,Tr) is solved with the value of Tr obtained during the solution of the differential equation to determine the time t for which the integral of the function dQr/dt(t,Tr) between t=0 and t=t is equal to the amount of heat produced up to the end of the previous time interval. The value for the time thus obtained is substituted in the function dQr/dt(t,Tr) and the value of dQr/dt is calculated and inserted in the heat balance equation being solved in the interval under consideration. The process is iterated until convergence is obtained for the time interval. This method is cumbersome and computationally intensive.

The second approach is simpler and is the one used in this paper. For each time interval used to solve the differential equation (1) it is considered that the conversion at the beginning of the interval is that at the end of the previous time interval. The conversion is defined as the integral (summation) of the calculated values of dQr/dt up to that time divided by the product of the monomer mass times the enthalpy of polymerization. The value of dQr/dt is obtained from the fitted function dQr/dt(x,Tr) for the value of Tr estimated by the differential equation solving algorithm (Runge-Kutta-Fehldberg) and the value of the conversion at the end of the previous time interval. The value of dQr/dt is inserted in the differential equation to calculate the time derivative. A new estimate of Tr is obtained for the corresponding value of dQr/dt. The new conversion is calculated at that point and used for the next iteration until convergence occurs.

The following sections describe the process applied to suspension and emulsion polymerization.

APPLICATION OF THE METHOD TO SUSPENSION POLYMERIZATION

In suspension polymerization the polymerization kinetics are similar to those occurring in a bulk process. The type of physical events taking place during the polymerization do not change with temperature, only their magnitude changes. The series of physical events that occur are radical generation (initiation), radical propagation (chain growth) and radical termination (chain termination). The rate of polymerization (Rp) is given by [3]

$$Rp = k_p\,[M]\,(f\,k_d\,[I]/k_t)^{0.5} \tag{4}$$

where k_p is the propagation rate constant, [M] is the monomer concentration, k_d is the initiator decomposition rate constant, f is the initiator efficiency, [I] is the initiator concentration and k_t is the termination rate constant. As the polymerization temperature changes only the values of the rate constant coefficients change.

Figure 1 shows the rate of heat generation by the polymerization (in watts) as a function of time for three different polymerization temperatures (60°C, 65°C and 70°C). From these plots, curves of dQr/dt as function of conversion can be obtained.

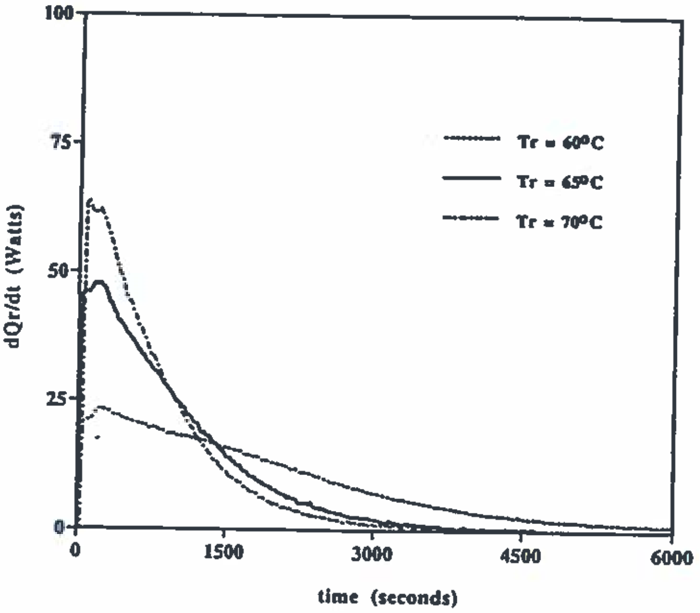

Figure 1: Evolution of dQr/dt as a function of time for suspension polymerization at three different temperatures.

Figure 2 shows curves of dQr/dt as a function of conversion for the three temperatures and the values fitted using the equation:

$$dQr/dt(x,Tr) = a - b\,x + c\,x^{1.5} - d\,e^{x} + f\,x^{0.5} \qquad (5)$$

The dependence of the coefficients with the polymerization temperature is obtained from Arhenius plots of the values of the coefficients versus temperature. These dependencies are:

$$\ln a = 36.50 - 10549.98/Tr \qquad (6)$$

$$\ln b = 51.41 - 15323.79/Tr \qquad (7)$$

$$\ln c = 44.99 - 13110.3/Tr \qquad (8)$$

$$\ln d = 38.02 - 11074.19/Tr \qquad (9)$$

$$\ln f = 48.68 - 14560.96/Tr \qquad (10)$$

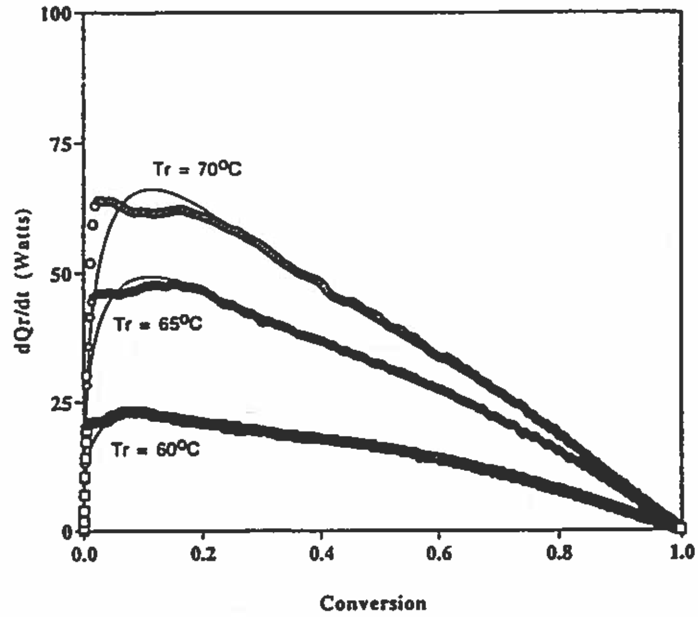

Figure 2: Evolution of dQr/dt as a function of conversion for suspension polymerization at three different temperatures. Symbols represent experimental results; continuous lines represent fitted equations.

The heat balance for the MP-10 reactor of the RC-1 calorimeter is given by a rearranged form of equation (1):

$$dTr/dt = dQr/dt(x,Tr) / (mCp) - UATr / (mCp) + UATj / (mCp) + $$
$$+ Qloss / (mCp) \qquad (11)$$

The equation was solved for two cases: one where the temperature of the jacket (Tj) in the RC-1 was kept constant at 60°C and another one where the temperature of the jacket was kept constant at 65°C. The value determined for UA in the RC-1 was 4.22 W/°K. The value of Qloss as a function of Tr was determined experimentally for the reactor from a plot of UA(Tr-Tj) versus Tr at isothermal values of Tr (from 60°C to 75°C) in the absence of any reaction. The relationship found was:

$$Qloss = 136.87 - 0.418\ Tr \qquad (12)$$

where Qloss has units of watts and Tr is in degrees Kelvin.

Figures 3 and 4 show the prediction of the model and the actual experimental curves obtained in the RC-1 by running polymerizations under isothermal jacket control at 60°C and 65°C respectively. The agreement is very good, with a small deviation at peak temperature.

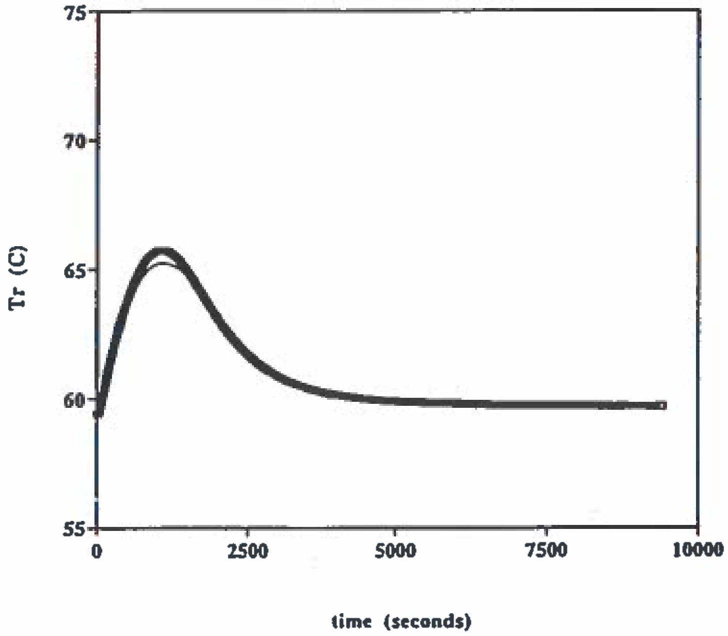

Figure 3: Comparison between the experimental results (symbols) and model predictions (continuous thin line) for the evolution of the reactor temperature (Tr) in a suspension polymerization conducted under constant Tj value of 60°C.

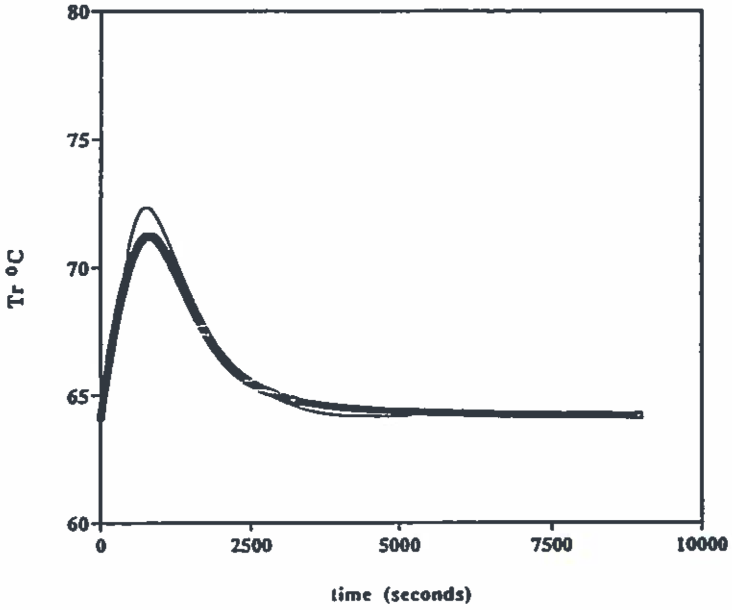

Figure 4: Comparison between the experimental results (symbols) and model predictions (continuous thin line) for the evolution of the reactor temperature (Tr) in a suspension polymerization conducted under constant Tj value of 65°C.

APPLICATION OF THE METHOD TO EMULSION POLYMERIZATION

The method presented in this paper was applied to an emulsion polymerization process. The kinetics of free radical emulsion polymerization are significantly different that those of solution, bulk or suspension free radical polymerization because of the different physical events that take place. Without getting into mechanistic details, the rate of polymerization in an emulsion polymerization process is given by [4]:

$$Rp = k_p [M]_p \bar{n} Np/N_A \tag{13}$$

where k_p is the propagation rate constant, $[M]_p$ is the monomer concentration in the polymer particles, $\bar{n}$ is the average number of radicals per polymer particle, Np is the concentration of polymer particles and N_A is the Avogradro number. The number of polymer particles is determined by the particle nucleation mechanism and stability of the particles. The average number of radicals per particle is determined by events such as radical entry, radical desorption and radical termination.

Because of the direct dependence of the rate of polymerization and therefore the rate of heat generation on the number of particles, the approach described before needs to be modified slightly. In emulsion polymerization, particle nucleation takes place over a very short conversion interval (less than 5% conversion). The number of particles is strongly dependent on the temperature over which the nucleation takes place. In systems where the number of particles is constant after the nucleation period is finished, it is safe to assume that the number of particles in a non-isothermal reactor is determined by the temperature at which the polymerization is started. Using this approximation, the only modification that needs to be done is the use of the function:

$$(1/Np(Tr))\ dQr/dt(x,Tr) \tag{14}$$

instead of dQr/dt(x,Tr), where Np(Tr) is the number of particles generated at the temperature Tr.

The heat balance for the MP-10 reactor of the RC-1 will be given by

$$dTr/dt = (Np(Tr_o)/Np(Tr))\ dQr/dt(x,Tr) / (mCp) - UATr / (mCp)$$

$$+ UA\ Tj / (mCp) + Qloss / (mCp) \tag{15}$$

where $Np(Tr_o)$ is the number of particles generated at the initial temperature Tr_o.

Figure 5 shows the rate of heat generation (dQr/dt) during the emulsion polymerization for three emulsion polymerizations carried in isothermal (Tr control) conditions at 60°C, 65°C and 70°C.

Notice the different experimental profiles of dQr/dt obtained for the emulsion polymerization compared to those obtained in the suspension polymerization process, this is a reflection of the different physical events taking place.

The dependence of the coefficients on the polymerization temperature is obtained, as in the case for the suspension polymerization process, from Arhenius plots of the values of each coefficients versus the temperature. The results are:

$$\ln a = -74.13 + 53754/Tr - 885197/Tr^2 \quad (17)$$

$$\ln b = 1.757 + 1743.2/Tr \quad (18)$$

$$\ln c = 248.95 - 161063.88/Tr + 26675041.13/Tr^2 \quad (19)$$

$$\ln d = 16.743 - 3612.37/Tr \quad (20)$$

$$\ln f = -58.021 + 42965.39/Tr - 7045340.96/Tr^2 \quad (21)$$

Figure 7 shows the number of particles generated as a function of the polymerization temperature. From this information an expression for the dependence of the number of particles generated as a function of temperature can be obtained

$$Np(Tr) = 4.86\ 10^{18} - (1.48\ 10^{21} / Tr) \quad (22)$$

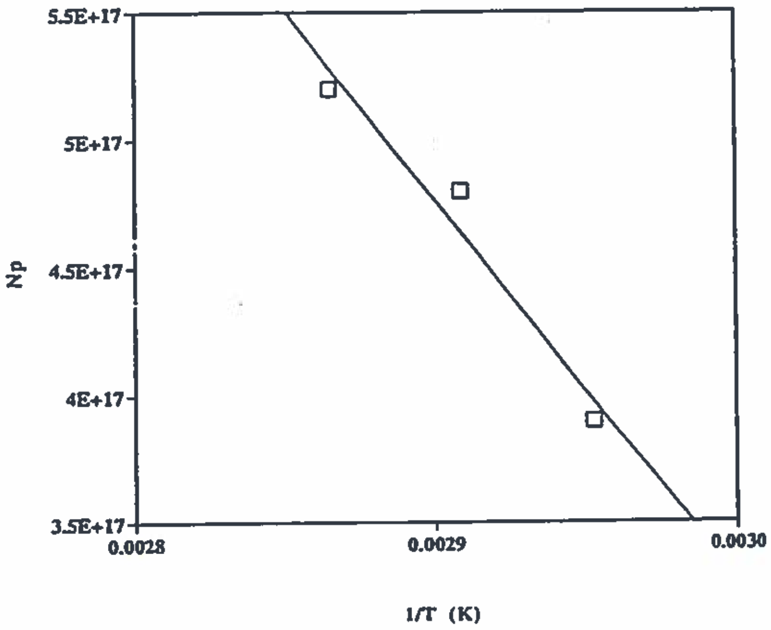

Figure 7: Number of polymer particles as a function of polymerization temperature.

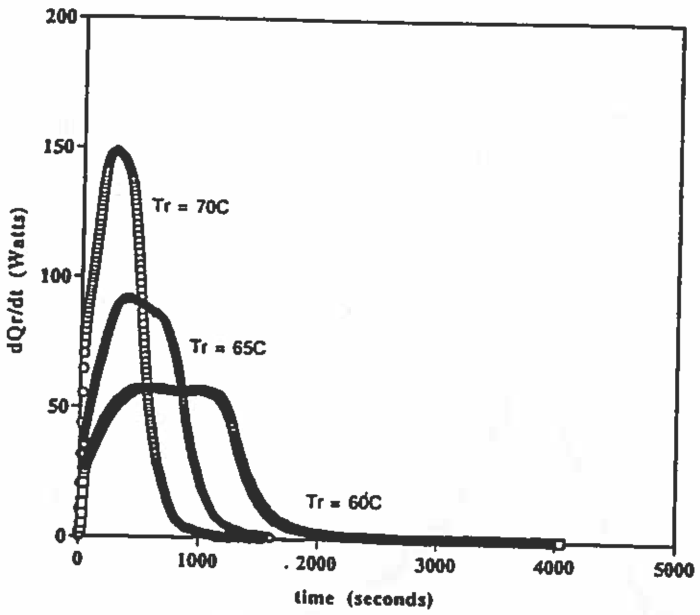

Figure 5: Evolution of dQr/dt as a function of time for emulsion polymerization at three different temperatures.

Figure 6 shows the experimental curves for dQr/dt as a function of conversion for the three temperatures and the fitted curves using the equation

$$dQr/dt(x,Tr) = -a + b\,x - c\,x^3 + d\,x^{0.5} + f\,e^{-x} \quad (16)$$

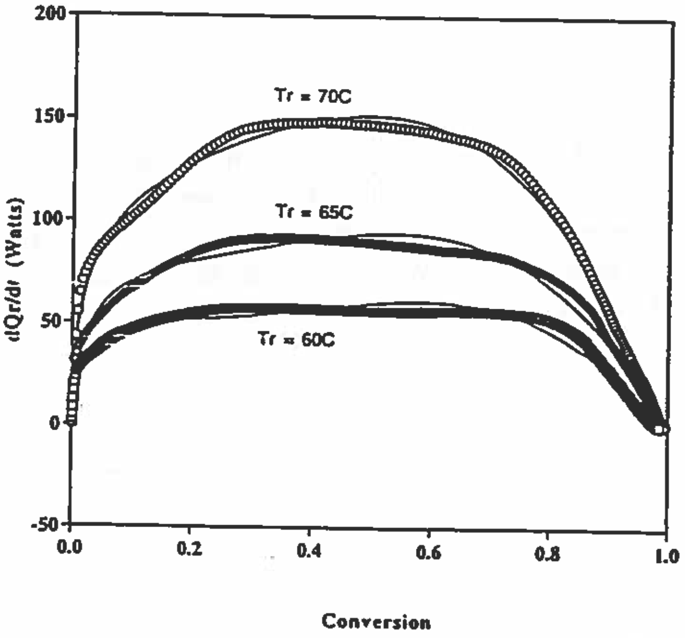

Figure 6: Evolution of dQr/dt as a function of conversion for emulsion polymerization at three different temperatures. Symbols represent experimental results; continuous lines represent fitted equations.

Figure 8 shows the predictions obtained when equation (15) was solved compared with the experimental values for an emulsion polymerization carried in the RC-1 calorimeter under constant Tj condition. In the experiment as well as in the simulation the temperature of the jacket was maintained at 60°C.

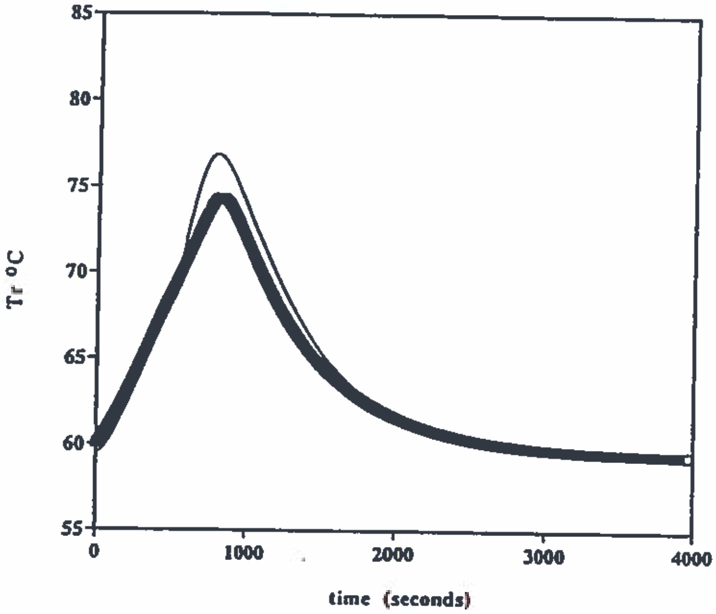

Figure 8: Comparison between the experimental results (symbols) and model predictions (continuous thin line) for the evolution of the reactor temperature (Tr) in an emulsion polymerization conducted under constant Tj value of 60°C.

CONCLUSIONS

A method has been presented to evaluate polymerization processes for scale-up purposes. The method circumvents the need of an accurate kinetic model to describe the polymerization process and the experimental determination of rate constants. The method relays on experimental kinetic information obtained in a reaction calorimeter. The method consists of the following steps:

1.- Experimental determination of kinetics:

A series of isothermal polymerizations are run at different temperatures in a reaction calorimeter such a Mettler's RC-1 reaction calorimeter.

2.- Curve fitting:

From the experimental results, curves of dQr/dt versus conversion are built and fit to a mathematical function. By using the same mathematical function for all the temperatures, the values of the coefficients of the mathematical function can be obtained as a function of temperature. At the end of this step a function dQr/dt(x,Tr) is obtained which provides values of dQr/dt for any value of conversion and temperature.

3.- Model validation:

3a.- The heat balance differential equation for the reactor of the calorimeter, is solved numerically for a constant value of Tj, using the function dQr/dt(x,Tr) to obtain the value of the rate of heat generation due to polymerization at any given conversion and reactor temperature. Predictions of the temperature of the RC-1 reactor as a function of time are obtained.

3b.- The model is validated by running polymerizations in the reaction calorimeter polymerizations under constant Tj control mode. The experimental values of the evolution of the reactor temperature as a function of time are compared with the predictions of step 3a.

4.- Model correction:

Adjustments are made to dQr/dt(x,Tr) until agreement is obtained between the predictions for the polymerization under constant Tj in the calorimeter and the experimental results.

5.- Predictions:

The heat balance equation for the reactor under consideration is solved using the function (Mr/Mrc1)dQr/dt(x,Tr), where Mrc1 is the mass of monomer in the calorimeter run and Mr is the mass of monomer in the reactor under consideration.

The method has been applied to suspension polymerization showing good agreement with experimental results. For emulsion polymerization the dependence of the number of polymer particles generated during the polymerization with the temperature is needed to estimate correctly the rate of heat generation.

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Contribution to the International Polymer Colloids Group Newsletter

E.S. Daniels, V.L. Dimonie, M.S. El-Aasser, A. Klein,
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The titles of our current research projects are given in the **Contents** of our *Graduate Research Progress Reports*, No. 42, July, 1994, which can be found at the end of this report. Summaries of progress in several research areas are presented here.

1. Details of the Emulsion Polymerization of Styrene Using a Reaction Calorimeter

Luis Varela de la Rosa

Emulsion polymerization has been traditionally described as a process consisting of three Intervals: Interval I, where latex particles are formed, Interval II, where the number of particles and the rate of polymerization are constant, and Interval III, where monomer droplets no longer exist and the rate of polymerization decreases. Although Interval I can be considered the most important stage because particles are formed here, Interval II has been described as being the most representative period of the emulsion polymerization process. The onset and end of this interval have been defined based on different parameters or variables. It has been reported that Interval II begins when micelles disappear and the number of polymer particles and the rate of polymerization reach steady values. However, the rate of polymerization has been typically obtained from the slope of the conversion-time curve, which appears to be approximately constant at some point in the process, and is usually assumed to be truly constant. Based on this assumption, a constant rate period is obtained which is considered characteristic of the emulsion polymerization process. The disappearance of monomer droplets leading to a decrease in the rate of polymerization, marks the end of Interval II.

The RC1 reaction calorimeter has shown obvious advantages over the traditional techniques of measuring emulsion polymerization reaction kinetics, such as gravimetry and gas chromatography. Using the calorimetric technique, the rate of polymerization is determined directly and a more detailed picture of the process is obtained. This technique, contrary to what was expected, has shown no Interval II in emulsion polymerizations of styrene performed above the critical micelle concentration (CMC) of the surfactant (sodium lauryl sulfate). These experiments were instead characterized by an increase in the heat of reaction (polymerization rate) to a maximum, which was experimentally determined to be the end of Interval I and the beginning of Interval III. This maximum was shown to be independent of both the emulsifier and initiator concentrations, and appears between 35 and 40% conversion as shown by the results presented in Figure 1. By knowing the conversion at which the maximum in the heat of reaction occurs, the monomer concentration in the polymer particles was determined to be 5.62 ± 0.07 mole/l. This

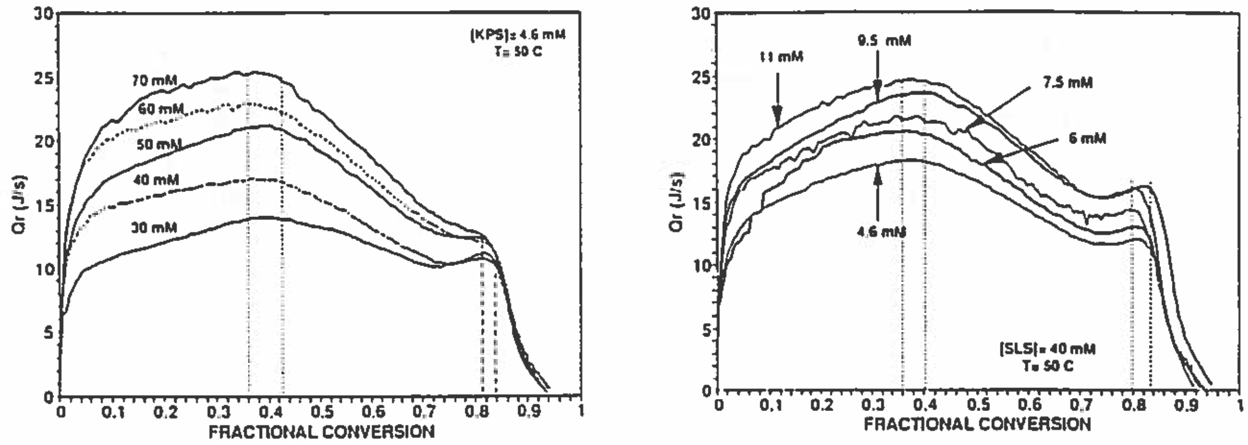

Figure 1: *Effect of emulsifier (left) and initiator (right) concentrations on the heat of reaction as a function of conversion for the emulsion polymerization of styrene in the RC1 reaction calorimeter; T= 50°C.*

value is close to the 5.48 mole/l reported in the literature. Combining this value with the rate of polymerization and number of polymer particles data, the average number of radicals per particle can be calculated. Thus, important kinetic parameters in emulsion polymerization can be calculated using the calorimetric technique.

The results reported in Figure 2, showing the evolution of the rate of polymerization and the number of particles, suggest that nucleation ends and monomer droplets disappear almost simultaneously, which is contrary to what has been reported where nucleation ends first, indicating the end of Interval I, and Interval II ends when monomer droplets disappear. However, as shown in Figure 3, measurements of the latex surface tension (T_s) suggest that micelles may

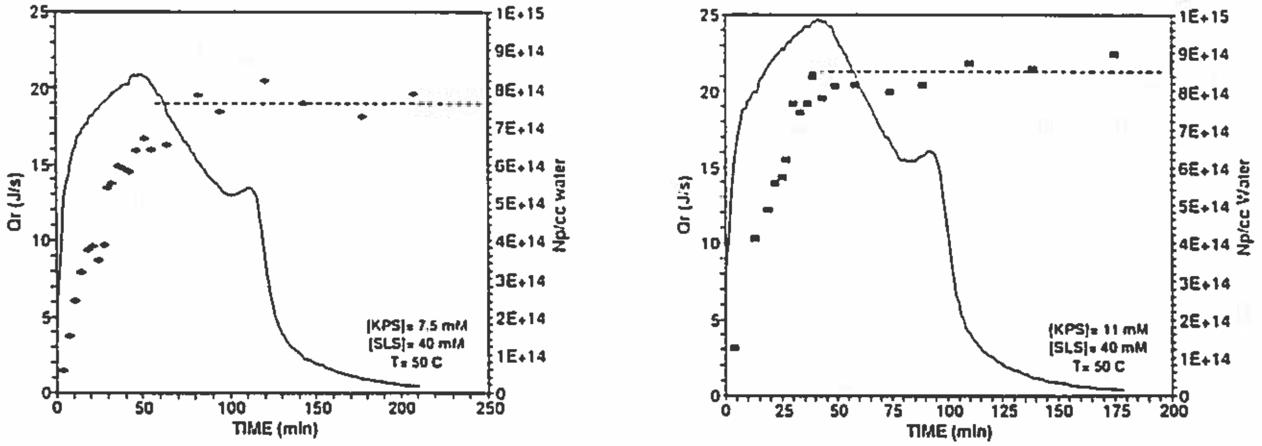

Figure 2: *Number of particles and heat of reaction as a function of time for the emulsion polymerization of styrene in the RC1 reaction calorimeter;*$[K_2S_2O_8] = 7.5$ *mM (left) and 11 mM (right);* $[SLS] = 40$ *mM, T = 50°C.*

disappear earlier in the reaction, leading to the conclusion that particle formation takes place by two nucleation mechanisms in the experiments conducted above the CMC: first micellar nucleation followed by homogeneous nucleation. By combining the rate of polymerization and the T_s results, it seems that the disappearance of micelles corresponds to a decrease in the slope of the heat of reaction curve. This change in the slope of the heat of reaction curve takes place between 5 and 10% conversion, and is also independent of both the emulsifier and initiator concentrations.

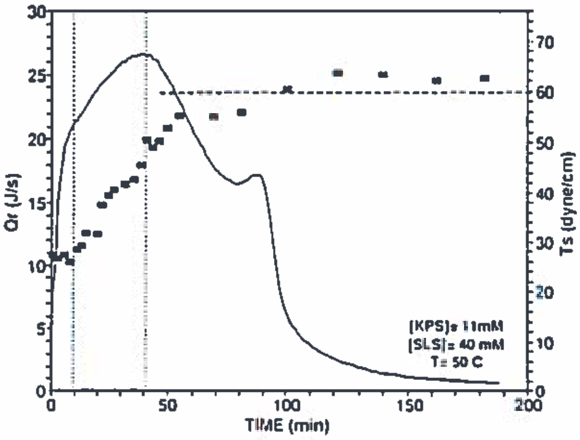

Figure 3: *Heat of reaction and surface tension as a function of time for the emulsion polymerization of styrene in the RC1 reaction calorimeter; [SLS]= 40 mM, [KPS]= 11 mM, T= 50°C.*

From these results, the emulsion polymerization of styrene performed above the CMC of SLS can still be divided into the three classical intervals, but with important differences, namely:

- Interval I: the rate of polymerization (heat of reaction) and number of particles increase. Micelle disappearance marks the end of this interval (indicated by the first change in the slope of the heat of reaction curve). Monomer droplets are present.

- Interval II: the rate of polymerization and number of particles increase. Particle formation takes place predominantly by homogeneous nucleation. Monomer droplets are present. The maximum in the heat of reaction curve determines the end of this interval and the end of nucleation.

- Interval III: the rate of polymerization decreases because the monomer concentration in the polymer particles decreases. The number of particles is constant. Monomer droplets disappear at the beginning of this interval (maximum in the heat of reaction curve).

2. Emulsion Copolymerization of Styrene and n-Butyl Acrylate Using an Automated Reaction Calorimeter

Eser Özdeğer

Styrene/n-butyl acrylate copolymers are commercially important for many paints, adhesives, and coatings. Differences in their monomer reactivities and water solubilities, and their glass transition temperatures makes it interesting to study them as a pair. In addition, their emulsion copolymerization using a nonionic surfactant as stabilizer has shown peculiarities in terms of the kinetics of the copolymerizations in recent studies of the effects of agitation on the polymerization.

In emulsion polymerization, the role of mixing is two-fold. In addition to maintaining a uniform temperature throughout the reactor, it controls the degree of dispersion of the immiscible oil (monomer) phase in the continuous aqueous medium. This is important throughout roughly the first half of the reaction in which the monomer droplets serve as reservoirs supplying monomer by diffusion to the growing (polymerizing) submicron polymer particles. The stability of the particles, as manifested by coagulum formation, can also be dependent on the shear to which the latex is subjected during various phases of the reaction.

In the preliminary studies using the RC1 Reaction Calorimeter, the impeller type and agitation speed used to form the emulsion were both shown to affect the kinetics of the copolymerization and the resulting particle size distribution. It was seen that for each impeller [A310 fluidfoil (Mixing Equipment Co.), turbine impeller (Mettler Toledo A.G.), and Rushton impeller (Mixing Equipment Co.)] and agitation speed, the heat of reaction curves which are proportional to rate of polymerization curves, did not follow the rate behavior observed in classical emulsion polymerization. In addition, each impeller resulted in a rate behavior that differed from the other two. Figure 4 shows the effect of impeller type on the kinetics and final latex particle size distribution of the emulsion copolymerization of styrene and n-butyl acrylate.

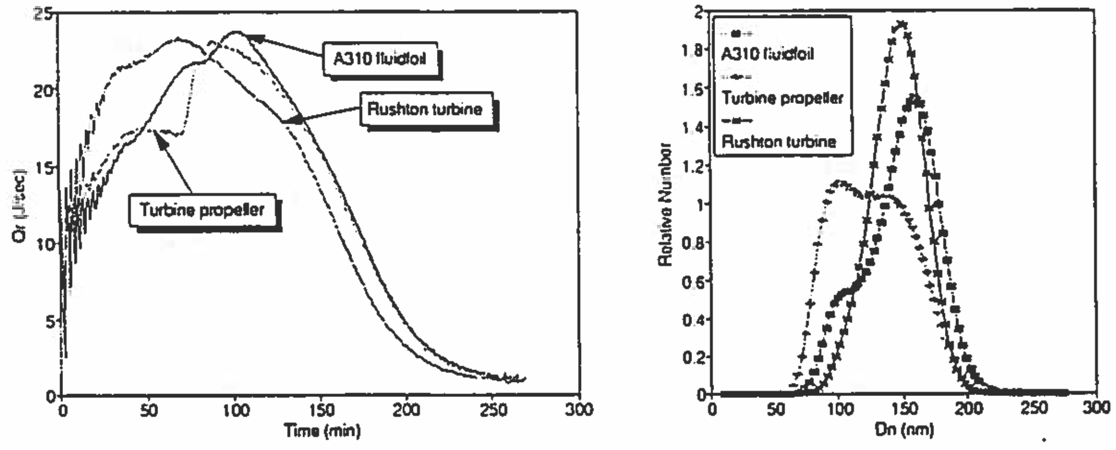

Figure 4: *Heat of reaction profiles with respect to time (left) and final latex particle size distributions (right) for the copolymerizations of styrene and n-butyl acrylate using different impellers;* $T_r = 70^{\circ}C$.

In order to explain these rate behaviors and determine the heats of reaction, homopolymerizations of styrene and n-butyl acrylate were carried out. It was seen that under the same experimental conditions, butyl acrylate and styrene exhibited very different reaction behaviors. Butyl acrylate polymerized quickly (high conversion in 45 - 50 min) with the nucleation of particles being followed by limited aggregation and a secondary nucleation, resulting in a broad unimodal particle size distribution. On the other hand, styrene polymerized slowly (high conversion in 10.5 hrs). Two distinct nucleation periods were found leading to a multimodal particle size distribution.

When the homopolymerizations were compared to the copolymerizations of styrene and n-butyl acrylate, it was seen that they have similarities as well as differences. The styrene homopolymerization resembled the styrene/n-butyl acrylate copolymerization in terms of the heat of reaction profiles with limited aggregation accompanying the initial nucleation. Also, secondary nucleation was seen to occur at ~ 40 % conversion for both of the polymerizations resulting in multimodal particle size distributions. Even though the same kind of nucleation scheme was observed for both the n-butyl acrylate homopolymerization and the styrene/n-butyl acrylate copolymerization, the butyl acrylate homopolymerization yielded a unimodal particle size distribution, whereas the copolymerization yielded a bimodal particle size distribution.

The solids content was shown to be an important process variable in studying the effect of agitation speed and impeller type. At 30% solids, it was seen that the impeller type had no effect while the impeller speed had little significant effect on both the kinetics and number of particles produced in the copolymerization of styrene and n-butyl acrylate. On the other hand, at 50% solids, the impeller type was shown to affect the nucleation of particles and thus the final particle size distribution. Using the A310 fluidfoil impeller, intermittent nucleation took place during the copolymerization of styrene and n-butyl acrylate resulting in a bimodal particle size distribution, whereas using the Rushton impeller, continuous nucleation took place resulting in a unimodal particle size distribution.

3. Polymerization of Miniemulsions Prepared from Polystyrene in Styrene Solutions

Christopher M. Miller

Recently, experimental results indicating differences between the polymerization kinetics of styrene miniemulsions prepared with and without small amounts of polystyrene added to the oil phase have been reported [C.M. Miller, P.J. Blythe, E.D. Sudol, C.A. Silebi, and M.S. El-Aasser, *J. Polym. Sci.: Part A: Polym. Chem.*, 32, 2365 (1994)]. In further studies, styrene miniemulsions and conventional emulsions prepared with and without the addition of a small amount of polystyrene to the oil phase were polymerized at 70°C in an automated reaction calorimeter. The results showed that miniemulsions prepared with as little as 0.05 weight percent polymer based on the oil phase exhibit a substantial increase in the polymerization rate and number of polymer particles produced over miniemulsions prepared in the absence of polymer. An increase in the polymerization rate was observed when either cetyl alcohol or hexadecane was used as the co-surfactant, however, the increase was greater for cetyl alcohol. In addition, the homogenization of a polymer solution without a co-surfactant was demonstrated to yield an unstable miniemulsion (i.e., a co-surfactant is required for the formation of a stable miniemulsion).

A more detailed look at the kinetics and mechanism of the polymerization of miniemulsions prepared from 1% polystyrene in styrene solutions was undertaken by conducting reactions with a varying potassium persulfate initiator concentration, and the results were compared with those for miniemulsions prepared in the absence of polymer. The final number of polymer particles was determined for both systems, and was shown to vary with the 0.31 power of the initiator concentration in the absence of polymer, but was independent of the initiator concentration for miniemulsions prepared from 1% polystyrene in styrene solutions. The final particle size distributions also differed when polystyrene was added to the miniemulsions. The miniemulsions prepared in the absence of polymer produced negatively skewed particle size distributions, the particle size decreasing with increasing initiator concentration. The miniemulsions prepared from 1% polystyrene in styrene solutions produced bimodal particle size distributions for all but the highest initiator concentration employed. By treating the system in an analogous fashion to seeded emulsion polymerization, it was demonstrated that the mechanism for polymerization of these miniemulsions proceeds by radical entry into highly monomer-swollen, pre-formed polymer particles.

The increased rate of polymerization and number of polymer produced when polymerizing miniemulsion droplets containing a small amount of dissolved polymer is attributed to a basic difference in the abilities of miniemulsion droplets and polymer particles to capture aqueous phase free radicals (i.e., radical capture efficiency). It is hypothesized that miniemulsions prepared from polystyrene in styrene solutions resemble the polymer particles formed in normal (i.e., no polymer) miniemulsion polymerizations at early conversions. This being the case, these polymer containing droplets are able to effectively compete with growing polymer particles for free radicals, whereas their counterparts which contain no polymer are not, and as a result, a greater fraction of the initial droplets become polymer particles. Based on this mechanism, it is speculated that the presence of the polymer increases the radical capture efficiency of the droplets by modifying either their interior (i.e., by increasing the interior viscosity thereby increasing the probability for a radical to propagate rather than exit) or the droplet/water interface (i.e., by disrupting a SLS/CA interfacial barrier to radical entry). Experimental results obtained through interfacial tension measurements indicated that the polystyrene does show some ability to modify the droplet/water interface.

4. Evaluation of Dimethyl Meta-Isopropenyl Benzyl Isocyanate (TMI) in Emulsion Polymerization

Samiuddin Mohammed

Dimethyl Meta-Isopropenyl Benzyl Isocyanate (TMI, Cytec Industries) is a bifunctional monomer possessing a double bond and an isocyanate group. TMI can be incorporated into the polymer backbone by copolymerizing it with various unsaturated monomers. Copolymers possessing pendant NCO groups are thus obtained. Subsequent crosslinking through the isocyanate group leads to polymers with improved properties. The main objective of this project is to evaluate the performance of TMI as a comonomer in emulsion polymerization. A model system comprising methyl methacrylate (MMA), n-butyl acrylate (BA), and TMI has been chosen, and several recipes have been developed in order to produce the terpolymer latexes. We expect the films obtained from these latexes to undergo crosslinking at ambient temperatures in the presence of moisture.

The kinetics of the emulsion terpolymerization of MMA/BA/TMI are being studied in detail. Polymerizations were carried out at low temperatures (40°C) in order to prevent the hydrolysis of TMI during the polymerization process. Redox initiators were used in order to work at this temperature. The NCO group of TMI was found to be very stable towards hydrolysis under these conditions. At 2 wt% TMI concentration (based on the oil phase), the order of incorporation of the monomers into the polymer was found to be MMA > TMI > BA. A favorable outcome of this result is that any monomer remaining at the end of the polymerization would be BA and not the isocyanate. At higher concentrations (> 5%), TMI was found to retard the polymerization process, and limiting conversions of around 45% were obtained while working below the critical micelle concentration (CMC) of the surfactant (Aerosol MA). Higher conversions could be obtained above the CMC, but in such cases a restriction was imposed on the particle size. While working above the CMC, the particle size was limited to the 40-60 nm range.

In order to overcome the problems of low conversion and particle sizes, several semi-continuous processes were designed. Using these processes, it was possible to incorporate high concentrations of TMI (5 - 10%) at appreciable polymerization rates. It was determined that it is necessary to feed the initiator semi-continuously, or in two shots, in order to obtain high conversions. The terpolymer composition could be controlled by adding the monomer semi-continuously as well, under "starved" conditions. The recipe used for the semi-continuous polymerizations is shown in Table 1. The conversion-time data for different TMI concentrations are shown in Figure 5. In these runs, the monomer was added in a batch mode, while the initiator was added semi-continuously over a period of 4 hr. Although the polymerization rate decreased with increasing TMI concentration, almost complete conversion was obtained even with a 20% TMI content.

Table 1: RECIPE USED FOR SEMI-CONTINUOUS EMULSION POLYMERIZATION OF MMA/BA/TMI

Component	Amount (gm)
Methyl methacrylate	12.00
n-Butyl acrylate	16.50
TMI	1.50 (5%)
Aerosol MA 80	0.90
Ammonium persulfate	0.1575
Potassium metabisulfite	0.1575
Ammonium iron (II) sulfate hydrate	0.0015
Distilled deionized (DDI) water	117.58

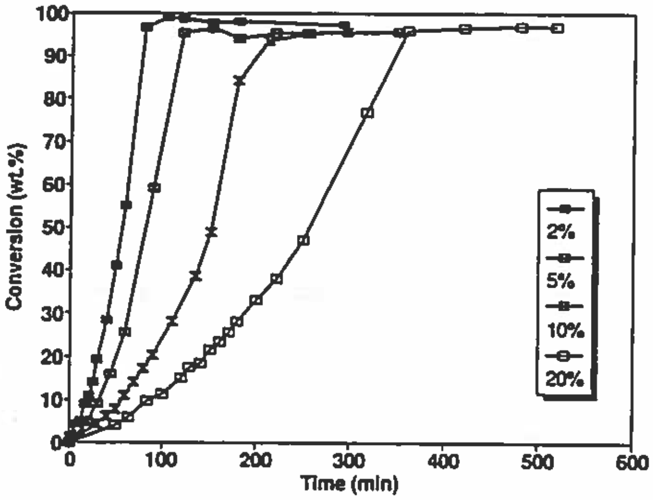

Figure 5: *Effect of TMI concentration on polymerization kinetics.*

5. Elastomeric Films from Structured Latexes

Yuan He

The objective of this program is to develop a model structured latex which is capable of forming a self-curable elastomeric film at low temperatures. In this model, a small amount of dimethyl meta-isopropenyl benzyl isocyanate (TMI®, Cytec Industries) was copolymerized with n-butyl acrylate (BA) onto poly(butadiene-*co*-styrene) ((P(Bd-St)) seed latex particles. The loci of isocyanate groups were controlled so that they were distributed in the interior portion of the PBA-based shell layer nearest to the P(Bd-St) core polymer. Polyol- or polyamide-types of polymeric surfactants, such as Tetronic® (Huntsman Co.) or Jeffamin® (BASF Co.) were then post-added into the latex system. These polymeric surfactants would tend to adsorb onto the surface of the structured latex particles with their hydrophilic functional groups (-OH or -NH_2) facing outward towards the water medium. In this way, the isocyanate groups and the -OH (or -NH_2) groups are separated in the shell layer of the structured particles as long as the particles remain surrounded by a water medium. In the final stage of the film formation process, the latex particles start to interact by coalescing with each other, and these two types of functional groups then approach each other via molecular interdiffusion. A crosslinked PBA network in the shell phase would then be formed by the crosslinking reaction between the isocyanate groups and the polymeric surfactant at low (e.g., room) temperature.

This concept was successfully applied to a P(BA-MMA)/P(BA-TMI) core/shell latex system. A major obstacle was encountered, however, when applying this model directly to a (PBd-St)/P(BA-TMI) core/shell latex system. The latexes prepared by the seeded emulsion polymerization of BA/TMI onto P(Bd-St) did not undergo much fusion, let alone form an elastomeric film. A series of studies using transmission electron microscopy (TEM), differential scanning calorimetry (DSC), and solvent extraction techniques indicated that a portion of the second-stage monomer was consumed to form a highly grafted/crosslinked P(Bd-St)/PBA core/shell interphase zone, as shown schematically in Figure 6. The amount of the second-stage monomer consumed to form this interphase zone was found to be significant, i.e., 50 and 100% of the weight of the high (>90%) and low (10%) gel-fraction P(Bd-St) seed particles, respectively. This interphase zone could consist of P(Bd-St)-*graft*-P(BA-TMI), P(Bd-St)-*cross*-P(BA-TMI), and P(Bd-St)-*ipn*-P(BA-TMI).

Reducing the amount of residual double bonds in the P(Bd-St) seed latex particles by hydrogenation was found to be an effective means of reducing the development of the interphase zone and the degree of crosslinking during the second-stage polymerization. Hydrogenation was carried out with a cupric-catalyzed hydrazine-hydrogen peroxide redox system. It was found that in addition to reaction conditions, such as temperature and pH, the cupric ion concentration at the P(Bd-St) particle surface was crucially important in determining the degree of hydrogenation. With this hydrogenated P(Bd-St) [H-P(Bd-St)] seed latex, the extent of the core/shell interphase zone was decreased, and the increase in the degree of crosslinking during the second stage polymerization was effectively suppressed. An elastomeric film was formed with this H-P(Bd-St)/P(BA-TMI) model latex.

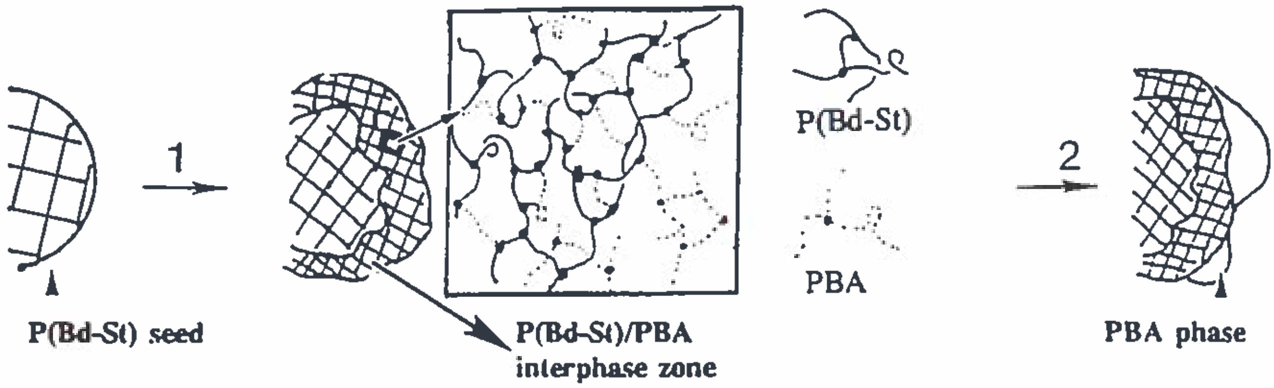

Figure 6: *Schematic illustration of the phase development in a P(Bd-St)/PBA core/shell latexes during the second stage polymerization.*

EMULSION POLYMERS INSTITUTE
Lehigh University

Graduate Research Progress Reports
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CONTENTS

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Abstracts:

" Dynamic Simulations of a Semiflexible Polymer Model"

Patrick S. Doyle, Alice P. Gast, Eric S. G. Shaqfeh

The configurations of deformed polymer molecules subject to flow manifest themselves in measurable quantities such as rheological coefficients and optical anisotropy. Computer simulations are a convenient means to simultaneously measure the stress, optical properties and configurations of a polymer model. There is a vast amount of theoretical work describing flexible and rigid polymer models while much less attention has been given to semiflexible polymer models. We have performed computer simulations of a semiflexible polymer model in simple shear and uniaxial elongational flows.

The polymer model is derived by considering a continuous flexible string with a finite bending modulus. In its continuous form the model is analogous to the well known Kratky-Porod model where semiflexibility is incorporated via a bending potential energy which is proportional to the square of the curvature. In its discrete form the model is similar to the Kramer's bead-rod model with an added bending term. The parameters in the model are the number of beads N, the persistence length P and the peclet number Pe. The beads act as points of isotropic friction distributed along the model and also as the discrete points we keep track of in the simulation. The persistence length is a dimensionless form of the bending parameter where a larger P describes more rigid polymers. A Pe is defined for the problem as the ratio

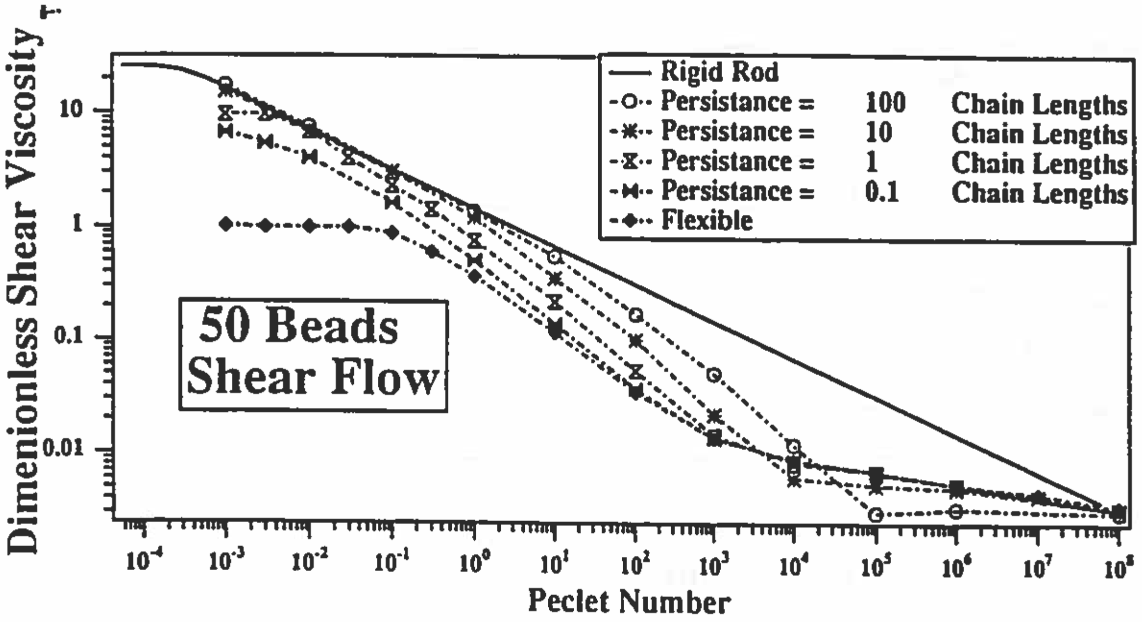

Figure 1: Plot of shear viscosity, made dimensionless with the flexible zero shear viscosity, verses Pe for a range of P. Rigid rod results are shown for comparison.

of the time for a bead to diffuse the interbead distance to the flow inverse shear or elongation rate. Trajectories are computed via a forward time stepping Brownian Dynamics algorithm which rigorously conserves constant contour length at each time step but neglects hydrodynamic interactions between the beads. Here we discuss results for N equal to 50 and a range of Pe and P in shear flow.

Subject to a moderate shear flow, with the flow direction being x and the gradient in the y direction, the model tends to align in the flow direction and eventually tumbles as brownian forces cause it to cross the zero shear axis. In figure 1, we plot the dimesionless shear viscosity verses Pe for a range of P. At low Pe we see a plateau region for all persistence lengths. As Pe is increased there is a region in which the viscosity shows power-law-like behavior, $\eta \propto Pe^n$. For the purely flexible, case n is approximately -1/2 and the rigid case is -1/3. For intermediate persistence lengths the power does not lie between -1/2 and -1/3 but takes on values smaller than -1/2. The thinning occurs due to the alignment of the model in the flow direction which decreases the velocity gradient across the the chain and thus the stress on

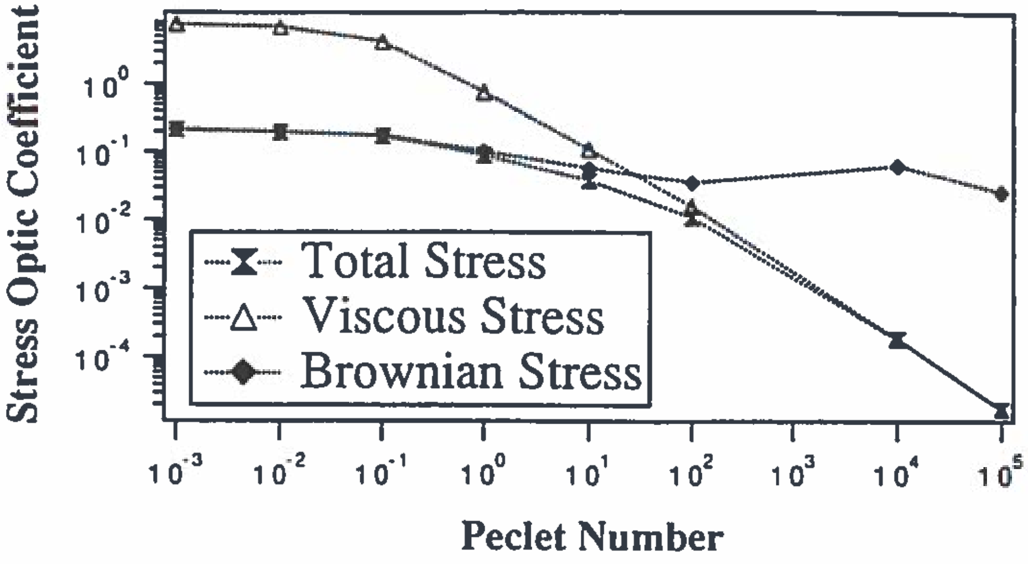

Figure 2: Plot of the stress optic coefficient verses Pe for a completely flexible chain (P=0.0).

the chain. All the chains show a global rotation which aligns the model in the flow direction but the more flexible ones also show a local unraveling which tends to delay the onset of shear thinning. At very large Pe numbers there is a second power law region with n equal to -1/10. In this region the length scale which governs the dynamics is no longer P but the discretized interbead distance. The stiffer chains thus take longer to reach the second power law region. The delay in the onset of shear thinning and the power law exponent are in reasonable agreement with the experimental results of Tam and Tui (*J. Rheology*, 33(2),257-280(1989)) who examined the steady shear properties of a range of semiflexible polymers in dilute concentrations.

The stress optic coefficient is calculated based on the x,y component of the stress tensor and the index of refraction due to the model. The coefficent is shown in figure 2 for the flexible case. A coefficent is calculated based on the brownian stress, viscous stress and also the total stress. At low Pe all three yield a relatively constant coefficient, but only the brownian stress yields a constant coefficient over a broad range of Pe. This seems plausible since the idea of a stress optic coefficient was originally derived for polymer melts where the stress from the model is purely brownian. In the near future we plan to investigate the dynamics of the chains near and tethered to interfaces.

“Interactions at Short Times between Polydisperse Charged Spheres”

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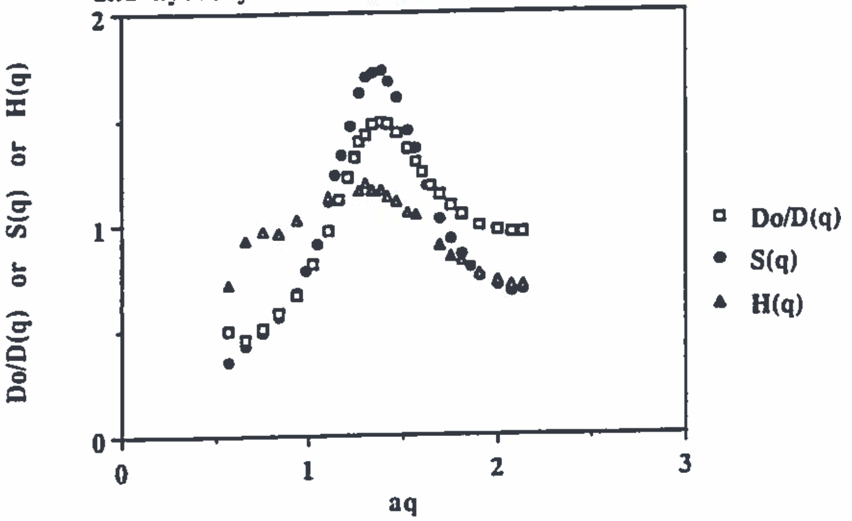
We investigate the local ordering and diffusion at short times of polydisperse, weakly charged silica spheres in a nearly optically matched, mixed solvent. We use 3-(trimethoxysilyl)propyl methacrylate-coated silica spheres in the mixture of pyridine and dimethylformamide (DMF) as our well defined model in developing an understanding of interparticle interactions in liquid. The average particle size in this study is 64 nm radius. The degree of size polydispersity determined by transmission electron microscopy and characterized with the unimodal continuous Schulz distribution is 17%. The particles are negatively charged with an average surface potential of 200 mV. Our suspension is nearly optically matched since the refractive index difference between the sterically coated silica particles and pyridine/DMF is less than 0.03. We limit our investigation to 15% particle concentration, above which we observe crystallization. We are interested in the dynamics at short times defined as times very long compared with the Brownian velocity relaxation time and very short compared with the time for a particle to execute a displacement comparable with the interparticle spacing.

Two classes of interactions can be identified: direct interparticle interactions, and indirect hydrodynamic interactions where the velocity field generated in the supporting fluid by the motion of one particle affects that of other particles. We use light scattering technique to probe the static and dynamic properties of the suspension. The static structure factor S(q) is determined from measurements of the angular dependence of the mean scattered intensity; q is the wavevector of the scattered light. The peaks in this factor

Diffusion coefficients, static structure factor and hydrodynamic function at 8% volume fraction.



indicate spatial correlations between particles due to the direct long-range interactions from electrostatic forces. Our measured static structure factors $S_M(q)$ demonstrate the influences of polydispersity particularly at long probing length scale q^{-1} and the first maxima. We also observe that S(q→ 0) of the polydisperse suspension is larger than that of the monodisperse suspension. In addition, the first maximum in the structure factor occurs at smaller q with slightly smaller magnitude. We study the dynamic properties via the effective diffusion coefficient $D_M(q)$. We obtain the $D_M(q)$ in the limit of short times from the initial decay of the measured dynamic structure factor $S_M(q,t)$ by applying the method of cumulants. It is usually assumed, particularly at low particle concentrations, that the long-range electrostatic interactions keep the particles far from each other. The short-range hydrodynamic interactions are diminished, and therefore are frequently neglected. Thus $D_M(q)$ mirrors S(q). We discover that this is not always the case. We observe the influence of hydrodynamic interactions on the diffusion of silica spheres. We calculate the hydrodynamic function H(q) from the expression $D_M(q) = D_o[H(q)/S(q)]$. Intuitively, we expect H(q) to be smaller than 1 since we associate hydrodynamics with friction. Interestingly, as shown in the figure, we find H(q) larger than 1 over a certain q range. Although this phenomenon has been reported before, the reasons are not yet understood. Encouraged by our observation in the importance of hydrodynamic effects at low volume fraction, we are motivated to test the validity of existing theories [G.Nägele.et.al Phys.Rev.E vol.47, 4, 1992 ; U.Genz and R.Klein Physica A vol.171, 1991 .]

Contributions to the IPCG Newsletter from
the Polymer Chemistry Group of Anton L. German,
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The following represents the summary of the thesis of Lilian F.J. Verdurmen-Noël and the summary of the thesis of Harold A.S. Schoonbrood. A copy of these theses is available on request.

Monomer partitioning and composition drift in emulsion copolymerization

by

Elisabeth, François, Johanna Verdurmen-Noël

Summary

The primary goal of the research described in the thesis of Lilian F.J. Verdurmen-Noël was gaining basic insight in copolymerization taking place in heterogeneous media, in particular emulsion copolymerization.

It was hoped that these insights, combined with the development of enhanced methods of on-line process monitoring, would contribute to a better control of composition drift in emulsion copolymerization, and hence to the preparation of well-defined emulsion copolymers.

In order to reach this goal, the following more specific aims were formulated:

(1) Development of a reliable and simple model to describe monomer partitioning of two monomers with limited water solubility, in such a way as to avoid the use of interaction parameters that are experimentally difficult to access and theoretically rather vague.

(2) Investigation and evaluation of the (theoretical) concept that minimum composition drift could be obtained by adjusting the monomer-to-water ratio for those monomer combinations in which the more water soluble monomer is also the more reactive one.

(3) Development and evaluation of reaction monitoring techniques that provide a large number of high-quality data over the entire conversion range.

In the following a summary will be given of the strategies followed to reach these aims, and some selected results will be shortly highlighted:

ad(1) Based on earlier work an extended model has been developed capable of describing monomer partitioning at partial swelling of latex particles by two monomers with limited water solubility. The most important and striking feature of this partitioning model is that the only parameters required are the individual homo-saturation values of the monomers in the polymer particles and the aqueous phase, which are readily accessible. Experimental verification of the model predictions for the monomer combination methyl acrylate-vinyl acetate shows excellent agreement.

The availability of the present model solves one of the major problems in modelling emulsion copolymerization, and allows the prediction of *i.a.* the compositional heterogeneity of emulsion copolymers.

In addition, the present model also allows prediction of the absolute monomer concentrations in the particle phase, which determine the rate of (co)polymerization. This is of great importance in determining optimal addition rate profiles, needed when preparing compositionally homogeneous copolymers in semi-continuous processes. The latter, however, is beyond the scope of this thesis.

ad(2) The reactivity-solubility concept was first tested for the emulsion copolymerization of methyl acrylate-indene, where methyl acrylate is the more reactive as well as the more water soluble monomer. It appears, when starting from any initial value within a wide range of monomer feed compositions, that indeed the composition drift can be minimised (almost zero) over the entire conversion range, simply by adjusting the monomer-to-water ratio.

A most rigorous test of the validity of the above concept is performed in a study of the effect of the monomer-to-water ratio on the copolymerization of methyl acrylate with a series of vinyl esters of strongly varying water solubility. The large difference in reactivity (for all these systems a factor of ca. 700), cannot be compensated by the small difference in water solubility between methyl acrylate and vinyl acetate, but it can be compensated by the larger difference in water solubility between methyl acrylate and the other (more hydrophobic) vinyl esters. The results clearly show that in essence the concept remains valid: *i.e.*, in all cases the composition drift is suppressed when decreasing the monomer-to-water ratio. Depending on the specific monomer combination some intrinsic or practical limitations may occur, however, preventing the composition drift to become (almost) zero.

These investigations provide and allow the utilization of a new handle on the compositional control in emulsion copolymerization; a tool that is unique in the sense that it does not exist in homogeneous (bulk or solution) copolymerization.

The present findings on the effects of monomer-to-water ratio and of monomer solubility in water are having important practical implications as well. For example, in those cases where the solids content in the reactor is changed, or where one of the monomers in the recipe is replaced (even by an equimolar amount of another monomer of equal reactivity), a copolymer product of different heterogeneity and thus different properties can be expected.

ad(3) The accurate and rapid determination of the partial conversion of the separate monomers is of key importance to understanding, modelling, and controlling emulsion copolymerization. The physical complexity of the systems (*e.g.*, the heterogeneity leading to monomer partitioning), calls for the combination of two on-line techniques: densimetry yielding the overall weight conversion, and gas chromatography providing the overall ratios of the residual monomers. Combination of these two data sets allows the calculation of the partial conversion of each monomer as a function of time, most importantly, without the need of an internal standard.

Adequate solutions have been proposed for non-ideal behaviour, as observed *e.g.* in the system methyl acrylate-vinyl acetate, where the specific volume of the monomers in the aqueous phase is different from that in the monomer droplet phase.

Even for this rather complex, non-ideal system comparison of the on-line data with off-line results and theoretical predictions gave satisfactory agreement, which validates this powerful combination of techniques, indispensable in monitoring emulsion copolymerization.

The method developed is certainly not restricted to the present systems, but could be applied, in principle, to any monomer combination. Extension of the method to monitor terpolymerization seems quite well feasible. Future developments also may include the instantaneous control of monomer addition, based on on-line measurements of monomer conversion data, allowing the preparation of tailor made copolymers in a single run. For example, the composition drift could be controlled in any desired manner by on-line measurement of the instantaneous monomer concentrations, and feed-back control of the addition rate of the more reactive monomer.

Emulsion Co-and Terpolymerization

Monomer partitioning, kinetics and control of microstructure and mechanical properties.

by

Harold A.S. Schoonbrood

Summary

In the thesis of Harold A.S. Schoonbrood investigations have been presented which are aimed at controlling an emulsion co- and terpolymerization in such a way that a product with desired properties is formed. The key to controlling an emulsion (co/ter)polymerization is understanding the relevant mechanisms. Here it was investigated how monomer characteristics determine the polymerization mechanisms and processes, how this understanding can be used to control emulsion co- and terpolymerizations leading to certain microstructures, and how the final properties are related to the microstructure.

One of the most important processes occurring in emulsion co- and terpolymerization is composition drift. This is determined by monomer partitioning and free radical copolymerization kinetics. A recently published model on monomer partitioning was carefully reviewed with respect to systems where the monomer molar volumes are not equal and also to systems where one of the monomers is water-soluble. In the first case the equations can be easily adapted, in the latter case the model is not applicable. The only monomer characteristics that are needed are its solubility in the polymer and aqueous phase and its molar volume.

The free radical kinetics of the styrene—methyl acrylate (S—MA) system were investigated in detail including both propagation and transfer to monomer. It was concluded that the transfer kinetics are dominated by the S-terminated radicals, whose concentration greatly exceeds that of MA-terminated radicals due to the propagation kinetics. A cross-transfer constant for S to MA could therefore be determined from the molecular weight distributions of the emulsion copolymers of these monomers. Transfer of acrylic radicals to polymer was also investigated with Gradient Polymer Elution Chromatography (GPEC). The terminal model was used to describe copolymer composition in the systems methyl methacrylate(MMA)—MA, S—2-hydroxyethyl methacrylate and S—MMA—MA. The latter system could be described with the pertaining binary reactivity ratios. A computer model was developed that can describe composition drift in emulsion co- and terpolymerizations. It uses the terminal model and the monomer partitioning model mentioned in the previous paragraph. The predictions obtained from this model were verified with ^{1}H NMR and GPEC. It was the first time a three-dimensional chemical composition distribution (CCD) was determined with ^{1}H NMR. This experimentally determined CCD was in agreement with the predicted CCD. It was also the first time GPEC was used to analyse the chemical composition distribution of a terpolymer.

The emulsion copolymerization kinetics are determined by even more monomer characteristics than composition drift, for instance by diffusion coefficients, transfer rate constants *etc*. An existing model for zero-one kinetics was extended and applied to the emulsion copolymerization of the system S and MA, which was shown to be a zero-one system. The rate-determining mechanisms of radical entry and radical exit were experimentally determined and could be described with existing models.

The knowledge gained was used to control emulsion copolymerizations with S and MA and emulsion terpolymerizations of S, MA and MMA. This resulted in the preparation of homogeneous co- and terpolymers, which was verified with GPEC. Also S–MA emulsion copolymers with very broad CCDs were prepared. These, and the homogeneous products of three different compositions, were analysed with respect to the relation microstructure-mechanical properties by applying for the first time the experimentally determined CCDs. It was shown that the extent of composition drift and thus also the microstructure, can have a large effect on the mechanical properties.

Contribution to the IPCG Newsletter from
the Sydney University Polymer Centre
Reporter: Bob Gilbert
Chemistry School, Sydney University,.NSW 2006, Australia.

The following abstracts from various members of the SUPC summarize current research directions.

Chain-length-dependent termination rate processes in free-radical polymerizations. 3. Styrene polymerizations with and without added inert diluent as an experimental test of model.
P.A.G.M. Scheren, G. T. Russell, D. F. Sangster, R.G. Gilbert and A.L. German. Macromolecules, submitted.
Experiments were performed to test a model for the kinetics of free-radical polymerization systems, including the dependence of the termination rate coefficients on the lengths of both chains involved. The model has few adjustable parameters, the values of which are moreover confined within fairly narrow limits. The data comprised the rate of polymerization in a seeded emulsion polymerization of styrene, with and without benzene as diluent, with initiation by persulfate and by γ-radiolysis. The latter can be switched off instantly, providing relaxation data which are sensitive to termination kinetics. Data from a single relaxation at a fixed weight-fraction polymer (w_p) were fitted to fix the unknown parameters, of which the only significant one is the probability p of reaction between two radicals upon encounter, incorporating the effect of spin multiplicity; this must lie between 0.25 and 1. Modelling using the value so obtained then successfully fitted: (a) relaxation data at the same w_p but with 15 mol % benzene diluent; (b) relaxation data with and without diluent over the range $0.5 \leq w_p \leq 0.8$; and (c) chemically initiated data over the same w_p range. This provides convincing evidence for the correctness of the termination model, which calculates the termination rate coefficients between two chains from the Smoluchowski equation, incorporating p, with diffusion coefficients (as a function of chain length and of w_p) obtained from a "universal" scaling law inferred from NMR data, and where the interaction distance for termination is the van der Waals radius of a monomeric unit; contributions from "reaction-diffusion" (whereby a chain end moves by propagating) are also important at high conversion. The data also support a model for initiator efficiency in emulsion polymerization, this model being based on competition between aqueous-phase propagation (to a sufficient degree of polymerization for surface activity) and termination.

Rate Determining Kinetic Mechanisms in the Seeded Emulsion Copolymerization of Styrene and Methyl Acrylate

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Abstract

A kinetic study of the seeded emulsion copolymerization of styrene (S) and the relatively water-soluble methyl acrylate (MA) was carried out so as to elucidate the mechanisms of radical entry into latex particles, radical exit from the latex particles, and the fate of radical species in the aqueous phase. Three seed latices of differing size were used, two of poly(S–co–MA) and one poly(S) latex. This means of determining kinetic parameters of emulsion copolymerization on a homopolymer seed ('heteroseeded polymerization') is possible, because the techniques used involve only a relative small change in conversion. This means that phase separation will not be a problem at the high monomer concentrations applied and that composition drift is negligible. Conditions were such that the system followed zero-one kinetics (Smith-Ewart cases 1 and 2) which means that no latex particles contain more than one growing radical. Data were obtained for the steady-state rate of polymerization with persulfate as initiator and for the non-steady-state relaxation kinetics in γ-radiolysis initiation experiments. The latter kinetics are dominated by radical loss mechanisms such as radical desorption and termination. It was possible to obtain a value for the chain transfer constant of styrene-terminated radicals to methyl acrylate from the molecular weight distributions. It was found that this copolymer system is retarded at very low conversions, possibly by oxygen. The data are consistent with the following mechanisms. Radical exit occurs via the same transfer-diffusion mechanism as found in a number of other systems, *i.e.* transfer of the radical activity to monomer(s) and subsequent desorption into the aqueous phase. These desorbed monomeric radicals always re-enter the particles and either terminate or propagate therein. Initiation by persulfate is inefficient, with 50-95 % of the persulfate-derived radicals undergoing termination in the aqueous phase. This is in accord with the mechanism for entry that states that the rate-determining events are aqueous-phase propagation and termination; radicals of a critical degree of polymerization enter a particle irreversibly and instantaneously. At high fractions of S in the S–MA system, although MA polymerizes quickly (high propagation rate constant, k_p), the occasional addition of S in the aqueous phase slows the propagation rate down considerably. Thereby it also decreases the probability of the attainment of a sufficiently high degree of polymerization for surface activity, perhaps 10-20 monomer units with the relatively water-soluble MA, so that there is considerable termination in the aqueous phase.

* The following publication has appeared since the previous Newsletter:

The measurement and meaning of rate coefficients in free-radical polymerizations.
J.P.A. Heuts, P.A. Clay, D.I. Christie, M.C. Piton, J. Hutovic, S.H. Kable, R.G. Gilbert.
Progress in Pacific Polymer Science; Proceedings, 3, 203-16, 1994.

INTERNATIONAL POLYMER COLLOID GROUP NEWSLETTER

Contribution from Norio Ise[1], Kensaku Ito[2],
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Reporter:Norio Ise

Ultra-Small-Angle X-ray Scattering Study of Colloidal Dispersions

(a) The USAXS study of colloidal silica dispersions was further extended by Konishi et al. using apparatus II (T. Konishi, N. Ise, H. Matsuoka, H. Yamaoka, I. S. Sogami, and T. Yoshiyama, Phys. Rev. B. in press). Several orders of Bragg diffraction were observed for aqueous dispersions in a vertically held glass capillary, as shown in Figure 1. The peaks appeared at each multiple angle of 150". The same profile was observed when the capillary was rotated around its axis by (60 x m)^{0} (m:integer). A different profile was found at (30 + 60 x m)^{0} with peaks at each multiple angle of 85". From all the information, it was concluded that a body-centered-cubic (bcc) lattice was maintained in the capillary, with the $[1\bar{1}1]$ direction of the single crystal being vertically upward and parallel to the capillary axis. It was inferred that the profile of Fig. 1-a corresponds to the (110) plane, with the distance d_{110} between the (110) planes being 2100 A. The first and second order peaks of Fig. 1-b are the (101) reflections while the peak at 170" may be simultaneously the first order of the (020) reflection. The lattice constant a was found to be 3000 A by using d_{110}. The closest interparticle distance $2D_{exp}$ was 2600, whereas the average distance from the concentration was 2900 A for bcc symmetry. Obviously, $2D_{exp}$ was smaller than $2D_0$, supporting our previous conclusion derived for ionic polymers and colloidal particles. In other words, the crystal occupies only 0.72 [= $(2600/2900)^3$] of the total dispersion volume and the rest (0.28) contains voids [1] and/or free particles [2].

It should be mentioned that the Hosemann plot [3] or the application of the Scherrer equation [4] to determine the size of the ordered structure was unsuccessful: the crystal was too large under the present conditions. The bcc symmetry and the lattice constant obtained above were confirmed to be correct by an independent Kossel line analysis by Sogami and Yoshiyama [5].

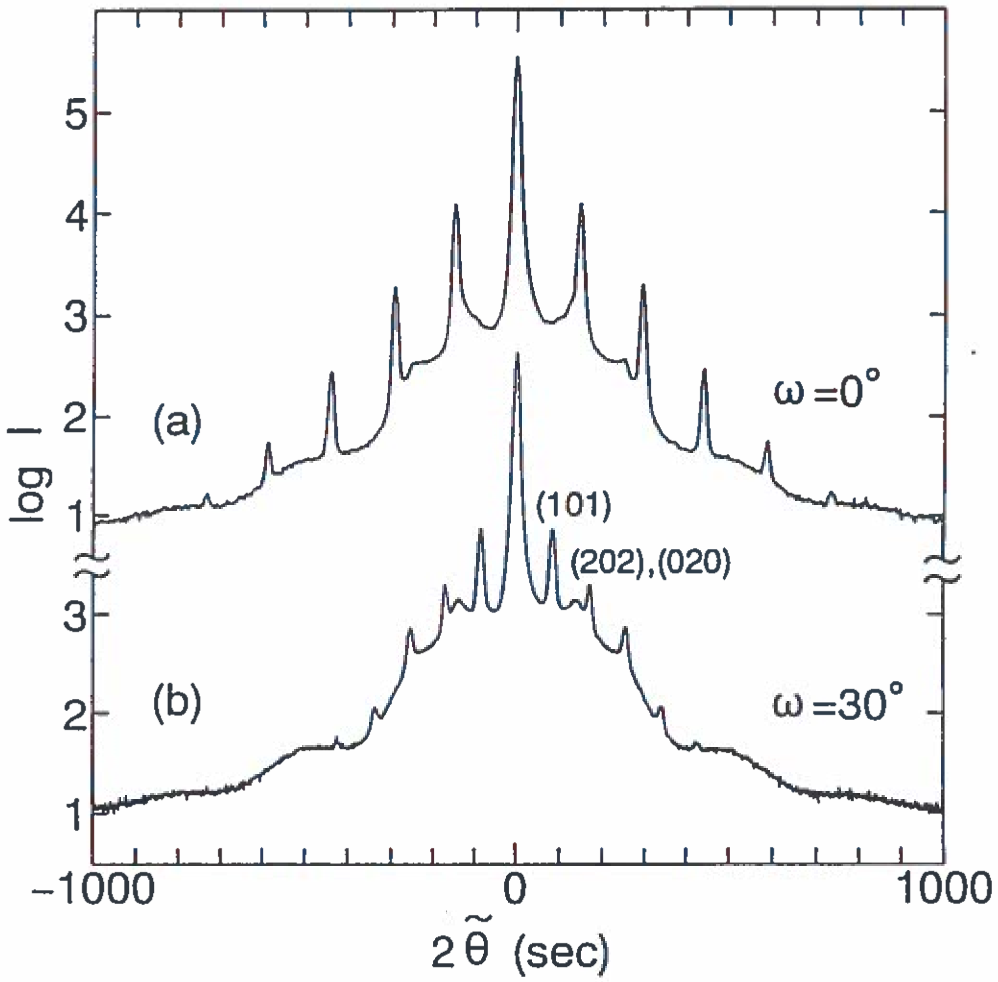

Figure 1. The logarithm of the USAXS intensity $I(2\tilde{\theta})$ in counts per second versus the rotation angle $2\tilde{\theta}$ of the second crystal of the Bonse-Hart camera. Sample: KE-P10W, Nippon Shokubai Co., Ltd. Osaka. concn.:3.76 vol%. radius:560 A, standard deviation: 8 %, net charge density: 0.06 $\mu C/cm^2$, analytical charge density: 0.24 $\mu C/cm^2$. Curve (a):rotation angle, $\omega = (60 \times m)^o$; (b) $\omega = (30 + 60 \times m)^o$

(b) Matsuoka et al. applied the USAXS apparatus I for polymethyl-methacrylate latex-water dispersion (H. Matsuoka, T. Harada, and H. Yamaoka, Langmuir, in press). They observed also clear Bragg peaks and detected shifts of the peak position with varying salt concentration. Most remarkable is that the Bragg spacing increased first with increasing salt concentration and, through a maximum, decreased, as is shown in Fig. 2, whereas the peak height simply became lower. The decreasing tendency of $2D_{exp}$ is consistent with the DLVO theory and also with the Sogami theory [6], while the increasing trend does not fit the theories. The slight change of the effective net charge of the particles at low salt concentrations would be an important factor to be considered.

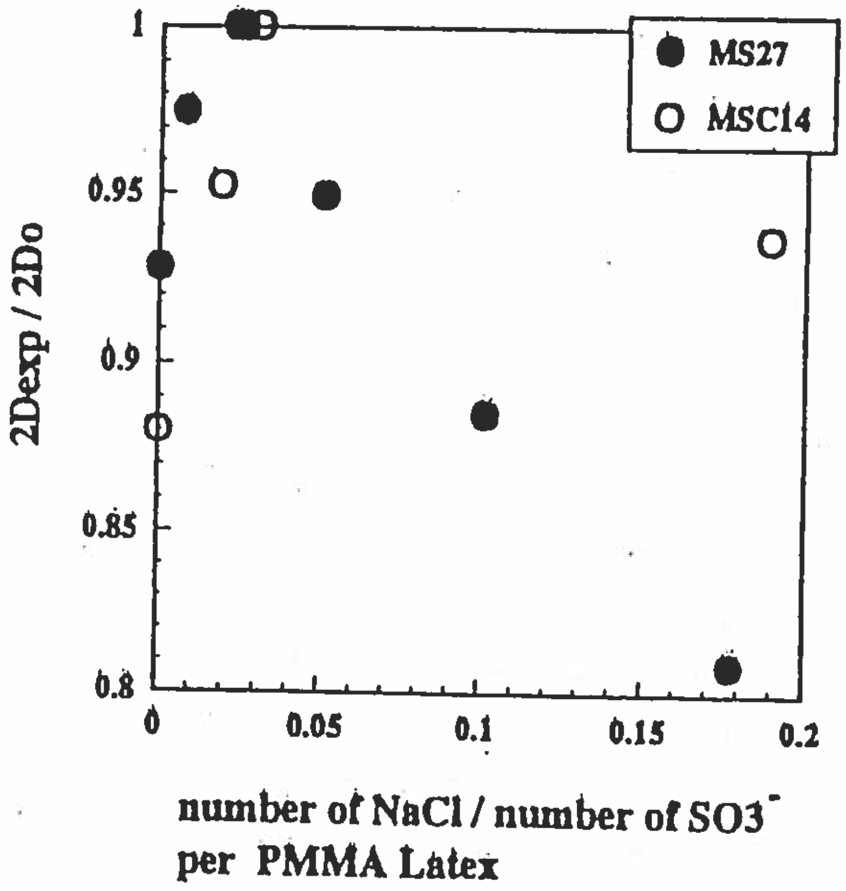

Figure 2.The interparticle distance $2D_{exp}$ as a function of added salt concentration (expressed in the ratio of NaCl molecules to latex charge number). Dispersion: polymethylmethacrylate-water. Particle radius: 1890 (MS27) and 1200 (MSC-14) A, charge density: about 3 $\mu m/cm^2$.

Positive Adsorption of Negative Latex Particles near Negatively Charged Glass Surface

It is generally believed that negatively charged ions are repelled by a similarly charged plate, and the concentration of these ions is small near the plate, and increases with distance to the bulk concentration. However, we had noticed in previous studies that the concentration of negatively charged latex particles was higher near a similarly charged glass surface by a confocal laser scanning microscope [2,7,8]. Thus, a more systematic study on this problem was initiated by Ito et al. (K. Ito, T. Muramoto, and H. Kitano, publication in preparation.)

In the course of the study, Thomas et al. reported the neutron reflection study for cationic micellar solutions above cmc [9]. They concluded that the cationic micelle concentration below the cationic monolayer at the air-solution interface was double the bulk concentration. Obviously, positive adsorption took place.

Ito et al. treated cover glasses with acid and washed with water thoroughly. The zeta-potential of the glass surface was found to be -70 to -90 mV. The latex sample was a styrene-styrenesulfonate copolymer, its diameter was 0.34 μm and the charge density was -1.1 $\mu C/cm^2$. After exten-

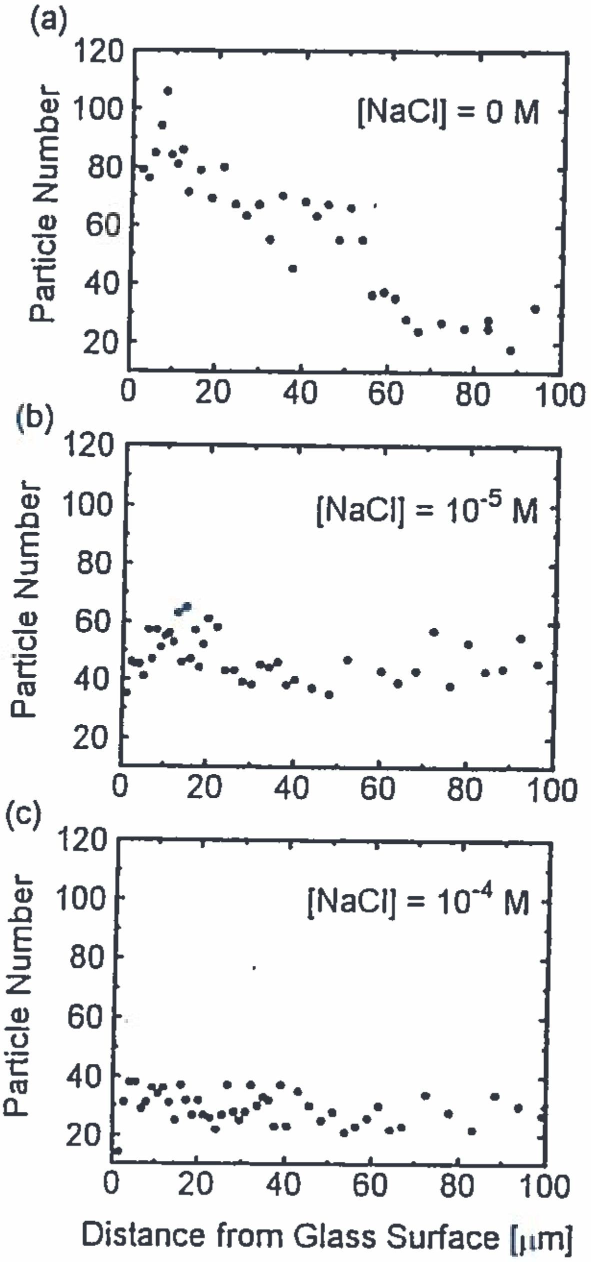

Figure 3. The number of particles as a function of distance from the cover glass. (a) deionized dispersion, (b) [NaCl] = 10^{-5}M, (c) [NaCl] = 10^{-4}M. Latex: styrene-styrenesulfonate copolymer, [Latex] = 0.01 %, diameter: 0.34 μm, charge density: 1.11 μC/cm^2.

sive purification of the dispersion, the particle number near the cover glass was directly measured by a confocal laser scanning microscope, and the micrographs were treated with Bio Scan Optimetric, Bio San Inc., Edmond, Washington, to obtain high contrast pictures and to count the particle number. Figure 3 represents the results. Clearly, the number of particles in the deionized condition decreased with distance between 3 and 50 μm. From the initial particle concentration, the depth of focus and the observed area, the average particle number was known to be 20 - 40. At about 5 μm in the deionized dispersion, the particle number was three time the bulk concentration. Positive adsorption occurred. However, the adsorption was hindered when the concentration of coexisting salt became higher, implying that the driving force of the positive adsorption was of electrostatic origin.

Considering the effect being very long-range, it seems natural to invoke an electrostatic interaction between particles. Intuitively, the charged interface would attract latex particles (say, at r = 5μm) through the intermediary of counterions. These particles would then attract distant particles (for example, r = 10μm) by the same mechanism. In other words, the particle at r = 10μm is attracted by the interface and particles in the region between 0 and 10 μm. Since the electrostatic influence of the interface is expected to diminish with increasing r, particles at very large distances (> 50 μm) are no longer affected by the interface so that it is plausible that these particles experience only the interaction from near-by particles and this interaction may be easily over-whelmed by the kinetic energy. Thus, the long-range adsorption would be possible.

The observed adsorption is clearly in disagreement with the accepted double-layer interaction theory. For example, the free energy of solutions containing curved surfaces (or charged spheres) was calculated by Overbeek by using the Debye-Hückel type potential [10]. Actually the integration of the product of the charge density and the potential was carried out from the particle surface to infinity. The positive adsorption observed provides the basis for the complete understanding of the double-layer phenomena.

A remark is necessary about the attraction. The attraction is generated through the intermediary of counterions, as was emphasized repeatedly by us. Thus, if two particles or the particle and the interface come very close to each other, the number of counterions in between would happen to be not abundant enough ro give rise to the attraction. Then the repulsion prevails. Under such a condition, only the repulsion is detected. In other words, in the very vicinity of the glass surface, the number of negative particles would be low as a result of the repulsion and increase with increasing distance from the surface, as was assumed by Overbeek. The observation of the positive adsorption shows that the use of the Debye-Hückel type potential is not generally warranted, though not totally incorrect.

Restricted Motion of a Particle Trapped Inside a Void in Colloidal Dispersion

Yoshida et al. further investigated the void structure in macroscopically homogeneous dispersion and noticed that some voids contained a small number of particles. Interestingly, the motion of the trapped particle was quite different from other particles in the surrounding regions (H. Yoshda, N. Ise, and T. Hashimoto, Phys. Rev. submitted).

Fig. 4 shows an (inverted-type) confocal laser scanning micrographic image of void structures in the internal region at a vertical distance of 28 μm from the cover glass. This structure was maintained for more than 3 hours although fluctuation of the interfaces of the voids was observed. The void structures could be easily destroyed by shaking the dispersion cell, which led to a homogeneous distribution. After leaving this randomized dispersion in the sample chamber for 3 days, voids were again formed.

As shown in Fig. 5, some voids contained particles. Fig. 5-a is a horizontal cut (parallel to the cover glass of the cell bottom) of such a void, whereas Fig. 2-b is a cross section of the void and particle in a plane perpendicular to the cover glass. It is obvious that the trapped particle really exist in isolation from other particles and the nearest neighbor particles from the trapped one were roughly 8 - 10 μm away in all directions.

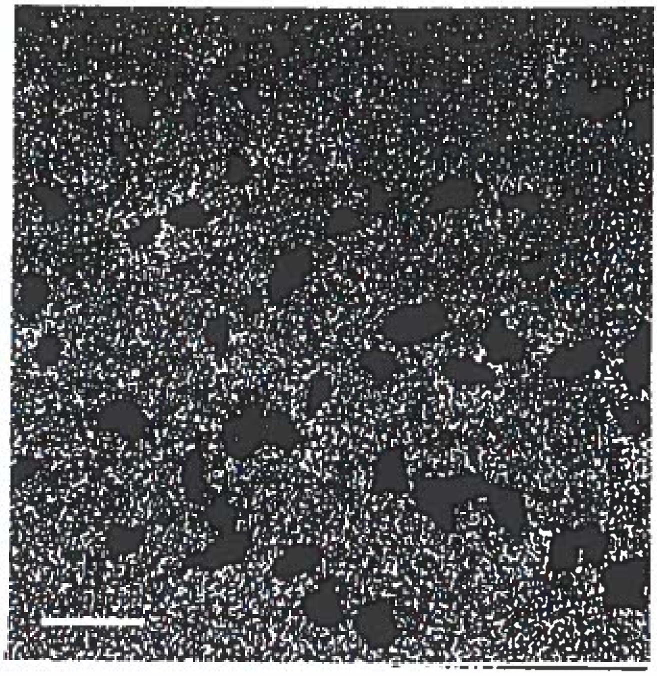

Figure 4. Void structure in a polymer latex dispersion observed by a confocal laser scanning microscope. Depth of focus: 0.5 μm, Scan time: 0.7 sec/frame. Latex: N700, latex diameter: 0.7 μm, analytical charge density: 3.9 $\mu C/cm^2$, [latex]: 1.0 %, dispersant: H_2O-D_2O (1:1) mixture, Scale bar at lower left corner: 50 μm.

In Fig. 6, trajectories of a trapped particle (a), a particle at the void interface (b) and a free particle (c) are compared. The free particle motion was obtained by an independent micrographic study of a particle in a dilute dispersion of 2.0 x 10^{-3} %. Clearly the diffusional motion of the trapped particle is highly damped in comparison with the others. Considering that the particle concentration is practically nil in the void over the experimental time scale, the diffusion of the trapped particle was expected to be the same as that of free particles. This was not the case, however.

According to the Einstein-Stokes equation, the diffusion of a non-interacting particle is determined by the temperature, the particle size, and viscosity of the medium. It is unrealistic to assume that the local temperature in the void is different from that of the surrounding region, since a small temperature difference would cause convection in the dispersion and destroy the structure. This was not observed. Particle aggregation, which would cause damped diffusion, can be ruled out, since monomeric and dimeric forms can be easily distinguished by the microscope. It is also difficult to admit that the local viscosity is higher in the void than in the bulk, though direct proof is not available.

We invoke here also a very long-range electrostatic interparticle interaction to explain the observed fact as follows. The particles in the surrounding region experience both (1) the interaction with neighboring particles and (2) that with distant particles. On the other hand, the trapped particle feel only the second interaction. Two features of these interactions must be noted. First, because of the large number of distant particles, the influence of their Brownian motion on the trapped particle would be smeared, though not completely. Therefore, the trapped particle is affected by the long-range interaction, weak or strong, homogeneously from all directions. This may be the cause of its restricted motion. Secondly, the influence of distant particles on the particles in the surrounding region would be less significant than that of their neighboring particles due to the difference in the working distances. This would cause random motion of the particles in the surrounding region.

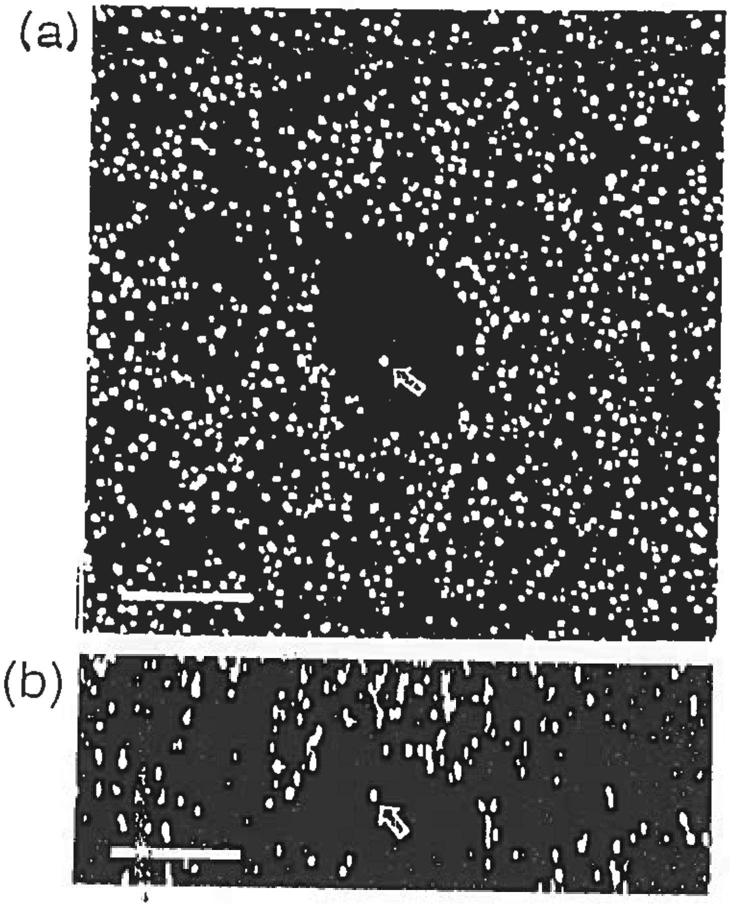

Figure 5. Micrographic images of a void containing a particle (pointed by arrow). Latex :N700, [latex]:1.0%. Scale bars at lower left corners: 20 μm. (a) cross section of a void at a distance of 15 μm parallel to the cover glass. (b) perpendicular cross section of the same void, obtained by computer-slicing of a 3D image of the void shown in (a), constructed from 24 horizontal cross sections (each 1.6 μm apart). The distances from the cover glass to the upper and lower edges of (b) are 39 μm and 2 μm, respectively.

It is to be noted that the positive adsorption discussed above and the restricted motion of the trapped particle point out the important role of the very long-range electrostatic interaction.

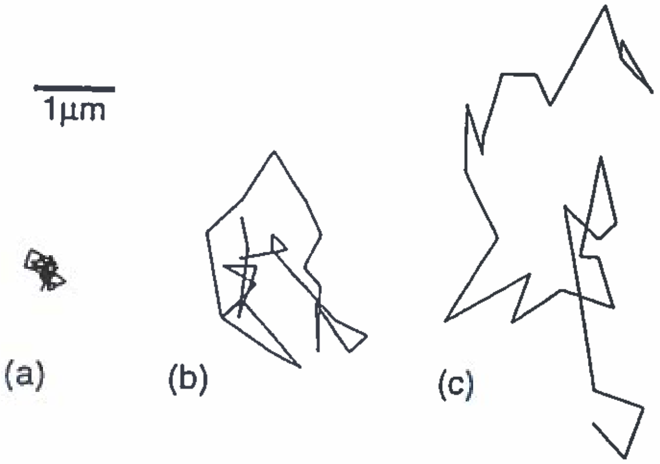

Figure 6. Trajectories of three particles, (a)trapped inside a void, (b) at the interface of the void, and (c)a free particle. The trajectory was obtained for 5.8 sec by analyzing scanned images (scan time: 0.2 sec/frame) with a Macintosh Quadra 650 personal computer with public domain image analyzing software (NIH Image, version 1.55, National Institutes of Health, USA).

Photothermal Compression of Colloidal Crystals
Paradoxes of the Repulsion-only Assumption

In 1985, Ise et al. found by microscopic method that the interparticle nearest neighbor distance ($2D_{exp}$) in the ordered crystal decreased with increasing temperature [11]. The compression of colloidal crystal was later studied by Asher et al. [12] by using absorption of high intensity radiation by dye molecules in colloidal spheres. The experimental data reported by Asher et al. which were interpreted by using the repulsive DLVO potential, were reanalyzed in terms of the Sogami potential [13] by Ise and Smalley (N. Ise and M. V. Smalley, Phys. Rev. B in press).

From the lattice constant measured by Kossel line analysis, it was first demonstrated that the volume fraction in the bcc crystal was 2.64 % whereas the overall, initial concentration was 2 %. This difference, which was not mentioned by Asher et al., implies that the crystal was not space-filling, but localized, and is in contradiction with the repulsion-only assumption, which requires the space-filling structure. Secondly, the compression could be reproduced by both the repulsive DLVO potential and the Sogami potential, which contains repulsive and attractive contributions. Thirdly, it is noted that the DLVO calculation was done with the renormalized charge number Z_{eff} = 1150, whereas the Sogami value was obtained using the net charge number Z_n = 308. According to the transference experiment by Ito et al. [14], which enables us to estimate the net charge number of macroions or particles in solutions with the least number of assumptions, the Z_{eff} is too large by a factor of 5 for particles under investigation, whereas the Z_n is of the correct magnitude. In conclusion, the interpretation in terms of the DLVO potential cannot quantitatively explain the observed contraction if a reasonable value for the net surface charge on the spheres is assumed.

In retrospect, we state that the structure factor (S(q)) of colloidal dispersion could be reproduced satisfactorily by Sood et al. using the Sogami potential [15], which had been earlier discussed exclusively in terms of the Yukawa or DLVO potential, and the elastic modulus was demonstrated by us[16] to be reproducible by the DLVO potential and by the Sogami potential as well. Very recently, Kepler and Fraden carried out an interesting measurement of the pair potential between colloidal particles [17]. They detected an attractive component much greater than predicted by the DLVO theory, but they did not ascribe it to the failure of the theory. However, Tata and Arora reanalyzed the potential curve and could reproduce it by the Sogami potential in a highly satisfactory manner [18]. These developments clearly show that, when it is demonstrated that the repulsion-only assumption or the repulsive DLVO potential can account for one particular phenomenon and the counterinterpretation in terms of the repulsion-attraction assumption, or the Sogami-type potential, is ignored, it is often concluded that the DLVO potential is the only correct one. This is obviously a dialectical error that was discussed in the cockroach experiment by Eigen [19], which must be avoided.

Viscosity Study of Latex Dispersions and Ionic Polymer Solutions

Yamanaka et al. further investigated the viscosity of latex dispersions, specifically the first-order electroviscous effect (J. Yamanaka, N. Ise, H. Miyoshi, and T. Yamaguchi, Phys. Rev. E. in press).

Aqueous dispersions of three kinds of colloidal silica and an ionic polymer latex, having particle radii of (0.04 - 0.5) μm, were measured at NaCl concentrations, C_s, of 5 x 10^{-5} to 10^{-3} M. The first-order electroviscous effect was estimated from the experiments, and compared with the Booth theory. The effect was found to decrease with increasing particle radius, a, as predicted by the theory. Furthermore, the function $Z(\kappa a)$ ($1/\kappa$: the Debye scareening length), introduced by Booth to discussed the deformability of the counterion cloud under a shear field, was estimated from the observed effect at several κa values between 0.9 and 15. The Z vs. κa plot thus obtained for colloids with various a values at various C_s's was well represented by a single curve, and decreased monotonically with increasing κa, whether κ or a was varied. This suggests that the Z really is a function of the product κa. In other words, it was shown that the deformability of the counterion cloud is determined by the ratio of the Debye screening length to the particle radius. On the basis of the present finding and previous studies [20], it was concluded that the Booth theory is satisfactory for description for large κa and small charge numbers. This result contributes to a better understanding of viscosity behavior of ionic polymer solutions [21].

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CONTRIBUTION TO THE INTERNATIONAL POLYMER COLLOIDS GROUP NEWSLETTER (OCT. 1994)

Contribution from the Department of Chemical Engineering,
Yonsei University, 134, Shinchon-dong, Sudeamoon-ku, Seoul, KOREA.

Reported by Jung-Hyun (Jay) Kim

Recently, our research group organized the Water-Soluble Resin and Emulsion Polymer Study Circle with support of Korea Ministry of Science and Technology. The activities of the study circle are discussion and review of emulsion polymer technology. Current researches accomplished in our lab. include : (1) composite polymer latex, (2) emulsion polymerization using alkali-soluble resin, (3) monodiseperse latex prepartion by membrane emulsification, (4) latex agglomeration, (5) water-soluble polyurethane polymerization. Some of the results were summarized in the following contributions. Also, New equipments were introduced : Dynamic Mechanical Thermal Analyzer (DMTA), Differential Scanning Calorimetry (DSC), Thermogravimetric Analyzer (TGA), Thin Layer Chrmatography with Flame Ionization Detection, Capillary Hydrodynamic Fractionation (CHDF) and Dynamic Light Scattering (DLS).

Grafting Reaction in Poly(n-butyl acrylate)-Poly(methyl methacrylate) Emulsion Polymerization

(Y. J. Park, J. H. Kim)

Latex particles which consist of poly (n-butyl acrylate) [p(n-BuA)] core and poly(methyl methacrylate) [PMMA] shell were prepared by two stage emulsion polymerization and grafting efficiency (GE) of these latex particles was determined by solvent extraction method. Kinetics of emulsion polymerization was applied to the grafting reaction and grafting efficiency was calculated. The results showed similar trend to the experimental values. Approximate value of grafting reaction constant was obtained by comparing experimental value with calculated grafting efficiency.

Grafting efficiency of the final core/shell structured latex was influenced by the type and amount of 1st stage crosslinking agent. Higher grafting efficiency was obtain in a semi-batch mode than in a batch process. The amount of initiator in 2nd stage shows little influence on the grafting efficiency of final latex.

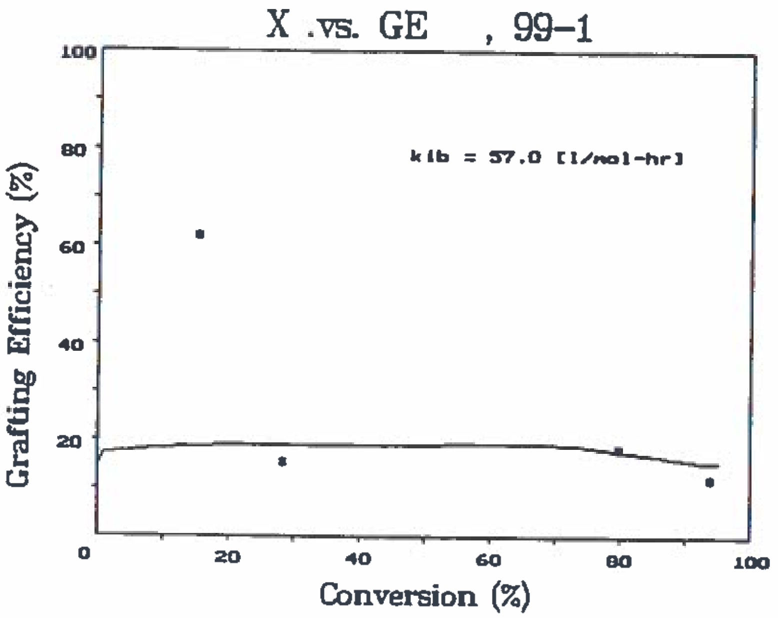

Fig. Grafting efficiency vs. conversion curve for core/shell latex. (*) : experimental data

Preparation of Monodispersed PB Latexes by Membrane Emulsification

(H. J. Lee, J. H. Kim)

As the new method for preparation of polybutadiene latexes with suitable particle size, membrane emulsification, which is capable of easy and uniformal control of particle size, was used in this study. The parameters were different type and amount of surfactants, amount of cetyl alcohol as additive, pressure etc. Two kinds of membrane was used. One is porous stainless steel (pore size : 1μm), the other is CaO-Al_2O_3-B_2O_3-SiO_2 type porous glass (pore size : 0.7μm).

Particle size and distribution of prepared latexes were characterized by PSA, TEM, optical microscopy and were compared with the emulsion by homogenizer (6400 rpm, 5 min). To investigate membrane emulsification mechanism, interfacial tension was calculated by Harkins-Brown equation.

In the case of porous stainless steel membrane, because of low hydrophilicity, membrane surface was wetted by polymer solution and then latex stability was breakdown. But emulsion by porous glass membrane was stable.

Highly monodisperse polybutadiene particles were produced by this new emulsification method. When amount of surfactant was more than 0.2 wt% (based on DDI water), stable emulsion was prepared. Critical pressure is 0.9 bar. Other parameters had no relationship with particle size and distribution. Therefore, the essential factor for determining the particle size was pore size of the membrane.

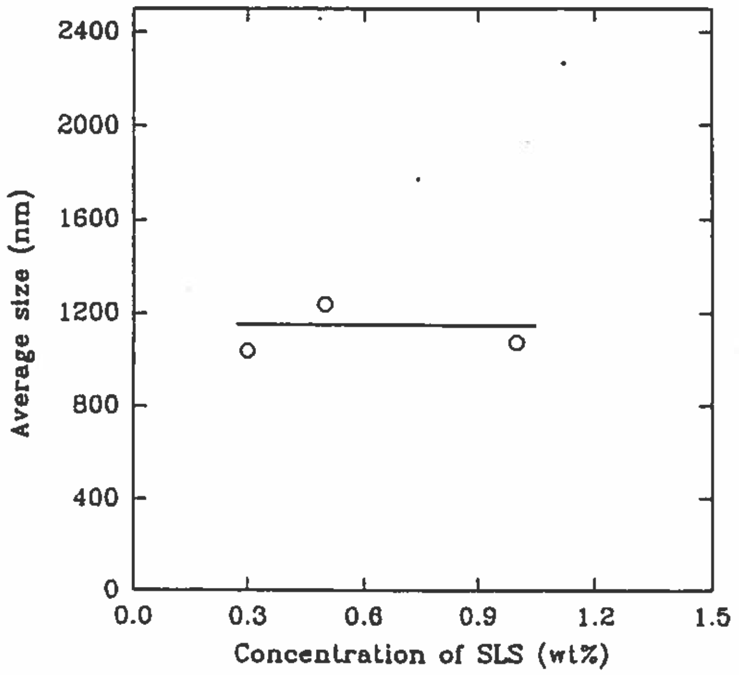

Fig. Change of the diameter prepared by (porous glass) membrane emulsification with SLS conc.

The development of rubber latex agglomeration process by using carboxylated agglomeration agent

(W. C. Shin, J. H. Kim)

In order to control the size of polybutadiene latex, the carboxylated agglomeration agent was prepared by two stage shot growth method and then polybutadiene latex was agglomerated by the agglomeration agent.

As a result, it was found that agglomeration effect was proportional to the concentration of H^+ ions which adhere to the stern layer of agglomeration agent.

The concentration of H^+ could be adjusted by the amount of acrylic acid and the pH of medium.

It is thought that this agglomeration phenomena results from hydrophilicity difference between agglomeration agent and polybutadiene latex. Therefore this phenomena is sensitive to the amount of carboxylic charge density and the pH of medium.

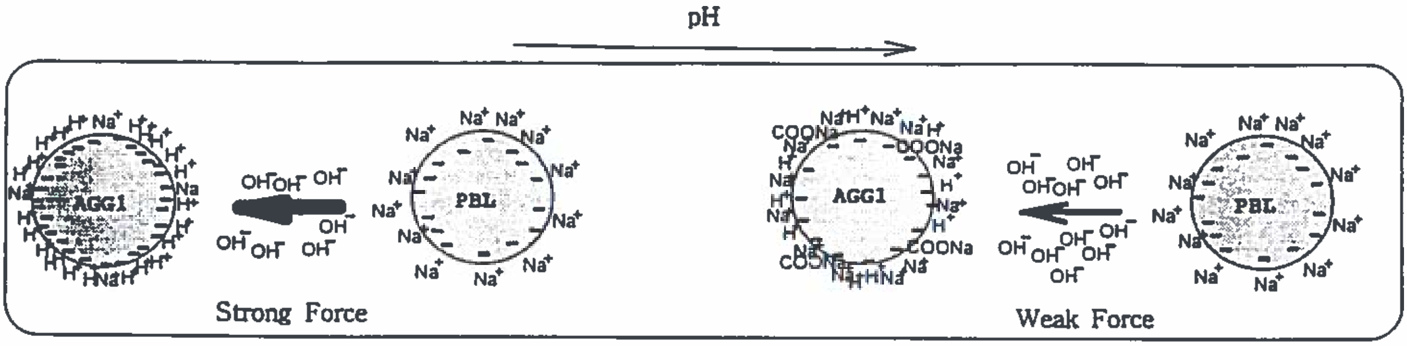

Fig. The sketch of agglomeration mechanism

Reaction Characteristics of Emulsion Copolymerization of Methyl Methacrylate and Butyl Acrylate with Alkali-Soluble Resin

(D. Y. Lee, J. H. Kim)

Alkali-soluble resin[poly(styrene/alpha-methylstyrene/acrylic acid)] was used as stabilizer/comonomer in the emulsion copolymerization of methyl methacylate and butyl acrylate. The roles of alkali-soluble resin(ASR) and the effects of various polymerization parameters on the size and its distribution were systematically investigated.

The latex was stabilized by grafting and adsorption of ASR, which results in formation of a very small and stable particle without the presence of any added surfactant. The grafting reaction of monomers onto ASR was observed by GPC and FT-IR analysis after using serum replacement technique. The particle size was found to increase with increasing amount of NH_4OH and pH of ASR solution. Also, the secondary particles were formed as the amount of NH_4OH was increased. It was found that the effect of NH_4OH on particle size and its distribution was greater than that of ASR concentration. The effect of NH_4OH on ASR conformation in solution, leading to a formation of polymer aggregate, was the main factor for explaining the formation of secondary particles.

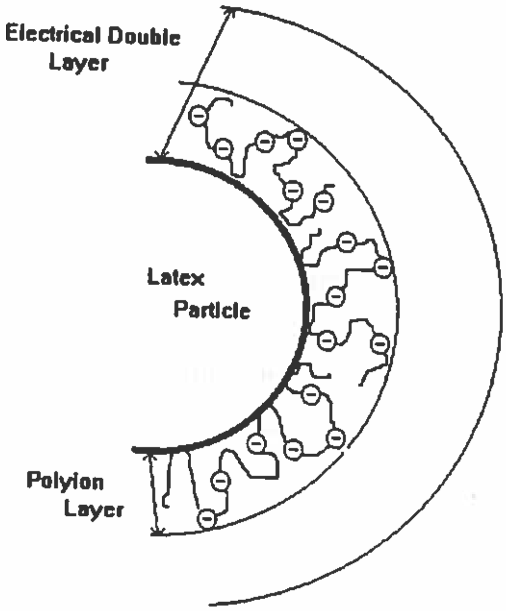

Fig. Schematic of Latex Particle with an Adsorbed and Grafted ASR (Polyelectrolyte).

International Polymer Colloid Group Newsletter

Contribution from the Department of Applied Chemistry, Keio University
Hiyoshi, Kohoku-ku, Yokohama 223 Japan

AFFINITY LATICES

Haruma Kawaguchi

Abstract: This is a short review of our recent studies on affinity latices. Hybrid particles carrying biospecific compounds to bind their complementary components were prepared and applied for bioseparation and cell activation. Optimal conditions for particle preparation, immobilization of biocompounds and procedure for application stage were discussed.

INTRODUCTION

Affinity latex particles are defined as particles having biospecific components such as DNA and antibodies on their surface, and used for bioseparation, diagnosis, cell stimulation, etc. via biospecific interactions. Gels and porous beads have been used as bioseparators so far. Latex particles are, however, expected to be superior to gel or porous beads in terms of sharpness and efficiency of protein purification because, in latex systems, binding and release are carried out only on the surface. In this paper, I would show some successful examples of affinity latices.

Particles were prepared by soap-free emulsion polymerization or precipitation polymerization. The latex particles were cleaned by repetitive centrifugation, decantation and redispersion and subsequently specific biocomponents were immobilized. The hybrid particles were mixed with blood or cell extracts upon application. The interactions between the immobilized component and its complementary counterpart were detected or measured under the most optimum conditions.

PREPARATION OF LATEX PARTICLES

Monomers used in the particle preparations were styrene (St, creating the core of the particles) and hydrophilic comonomers including glycidyl methacrylate (GMA), acrylamide (AAm) and methacrylic acid (MAc) (attributing to the shell of the particles). Azobis compounds were used as the initiator for soap-free emulsion copolymerization of St with GMA. Post polymerization of GMA was necessary to establish the poly-St core / poly-GMA shell structure. The particles themselves should have no interaction with non-specific compounds in blood or cell extracts. Poly-St core / poly-GMA shell particles showed less non-specific adsorption of proteins and other biocompounds more than expected.

Soap-free emulsion copolymerization of St with AAm resulted in the formation of particles having poly-AAm-rich skin layer. Amide groups of the surface layer could be converted to amine groups by the Hofmann reaction and to carboxyl groups by hydrolysis. Both groups served as binding sites with biocompounds.

Hydrophilic particles – hydrogel microspheres -- were prepared in alcohols by precipitation copolymerization of AAm, MAc and a closslinker, usually methylenebisacrylamide (MBAAm). Addition of p-nitrophenyl acrylate into the recipe resulted in the formation of monodisperse reactive hydrogel microspheres which were convertible to novel particles by modifying the active ester moiety.

IMMOBILIZATION OF BIOSPECIFIC COMPONENTS

The orientation of immobilized biocomponents is crucial in most cases of affinity latices. Biocomponents are asymmetric and should be immobilized on the particles in an orientation exposing their specific domains towards the medium in order to react with their complementary components. Many efforts have been done to immobilize antibodies onto particles in a desirable orientation in which the Fab fragment faces towards the medium while Fc fragment is bound to the particle and several methods have been proposed to immobilize DNA on substrates. DNA chains had better be immobilized at one end of their chains for the specific purposes. Immobilization of DNA with one chain end on poly-St core / poly-GMA shell particles were successfully performed under mild conditions using double stranded DNA having protruding chain end. DNAs were ligated prior to immobilization since the part of the DNA chains adjacent to the particle surface exhibited no activity to catch its complementary compounds due to steric hindrance. Namely, that part of DNA serves only as a spacer. This was also the case for functional peptide-carrying affinity particles. Sometimes additional spacers were bound to the particles prior to immobilization of functional compounds. For example, ethyleneglycol diglycidylether (EGDE) was used as a hydrophilic spacer to prepare a specific protein- and peptide-carrying particles.

USE OF AFFINITY LATICES

The optimal conditions for the application stage of affinity latices were obtained via trial and error. In bioseparation, only the complementary compounds were bound on the particles through specific interaction with the immobilized compounds. And after separation of the particles from the supernatant, the complementary compounds were released from the particles by changing the ionic strength or temperature of the solution. Purified compounds were examined by foot printing, Western blotting, etc. to confirm that they retained their original functions.

Sequence-specific double stranded DNA-carrying particles were used to purify some transcription factors. The results are shown in the left column of Table 1 and compared with the results obtained using sepharose gels. Affinity latices were superior to the conventional affinity gel separators in terms of efficiency and processability for the purification of transcription factors.

Table 1 Comparison between latex particles and sepharose gels

	Latex particles	Sepharose gels
Procedure	batch-wise	column
Time for purification	2 hrs	1 - 2 weeks
Number of steps	1	4 - 5
Recovery of transcription factor E4TF3 (43kD) from 1 mg nuclear extract	0.25 μg	0.02 μg
Concentration of transcription factor purified	high	low
Direct purification from crude nuclear extracts	possible	imposible
Non-specific adsorption	very low	high
Mechanical strength of carrier	high	low

Because double stranded DNAs were immobilized at the protruding chain end on our DNA-carrying particles, the unbound counterpart of double stranded chains could be released from the particles by denaturing. Resulting single strand DNA-carrying particles could re-bind the complementary DNA (564 bp) specifically among the mixture of DNAs of different chain lengths (from 125 to 23130 bp) within 30 min.

RGDS-carrying affinity latex particles were used for purification of its receptor released from cell mebrane. RGDS-carrying particles could specifically bind its receptor proteins from crude octylglucoside extracts. The receptor proteins bound to on-surface RGDS were not easily washed away with 0.1 M NaCl but released with 1 M NaCl. The specific binding of the receptor proteins was inhibited when free RGDS coexisted with RGDS-carrying particles during the binding stage.

RGDS-carrying affinity particles were also used for cell activation. The dependence of polymorphonuclear leucocytes (PMNs) response was examined when they contacted with RGDS-carrying particles. The extent of cell response was assessed with oxygen consumption by PMNs. A large amount of oxygen consumption indicates that the particles gave strong stimuli to PMNs. The carrier particles were partially-hydrolysed St-AAm copolymer (SAD) particles and AAm-MAc-MBAAm hydrogel (AM) particles. Remarkable oxygen consumption was observed in the system of SAD particles but not in AM particle system. Namely, hydrogel microspheres gave no significant stimulation of cells. Thermosensitive particles composed of poly(N-isopropylacrylamide) discontinuously below and above the transition temperature changed the extent of interactions with proteins and cells.

ACKNOWLEDGEMENT

The author would like to thank Professor H.Handa, Faculty of Life Science & Technology, Tokyo Institute of Technology, for his cooperation during this work.

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RGDS-carrying affinity latices

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Contribution to IPCG Newsletter

by

Dr. Peter A. Lovell

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UK Polymer Colloids Forum

In the previous newsletter, I announced the creation of the UK Polymer Colloids Forum, of which I am chairman. I am pleased to say that support for the activities of the Forum is growing and that we now have just over 170 people registered with the Forum, almost all of whom are UK-based. Please let me know by fax (+44 161 200 3586) if you would like to register and be added to the mailing list. You will then receive directly all information and circulars concerning the Forum and its activities.

The second meeting of the Forum took place at Keele University from 22-23 Septmeber 1994 and was attended by 68 people. The meeting proved to be a great success, both scientifically and socially. The proceedings are summarised in Sandy Dunn's contribution to this issue of the newsletter.

The next meeting of the Forum is scheduled for 19-20 September 1995 and will again be held at Keele University. Dr. Paul Reynolds of Bristol University is organising the meeting. It is hoped that the first circular and call for papers will be ready by the end of this year.

Toughening of Epoxy Resins using Multi-Phase Particles

Sponsors: ICI Acrylics

Research worker: Dorian Pierre

Three-layer toughening particles designed for use with epoxy resins have been prepared using procedures adapted from those described for preparation of three-layer PMMA toughening particles [1]. The only differences are that the rubbery layer is crosslinked poly(n-butyl acrylate) and the outer layers of the particles comprise poly[(methyl methacrylate)-*co*-(glycidyl methacrylate)-*co*-(ethyl acrylate)] with 20.0 wt.-% glycidyl methacrylate and 4.0 wt.-% ethyl acrylate repeat units. In each case, the rubbery layers and the inner glassy layers are crosslinked, and each layer is graftlinked to the adjacent layer(s) using allyl methacrylate (ALMA). The range of particles prepared are shown schematically in Figure 1 together with the nomenclature used to define them, e.g. GM(28/10) is a particle with outside diameters of the rubbery annulus and glassy core of 0.28 and 0.10 µm respectively. Data from preparation of the GM(47/15) particles are shown in Figure 2 and are representative of the preparations.

After isolation by coagulation and drying, the particles were blended at different levels into bisphenol-A diglycidylether (DGEBA) (Epikote 828, *ex*. Shell) using a Silverson L4R high shear mixer fitted with a standard disperser head. After de-gassing under vacuum, piperidine was mixed in and the resin cured at 120 °C for a period of 16 h. The epoxy resin matrix has a T_g of 86±1 °C (measured by DSC) which is unaffected by the toughening particles.

Contribution to IPCG Newsletter

Peter A. Lovell, Manchester Materials Science Centre, University of Manchester & UMIST, UK

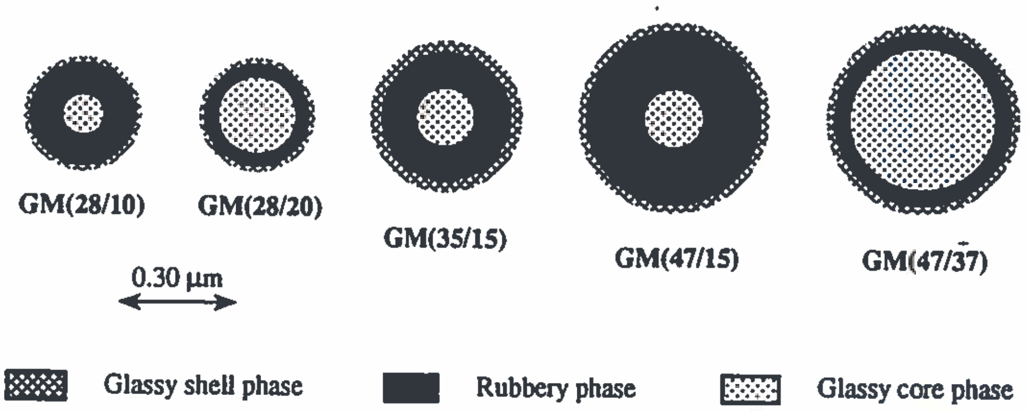

Figure 1. Schematic diagrams of sections through the equators of the toughening particles showing their sizes and internal structures.

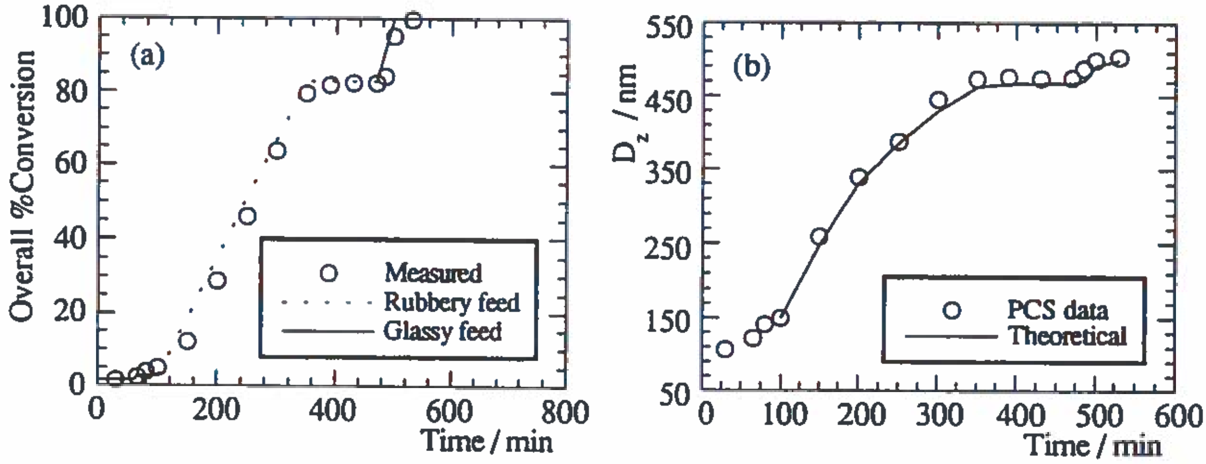

Figure 2. Variation of (a) overall % conversion and (b) z-average particle diameter (D_z) with reaction time for preparation of the GM(47/15) toughening particles.

The results from tensile testing show that the toughening particles have the usual effect of increasing matrix ductility (ultimate strains up to about 10% are achieved) at the expense of reductions in modulus and fracture stress. The values of Young's modulus (E) are plotted against the volume fraction of rubber (V_r) in Figure 3 which shows that E is controlled by V_r.

The effects of particle size and morphology upon the critical strain energy release rate (G_{Ic}) under impact loading have been investigated. Figure 4 shows the variation of impact G_{Ic} with particle volume fraction (V_p), which excludes the outer layer but includes the internal PMMA core of the particles. The data presented in Figure 4a indicate that G_{Ic} depends upon particle size and suggest that rubbery layer diameters ≥ 0.35 mm are an advantage. Figure 4b shows that increasing the size of the glassy core has a detrimental effect upon toughness, this most clearly being evident from the data for the GM(47/15) and GM(47/37) particles. These results may be interpreted in terms of the micromechanics of deformation. For rubber-toughened epoxy resins, deformation proceeds by shear yielding of the matrix which itself is initiated by cavitation of the rubbery particles. The cavities dilate considerably in conventional, rubber-toughened epoxy resins in which carboxyl-terminated poly(butadiene-*co*-acrylonitrile) (CTBN) liquid rubbers are employed. In the GM series of particles, the rigid glassy core can be expected to constrain the cavitated rubbery layer and

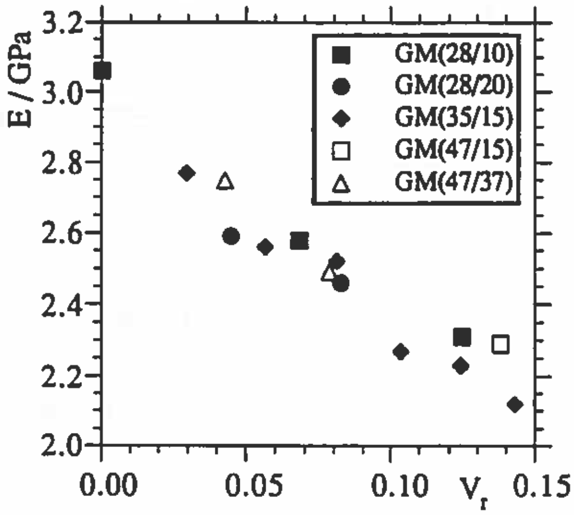

Figure 3. Plot showing the variation of Young's modulus (E) with volume fraction of rubber (V_r) for each of the rubber-toughened epoxy resin materials.

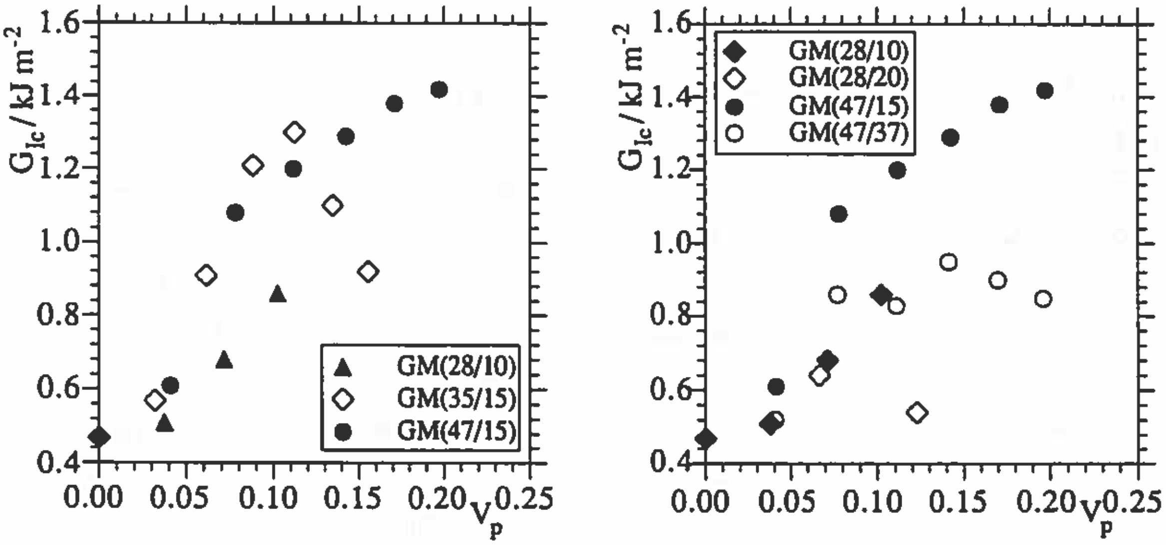

Figure 4. Variation of 0.3 m s^{-1} impact values of the critical strain energy release rate (G_{Ic}) with volume fraction of particles (V_p) for rubber-toughened epoxy resin materials. (a) Data showing the effect of particle size. (b) Data showing the effect of particle morphology.

limit its dilation, thereby reducing the ability of the matrix to shear yield and reducing toughness. This interpretation of the observed effects of particle morphology is in the process of being investigated more thoroughly with experiments that probe deformation mechanisms.

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International Polymer Colloids Group Newsletter

Contribution by M. Nomura

Meeting News in Japan:

(1) **The 8th Polymeric Microsheres Symposium (domestic)** is to be held in Fukui University from November 9-12, 1994. In this symposium, 54 papers will be presented and the number of participants would be around 300, most of whom are from companies. Preprints, though written in Japanese, are available from M. Nomura.

(2) 5th SPSJ International Polymer Conference organized by The society of Polymer Science, Japan is to be held in Osaka from November 28 to December 2, 1994. In this conference, 7 sessions are provided and one of them is "Polymer Particles". In this session, 17 oral and 8 poster papers are to be presented. Dr. El-Aasser and Dr. J. Ugelstad are invited speakers.

Recent Research Activity of Our Group (M. Nomura and H. Tobita):

Papers and Principal Presentation:

(1) Molecular Weight Distribution in Emulsion polymerization, H. Tobita, Y. Takada and M. Nomura, *Macromolecules*, **27**, 3804 (1994)

In this paper, a new Monte Carlo simulation model is proposed for emulsion polymerization. This Monte Carlo simulation model can give very detailed information such as the full distribution of the dead polymer molecular weights and macroradicals in the polymer particles. This simulation model predicts that the effect of long-chain branching on molecular weight distribution is significant with the formation of very high-molecular weight chains, if active terminal double bonds are formed and polymerize.

(2) Kinetics and mechanisms of Unseeded Emulsion Polymerization of Methyl Methacrylate, M. Nomura and K. Fujita, *Polymer Reaction Engineering*, in printing.

(3) An Experimental Study on Saturation Swelling of Styrene-Acrylonitrile Copolymer Particles with Styrene and Acrylonitrile Monomers, M. Nomura, X. Liu, K. Ishitani and K. Fujita, *J. Polymer Sci., Polym. Phy. Ed.*, in Printing,

This paper is to be presented in 5th SPSJ International Polymer Conference to be held in Osaka from November 28 to December 2, 1994. The manuscript of my presentation is shown in the next page.

Swelling of poly(styrene-*co*–acrylonitrile) latex particles with a styrene and acrylonitrile monomer mixture

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The knowledge of equilibrium and partial swelling of poly(styrene-*co*-acrylonitrile) (SAN) latex particles with a styrene (St) and acrylonitrile (AN) monomer mixture is of great importance for emulsion copolymerization of St and AN, because the knowledge of monomer partitioning among the three different phases, that is, the water, monomer droplet and polymer particle phases, determine the rate of copolymerization, the composition of copolymer produced and so on. In this study, therefore, the effects of the copolymer composition and the compositional inhomogeneity in SAN copolymer particles on their swelling behavior were examined.

Experiments: SAN copolymer latex particles with different copolymer composition and in the range of 100±20 nm in diameter were synthesized with conventional batch and semicontinuous emulsion copolymerization of St and AN with sodium lauryl sulfate (NaLS) and potassium persulfate ($K_2S_2O_8$) as emulsifier and initiator, respectively. Swelling experiments were carried out as follows: About 20 cm^3 SAN copolymer latex of known solid content and copolymer composition thus prepared was mixed with a large quantity of St and AN monomer mixture of known composition in a 100 cm^3 flask and was agitated for 4 hours at 50°C to attain equilibrium. Then, an aliquot of the mixture was transferred into a centrifuge tube and the monomer droplet phase in the mixture was immediately separated as a monomer layer from the serum consisting of the monomer-swollen polymer particles and water by centrifugation at 3700 rpm for 30 min. The concentrations of St and AN monomers in the monomer layer, which were in equilibrium with those in SAN copolymer particles, was measured by gas chromatography. From the bottom of the centrifuge tube, a small quantity of the serum containing monomer-swollen polymer particles and water was withdrawn by a syringe, weighed and transferred into a 100 cm^3 volumetric flask containing methanol to precipitate SAN copolymer in the monomer-swollen particles. The weight of precipitated copolymer and the concentration of each monomer in the filtrate were measured respectively. Using these data and the separately determined water solubility of St and AN monomers at 50°C, the equilibrium concentrations of St and AN in the polymer particles, $[M_S]_p$ and $[M_A]_p$ versus AN weight fraction in monomer droplets, ϕ_{ad} was calculated and shown in Fig 1. It was found that the copolymer composition of SAN latex particles had little or no influence on the swellability of these latex particles with a St and AN monomer mixture as long as the weight fraction of AN units in SAN latex particles, H_A, was less than around 0.6. It was found that all the saturation swelling data presented so far can be expressed by the following empirical equations:

$$\frac{1}{[M_A]_p} = A + \frac{B}{\phi_{Ad}} \quad (1), \qquad \frac{1}{[M_S]_p} = C + \frac{D}{1-\phi_{Ad}} \quad (2)$$

The numerical values, A, B, C and D experimentally determined are shown in Fig. 2. The solid and dotted lines in Fig. 1 are drawn using Eqs.(1) and (2) and these values to compare with the experimental data. It is seen that these empirical equations predicts very well the swelling behavior of SAN copolymer particles with St and AN monomers.

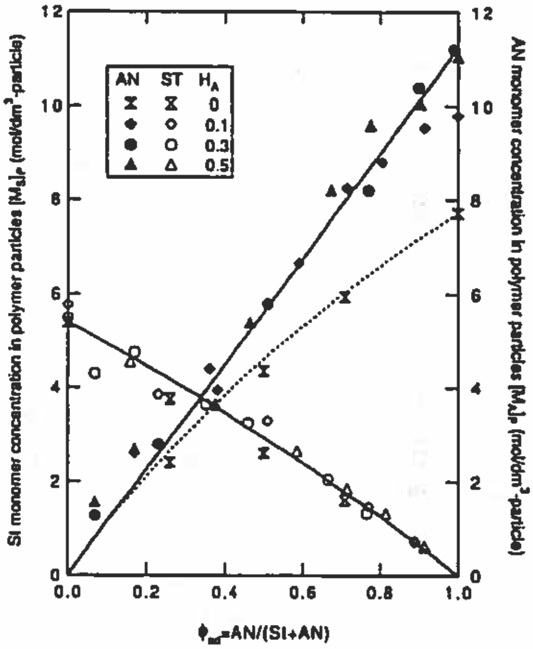

Fig. 1 $[M_s]_p$ and $[M_A]_p$ versus ϕ_{ad}

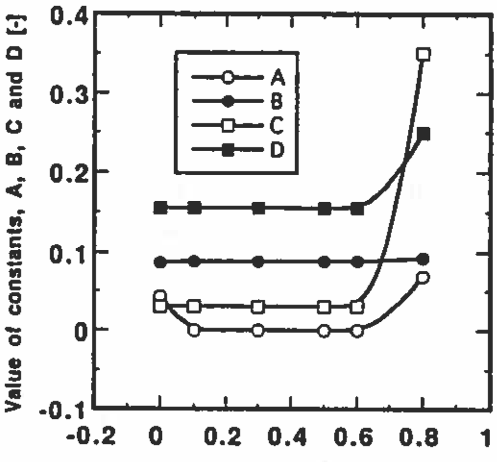

Fig.2 Variation of values of A,B, C and D with H_A

Temperature dependent contact angles of water on poly(N-isopropylacrylamide) gels.

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October 2, 1994

Abstract

The advancing contact angles of water on cross-linked poly(N-isopropylacrylamide) water swollen gels were a sensitive function of temperature. From 25 to 35 °C the angles were close to 40 ° whereas from 35 to 50 °C the angles were about 90 °. The abrupt change in wetting corresponded to the temperature range in which the gel shrank from about 90 to 20 wt % water upon heating. It is speculated that the propyl groups preferentially occupied the air water interface.

Introduction

This communication describes results of the first reported contact angle measurements on water swollen cross-linked poly(N-isopropylacrylamide), polyNIPAM, gels which show unique behavior as a function of temperature. Many papers in the last decade have discussed the swelling properties of cross-linked polyNIPAM gels in water [1]. This is an interesting system because the gels are highly swollen (typically 90% by wt water) up to 32 °C whereas at higher temperatures the gels expel most of the water to leave about 2 water molecules per amide unit. Temperature sensitive swelling has been observed in both macroscopic[2] and microscopic colloidal microgels[3] and the volume phase transition temperature (i.e. the temperature corresponding to the greatest change in volume), Tv, is in the range 31-35 °C. This behavior reflects the fact that linear polyNIPAM has a lower critical solution temperature in water at 32 °C[4].

Figure 1 shows the advancing contact angle of water as a function of temperature. The behavior was remarkable. At 25 °C when the gel contained about 90 % water, the contact angle was 42 °. Around the Tv (about 36 °C) the contact angle jumped to 90 ° which corresponds to values for water on alkane surfaces.

The arrows in Figure 1 show the direction in which the temperature was changed. Although a minimum of 30 minutes was given for equilibration, we believe the scatter reflects incomplete swelling or de-swelling of the gel. Slow de-swelling kinetics have been reported by others[5].

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The results can most obviously be interpreted by assuming that propyl groups tend to concentrate at the air/water interface at all temperatures. At high temperatures the result is an alkane-like surface of packed propyl groups whereas at low temperature there are some water or amide groups mixed in at the interface.

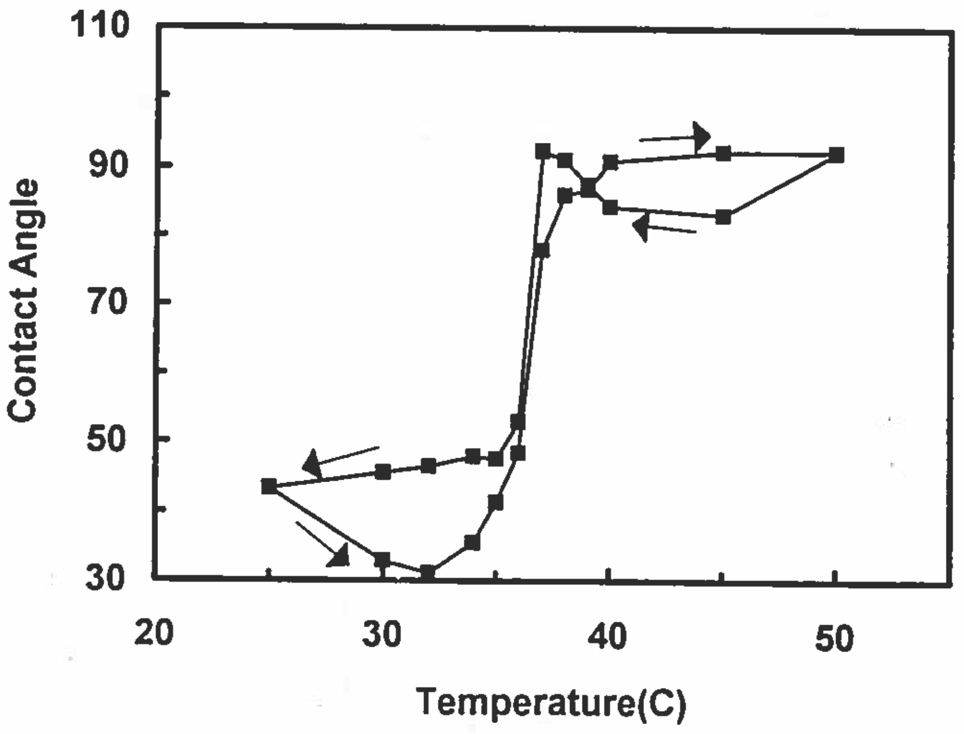
Attempts to measure a contact angle by the captive bubble method with the gel immersed in water were unsuccessful. Below Tv, the bubbles did not adhere indicating a contact angle of zero. At higher temperatures the results were erratic; in some cases the captive bubble would adhere to give a contact angle whereas a in repeated measurement at the same location the air bubble did not displace water from the surface. Perhaps with immersed gels the more polar amide groups were facing the water phase. The concept of polymers and gels orienting to give the minimum interfacial tension has been proposed by others[6].

High contact angles for water on other types of hydrogels has been reported. For example, Holly and Refojo reported advancing contact angles between 60 and 85 ° for cross-linked poly(2-hydroxyethyl methacrylate) swollen containing 30 to 40% water[7]. Similarly Chappuis et al. showed that saline solution had an advancing contact angle of 100 °C on animal cartilage[8] . Therefore, we conclude that the polyNIPAM results are not un-reasonable.

The swelling behavior of polyNIPAM gels is influenced by solvent composition, surfactant and the presence of acrylamide or other co-monomers. We speculate that the contact angle will also be sensitive to these factors and work is in progress to verify this.

In summary, we believe the results in Table 1 are the first reported contact angles for water on polyNIPAM gels and we do not know of any other system where the contact angles are such a strong function of temperature.

Figure 1 The advancing contact angle of water on cross-linked polyNIPAM gel swollen with water. The initial measurement was made at 25 °C and the arrows indicate the direction of temperature change.



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Polystyrene latex deposition onto polyethylene film consecutively treated with cationic and anionic polymer

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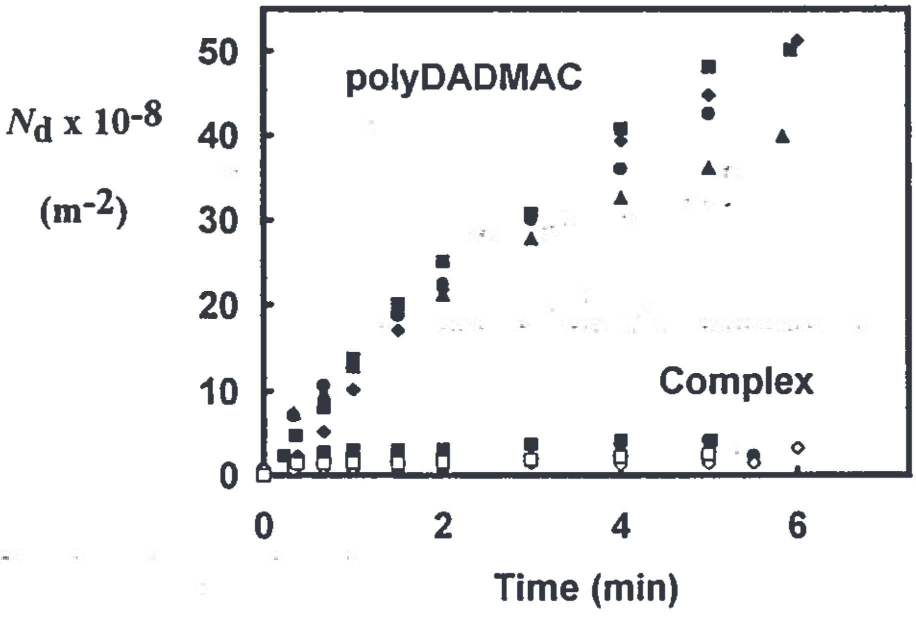
October 2, 1994

Abstract:

The effects of treating polyethylene film by consecutive adsorption of poly(diallyldimethyl ammonium chloride), polyDADMAC, followed by poly(sodium p-styrene sulfonate), PSS, on the deposition rate of aqueous polystyrene latex was investigated with the impinging jet technique. Rapid initial deposition occurred on films treated with polyDADMAC, however, significant blocking occurred. Deposition decreased with the concentration of polyDADMAC used to treat the PE film.

Film treatment with polyDADMAC followed by PSS to give an adsorbed polyelectrolyte complex gave decreased deposition rates. The molecular weight of PSS was not a significant variable in the range 5,400 to 1,200,000. It was concluded that PSS increased the electrostatic repulsion between the PE film and the latex particles.

Particle deposition versus time for polyDADMAC and complex coated films. The polyDADMAC and PSS solution concentrations were 0.1% and the soaking time was 48 h for each polymer. Different symbols denote replicated experiments. Re = 75, VP =0, [Latex] = 1.1×10^7 cm^{-3}.



Contribution to IPCG Newsletter From Laboratoire de Chimie des Procédés de Polymérisation
(LCPP-CNRS)
and Unité Mixte CNRS-bioMérieux
Lyon-France

(submitted by C. Pichot)

Maleic anhydryde hemiester derivatives as reactive surfactants

(A. Zicmanis, T. Hamaide, A.Guyot, LCPP)

Hemiesters themselves can be used at pH 7 and more as anionic surfactants in the polymerization of styrene. Small and monodisperse particles(100 nm) are obtained with no coagulum with small amount of surfactants (2.10^{-3} mole/l); Up to 70 % of the surfactant remain attached to the latex after ion exchange resin treatment. Upon flocculation with $CaCl_2$, almost no surfactant stays in the serum.

The hemiester have been engaged as initiators in the catalytic polymerization of ethylene oxide. It results in nonionic surfactant with a reactive double bond in between the two amphiphilic parts. These surfactants have been used in dispersion polymerization of styrene as well as with styrene-butyl acrylate binary system.

In batch emulsion polymerization, monodisperse particles (200-300nm) can be prepared; however a large amount of coagulum is also produced. Seeded copolymerizations of styrene and butyl acrylate give much better results provided continuous feed of both the monomer mixture and the surfactants is carried out. Up to 40% of the surfactant can be attached to the latex after serum exchange treatment.

Finally, in dispersion polymerization in hydroalcoholic medium, monodisperse particles in the micron size are easily obtained if enough surfactant is introduced. However, although the comsumption of the maleic derivative, as copolymer with styrene is very fast, only 2% of the surfactant remains fixed onto the polymer particles. The serum contains most of the renaining surfactant moieties and also polystyrene oligomers.

Surface functionalization of polystyrene latex particles with a liposaccharidic monomer

(J. Revilla, A. Elaissari, C. Pichot, (U.M CNRS-bioMerieux), B. Gallot (LMOPS))

Emulsifier-free polystyrene latexes with immobilized carbohydrate residues have been prepared by batch or seed (co)polymerization of styrene in the presence of 11-(N-p-vinylbenzyl)amido undecanoyl maltobionamide (LIMA).

CMC and molecular surface area of LIMA were determined by surface tension and fluorescence measurements. Batch polymerization of LIMA with styrene was first performed using potassium persulfate, proving the efficiency of LIMA as emulsifier. Seed copolymerization was then investigated using polystyrene seed particles with varying experimental conditions (especially the LIMA surface coverage). Material balance of LIMA between aqueous phase and particles was obtained by separating both phases by ultracentrifugation and it was found that the surface-active monomer is preferentially on or in the particle (nearly 100 % in batch and at most 70% in seed copolymerization). The presence of the carbohydrate residues at the particle surface was directly evidenced by ^{1}H NMR, ESCA analysis and electrophoretic mobility.

Preparation and characterization of cationic N-isopropyl acrylamide copolymer latexes (F. Meunier, A. Elaissari, C. Pichot (U.M CNRS-bioMerieux))

Cationic poly(N-isopropylacrylamide (NIPAM)) copolymer latexes have been prepared at 70°C using Methylenebisacrylamide (MBA) as crosslinking agent, 2-2'-Azobis-(2-Amidinopropane hydrochloride) (V50) as initiator and in the presence of 2-Aminoethylmethacrylate hydrochloride (AEM). It was found that the concentration of AEM plays a major role on the polymerization kinetics and particle nucleation. However too a high concentration (2-5 mole%/ NIPAM) caused the latex to be polydisperse together with the production of large amounts of polyelectrolytes. The presence of surface amino groups on the final particles under protected form was revealed both by a U.V spectrometry and NMR methods. It was undirectly evidenced through the electrophoretic mobility behavior of the latex particles (below and above the lower critical solubility temperature of the poly(NIPAM)) as well as by their stability against a monovalent electrolyte.

Preparation of model amino functionalized polystyrene latexes for interaction study with nucleic probes (F. Ganachaud, A. Elaissari, C. Pichot, (U.M CNRS-bioMerieux))

Emulsifier-free (co)polymerization of styrene with vinyl benzyl amine hydrochloride (VBAH) was carried out using batch and shot growth processes and 2-2'-Azobis-(2-Amidinopropane hydrochloride) as a cationic initiator. In a batch process, the surface functionalization was controlled by the amonut of VBAH but led to too small particle size. On the contrary, shot groth process allows one to control the size and then the incorporation of the functional monomer. The characterization of the surface amino groups was performed by a fluorescence method which enables one to titrate residual monomer in the serum and to determine the amount of VBAH directly on the latex particles. The total surface charge density seems to level off at 20 µC/cm2. Studies are currently investigated concerning the adsorption behavior of various nucleic probes onto these model reactive latexes with special emphasis on the influence of ionic strength and pH.

Thesis and recent papers:

"Emulsion polymerization in the presence of nonionic surfmers".
Annie Filet - (LCPP)- Univ. Lyon I, April 1994

"Modelisation of particle structuration in latex".
Yvon Durant - (LCPP)- Univ. Lyon I, April 1994 (in collaboration with Prof. D. Sundberg - Univ.New Hampshire - USA)

"Synthesis and characterization of cationic amino functionalized polystyrene latexes".
T. Delair, V. Marguet, C. Pichot, B. Mandrand in Colloid Polym. Sci., 272,962 (1994)

"Recent developments in the preparation of functionalized polymeric microsheres"
C. Pichot in Macromolecular Symposia, Oct (1994)

POLYMER COLLOIDS NEWSLETTER CONTRIBUTION

from The University of Akron
Submitted by Irja Piirma

Emulsion Copolymerization of p-Methylstyrene and Methyl Methacrylate with Water Soluble and Monomer Soluble Initiators.

Work carried out by Dr. Rosa Carceller

ABSTRACT

The objective of the study was to study the mechanism and obtain kinetic data for the aqueous emulsion copolymerization of p-methylstyrene (PMS) and methyl methacrylate (MMA) with water soluble potassium persulfate (PPS) and monomer soluble azobisisobutyronitrile (AIBN). The particles were stabilized with sodium dodecyl sulfate.

Under the same experimental conditions, i.e. initiator concentration and polymerization temperature, the PPS system created a much larger number and smaller particles than did the polymeriazations with AIBN. An increase in the PPS concentration from 2x10-4 to 7x10-4mol increased the polymerization rate four-fold. There was an initial increase in rate with increasing AIBN concentration, but additional increase did not increase the rate any further.

Additional work is planned to determine the differences and similarities in the behavior of the two initiators as far as particle numbers and sizes are concerned, also to determine the copolymer compositions, and how these are affected by the different mechanisms of these polymerizations.

Contribution to IPCG Newsletter

EMULSION POLYMERIZATION OF STYRENE WITH p.tBu TOLUENE THIOL AS TRANSFER AGENT

O. LAMBERT, Ph. DUMAS and G. RIESS

Laboratoire de Chimie Macromoléculaire, ENSC, CRPCSS
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Introduction

Mercaptans are commonly used as chain transfer agents (CTA) in emulsion polymerization for controlling the molecular weight of polymers. p.tBu toluene thiol (PBTT) is an odorless mercaptan and we have studied its efficiency in the emulsion polymerization of styrene. Moreover, its very low solubility and diffusion rate in water have allowed us to obtain new data on the locus of polymerization initiated by oil-soluble initiators.

Experimental

Typical emulsion recipe :

- styrene : 70 g
- sodium dodecylsulfate : 2 g
- potassium persulfate or AIBN : with a ratio ; initiator/monomer of 1 % (in w/w)
- water : 225 g
- thiol : variable amount

Experiments are run at 70°C, with an impeller speed of 200 rpm, either in batch or in a continuous process in which only the thiol is continuously added during the second stage of the emulsion polymerization.

Results and discussion

a) Hydrosoluble initiator

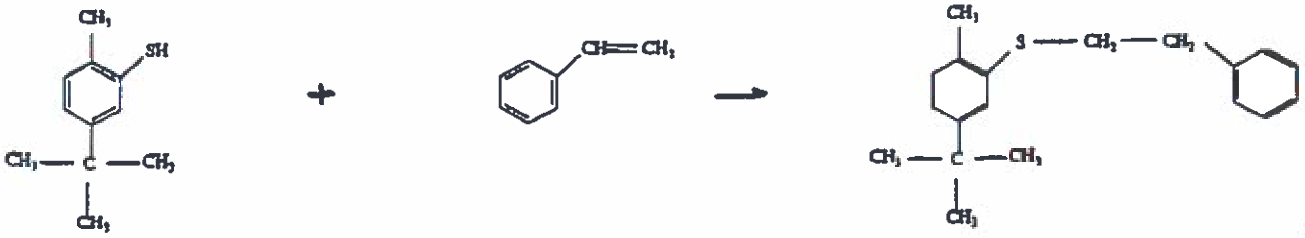
Emulsion was run in batch and initiated by $K_2S_2O_8$. The chain transfer constant of PBTT was calculated by plotting $1/DP_n$ versus the ratio [PBTT]/[monomer] (fig. 1). For ratio higher than 1,25 % (w/w-thiol/monomer) we observed practically no effect of the concentration of thiol on the molecular weight of polymer. The transfer constant is obtained from the steep slope. This value (0.12) is smaller than those obtained with the same thiol in bulk and also with an aliphatic thiol (tert dodecylmercaptan) in the same conditions (see table 1).

This small efficiency depends of it small rate of diffusion as reported for aliphatic thiols (1) and also from the presence of a secondary reaction suggested by the absence of effect on molecular weight of polymer for high thiol concentrations.

The results of ^{1}H-NMR study are reported on fig. 2. Initially, the medium part of the spectrum consists of ethylenic protons of styrene (around 5.5 ppm) and proton of thiol (3.3 ppm). After 1 hour at 80°C, these signals disappear and are replaced by 2 quadruplets (around 3 ppm) corresponding to the sequence :

$$- CH_2 - CH_2 - S -$$

coming from the addition of the thiol on the double C - C bound of styrene :



In order to check this addition in our emulsions, we run an experiment with a high ratio thiol/monomer (10 % w/w) and at the end of polymerization, we have isolated the product of addition. About 1/3 of PBTT adds to styrene.

This Michael type reaction between styrene and an aromatic thiol was also described in an anionic copolymerization of methyl methacrylate (2).

In order to minimize this secondary reaction between thiol and monomer, we have added thiol continuously during the second stage of the emulsion polymerization. SEC chromatograms are reported on fig. 3. The molecular weights obtained by this continuous process are roughly half of those obtained by a batch method for a same total thiol concentration.

b) Oil-soluble initiator

One series of emulsions initiated by AIBN were run in batch. Two typical SEC chromatograms are reported on fig. 4. For small conversions, we observe a bimodal distribution which becomes unimodal after approximatively 30 % of conversion. Only the high molecular weight peak survives.

Fraction of high molecular weight (M_{peak} around 10^6) is similar to that obtained without CTA (emulsion initiated by AIBN at 70°C). In marked contrast, the fraction of low molecular weight (M_{peak} of about 60,000) is very similar to the polymer obtained with an aliphatic thiol as CTA (emulsion initiated by AIBN at 70°C).

This implies that high molecular weight polymers are obtained in particles and low molecular weight polymers are formed in monomer droplets where practically all the PBTT is confined.

These results are in agreement with NOMURA's results (3) showing that the principal locus of the polymerization shifts at a comparatively early stage from the monomer droplets to the resulting polymer particles.

Another series was run with a continuous addition of PBTT during the second stage of the emulsion. With this continuous addition we can see, on fig. 5, that monomer droplets remain a locus of polymerization at all stages. Moreover, its contribution seems to increase with the conversion.

Our results show that different mechanisms can operate in the emulsion of styrene initiated by AIBN in presence of PBTT as transfer agent. The main factor seems to be the thiol concentration in the monomer droplets ; with large concentration (batch) Michael reaction between thiol and monomer seems predominant whereas for low concentration (continuous addition of thiol) chain transfer is favoured.

Conclusion

In emulsion polymerization of styrene in presence of PBTT as CTA, we have observed a competition between the expected chain transfer reaction and a Michael type addition on styrene.

In the case of an organo-soluble initiator, we have two locus of polymerization. When chain transfer reaction is favoured (continuous addition of thiol) the droplets are the principal locus of polymerization. This can be attributed to the high hydrophoby of thiols radicals that remain confined in the monomer droplets.

Acknowledgments

We thank the 'Société Française HOECHST' for financial support and Mr F. VUILLEMIN for helpful discussions.

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table 1. Transfer constants for emulsion and bulk polymerizations of styrene.

THIOL	Cs	Conditions
ter-dodecyl mercaptan	0,81	Emulsion, 70°C
PBTT	0,12	Emulsion, 70°C
PBTT	1,43	Bulk, 80°C

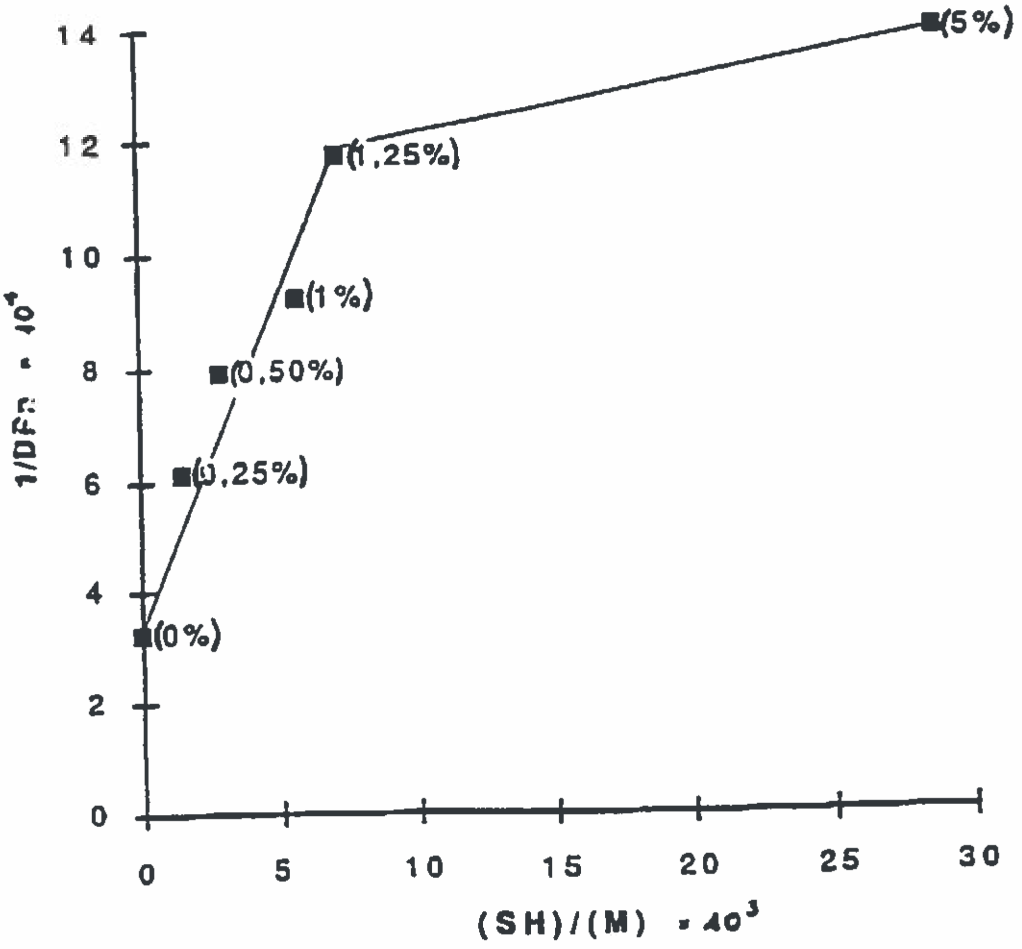

fig. 1. Effect of thiol concentration on molecular weights. In brackets, the ratio PBTT / Styrene in $^{w}/_{w}$.

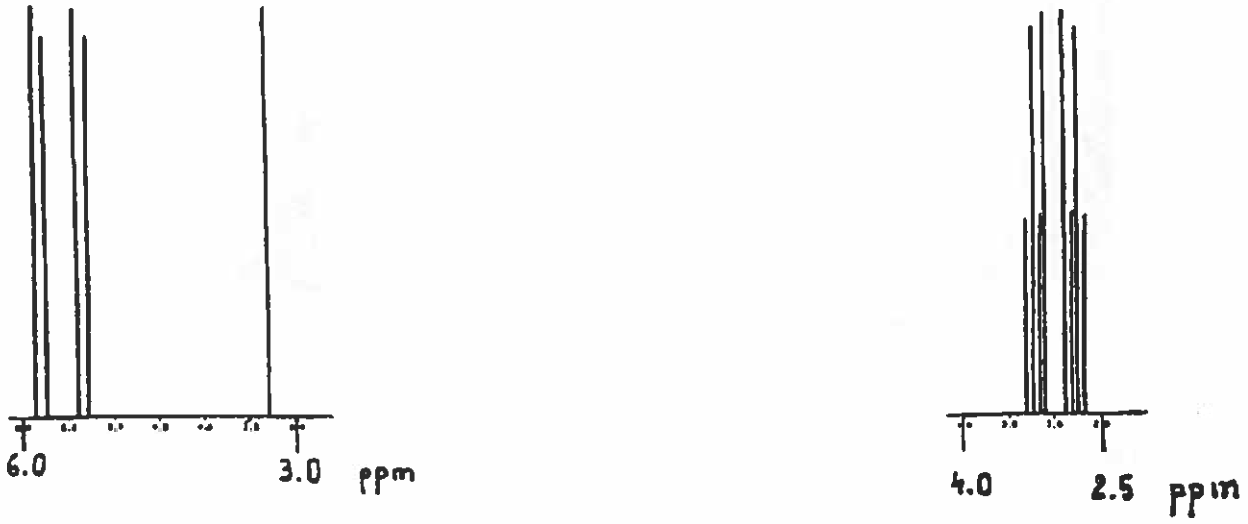

fig. 2. ^{1}H. NMR study of the reaction between PBTT and styrene.

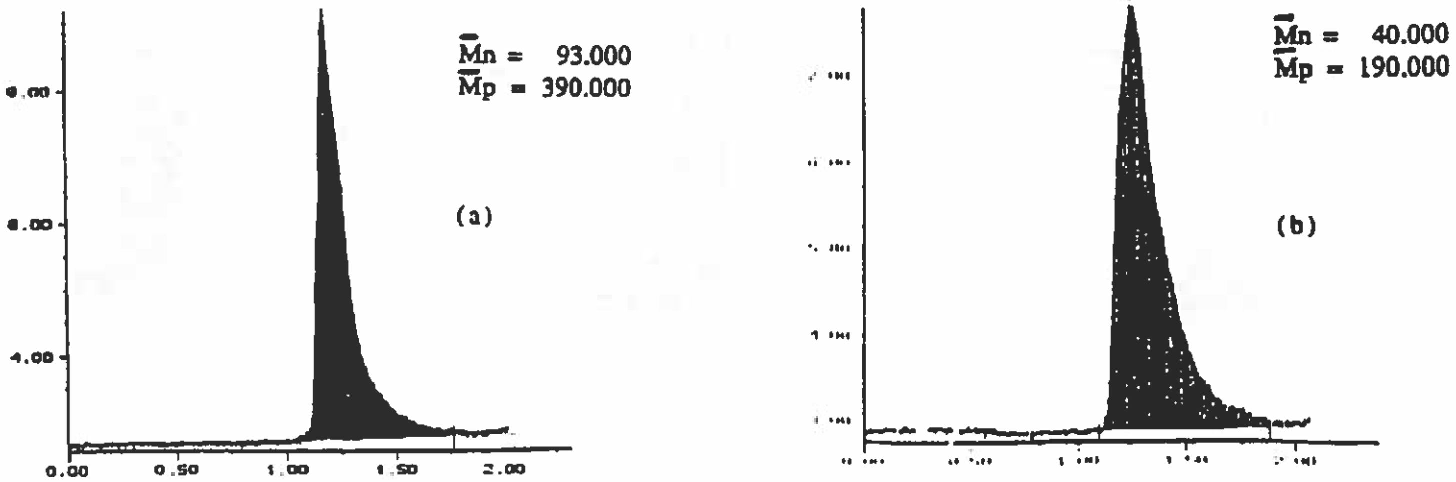

fig. 3. Emulsion initiated by potassium persulfate.
SEC chromatograms for polymers obtained at complete conversion. (a) batch and (b) continuous addition of thiol (thiol / styrene = 1% in $^w/_w$).

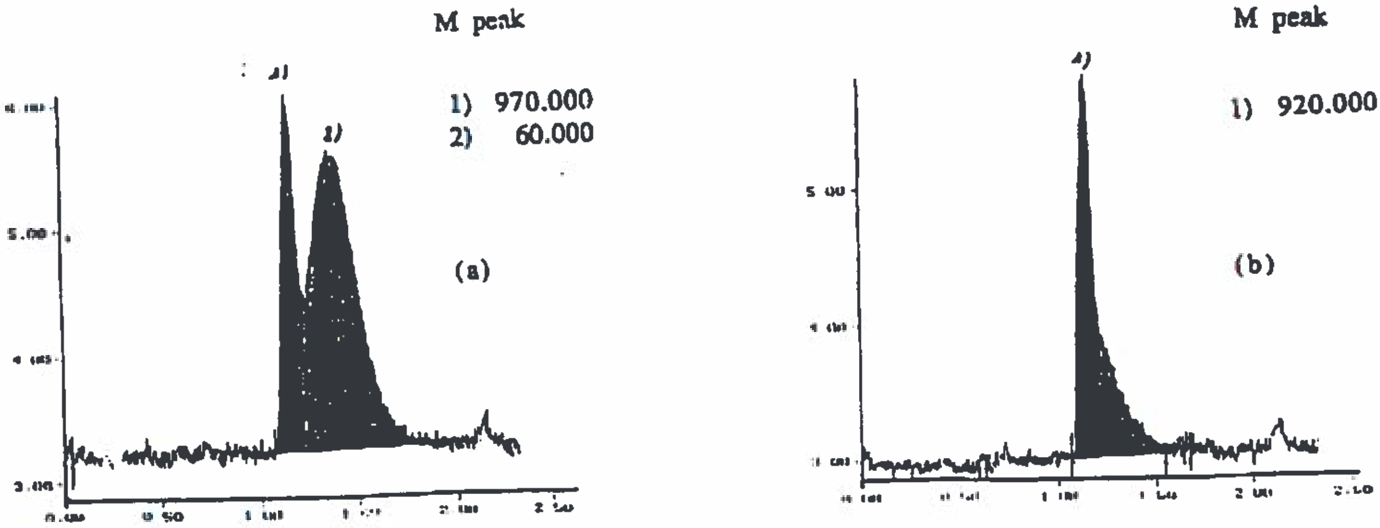

fig. 4. Emulsion (in batch with thiol / monomer = 1% in $^w/_w$) initiated by AIBN.
SEC chromatograms for polymers obtained at partial conversions.
(a) 11% and (b) 33%.

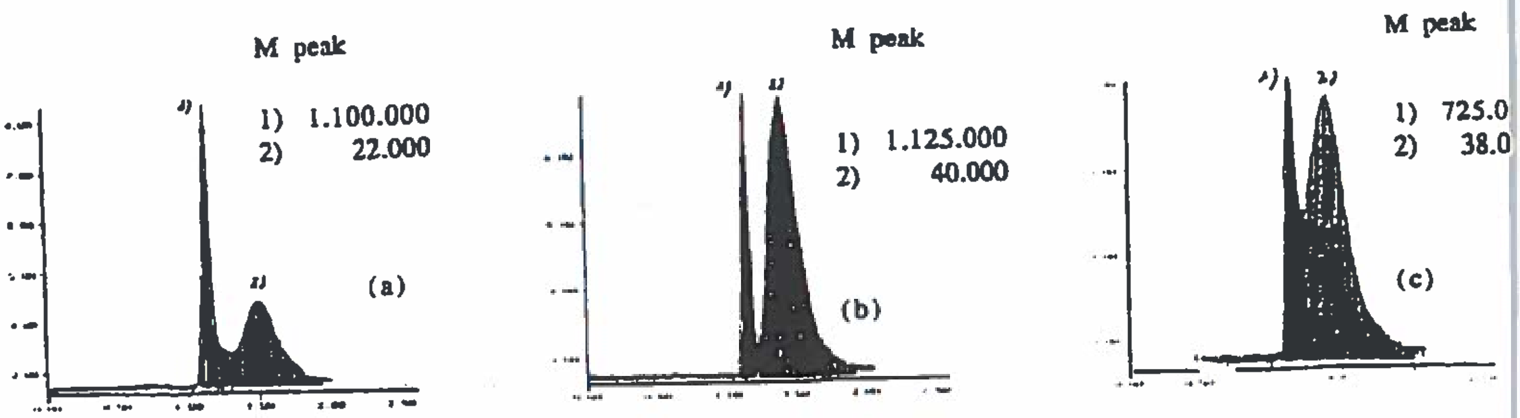

fig. 5. Emulsion initiated by AIBN with continuous addition of thiol (thiol / monomer = 1% in $^w/_w$).
SEC chromatograms for polymers obtained at partial conversions.
(a) 16%, (b) 55% and (c) 78%.

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Robert L. Rowell, *Associate Editor*

POLYMER COLLOID GROUP NEWSLETTER

THE ELECTRODYNAMIC POTENTIAL; A MEASUREMENT OF DOUBLE-LAYER DISPLACEMENT. R. L. Rowell, R.J. Bishop, L. Yezek and G.M. Aval[1], Department of Chemistry, University of Massachusetts, Amherst, MA 01003-4510.

We combine the hydrodynamic theory of uncharged particles with the electrophoretic theory of charged particles by defining a new and directly measurable quantity, the electrodynamic potential g as the ratio of the diffusion constant D to the electrophoretic mobility U, $g=D/U$. The charge separation in a particle undergoing electrophoretic mobility is measured by g whereas the classical ζ-potential is a measure of the excess charge at the surface of shear. We relate g to double-layer theory by $g=fkT/6\zeta\varepsilon_r\varepsilon_0 r_h$ where f is a double layer factor, ε_r the relative dielectric constant, ε_0 the permittivity of vacuum and r_h the hydrodynamic radius. In the Hückel model $f=6$ while in the Smoluchowski model $f=4$. In a similar manner we relate g to the charge Q on a particle by $g=fkT/6Q$. The concept of the electro-dynamic potential is generally applicable to particles of all shapes in both aqueous and non aqueous media and may be used as a direct probe of the electrical properties of colloids, polyelectrolytes, charged macromolecular systems, micelles and smaller ionic systems limited only by the separate measurability of D and U. Applications of the theory are discussed.

[1] On leave from Teacher Training University, Tehran, Iran.

From: Vivian T. Stannett
Chemical Engineering Department
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Richard Gilbert (Wood and Paper Science Department) and I have now published our work, mentioned briefly earlier, on the radiation induced inverse emulsion polymerization of N-vinyl pyrrolidone.

Excellent yields at rapid polymerization rates were obtained with high molecular weights of 1-3 million. The particle sizes were rather broad and between 320 and 1800 nm.

Full details may be found in our paper "Radiation Initiated Inverse Polymerization of Vinyl Pyrrolidone" by M. B. Taylor, R. D. Gilbert, V. T. Stannett and J. L. Williams. J. Appl. Polym. Sci. 53, 1385-1390. (September 1994).

Reprints will be sent on request.

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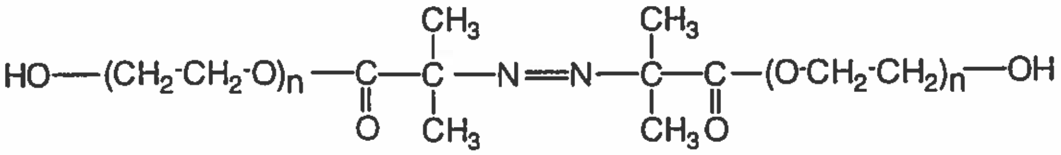
Contribution to the IPCG-Newsletter
Reporter: Klaus Tauer

BLOCK COPOLYMER LATEX PARTICLES - INVESTIGATION OF THE PARTICLE STRUCTURE

With Poly(ethylene glycol)-azo-initiators (PEGA) (Formula 1) with molecular weights of the poly(ethylene glycol) chain (PEG) equal or greater 2.000 g/mol completely electrolyte free, stable polymer dispersion can be prepared. We have investigated PEGA from PEG with molecular weights of 2.000 g/mol and 10.000 g/mol corresponding to an ethylene glycol chain length n of ca. 50 and 250, respectively.



$$HO-(CH_2\text{-}CH_2\text{-}O)_n-\underset{\substack{\|\\O}}{C}-\overset{\substack{CH_3\\|}}{\underset{\substack{|\\CH_3}}{C}}-N{=}N-\overset{\substack{CH_3\\|}}{\underset{\substack{|\\CH_3}}{C}}-\underset{\substack{\|\\O}}{C}-(O\text{-}CH_2\text{-}CH_2)_n-OH$$

Formula 1

A schematic picture of the expected particle structure is shown in Fig. 1.

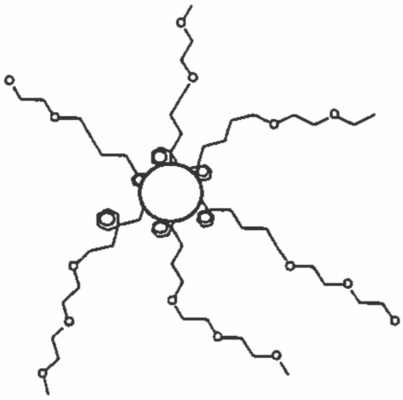
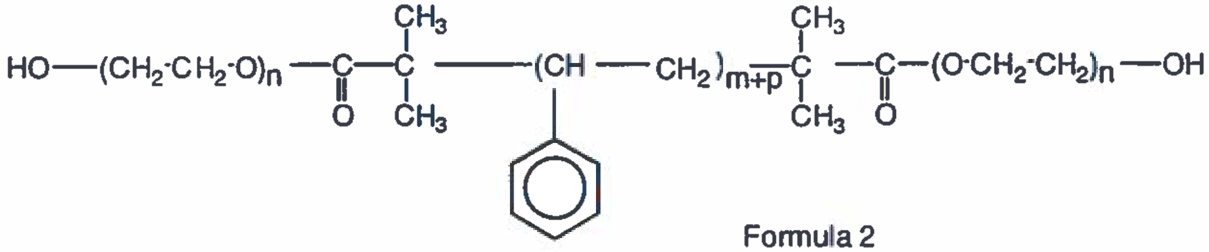


Fig.1 Schematic representation of the block copolymer latex particle structure
__Core:__ PS or PMMA
__Shell:__ PEG

The latex particles consist of a hydrophobic core (poly(styrene) [PS] or poly (methyl methacrylate) [PMMA]) and the covalently bound hydrophilic PEG shell. If the core of these particles is cross linked it should be possible to investigate the properties of the particles and their stability behaviour in different dispersing agents which are solvents for PEG. Furthermore, such latex particles are model systems for investigations of the mechanism of steric stabilisation.

The polymer structure obtained by this way of initiation should be in the case of styrene (STY) as monomer a triblock copolymer due to the fact that the termination event is the recombination of two growing chains (Formula 2). In the case of methyl methacrylate (MMA) the block copolymer should be a diblock, cause the main termination event is the disproportionation reaction of two growing radicals.



$$HO-(CH_2\text{-}CH_2\text{-}O)_n-\underset{\underset{O}{\|}}{C}-\overset{CH_3}{\underset{CH_3}{C}}-(\underset{C_6H_5}{CH}-CH_2)_{m+p}-\overset{CH_3}{\underset{CH_3}{C}}-\underset{\underset{O}{\|}}{C}-(O\text{-}CH_2\text{-}CH_2)_n-OH$$

Formula 2

The same results are obtained when instead of the PEGA with thermal initiation a redox initiator system consisting of Ce^{4+} and a hydroxyl group containing organic compound (PEG, PEGA) is used. In this case the emulsion polymerisation can be carried out with PEG as well as with PEGA at low temperatures in the absence of additional stabilising agents if the PEG chain length is appropriate to ensure particle stabilisation. Using styrene as monomer the polymerization rate is very low. However, it is possible to increase the rate either by increasing the temperature or by addition of a small amount of a water soluble comonomer as for instance MMA or acrylo nitrile.

Not only the structure of the block copolymers of STY and MMA differs from each other but also the structure of the block copolymer particles. Comparing transmission electron microscopy (TEM) photographs the difference between STY (Fig. 2) and MMA (Fig. 3) block copolymer particles is clearly to be seen. The particles have been deposited on the EM grid by suspension preparation. The TEM photographs of the STY block copolymer particles look like ordinary latex particles with a spherical shape and a size distribution in between ca. 70 nm and ca. 300 nm. Contrary to this, the MMA block copolymer particles look extremely different: they are much smaller (ca. 80 nm in diameter) and non spherical. Furthermore, it appears as if this particles are aggregates of smaller but also non spherical objects. One can speculate whether or not these smaller objects are block copolymer micelles. Fig. 4 makes the difference clear in the particle size distribution (PSD) of both kinds of block copolymer particles. The PSD's were estimated by counting the TEM photographs.

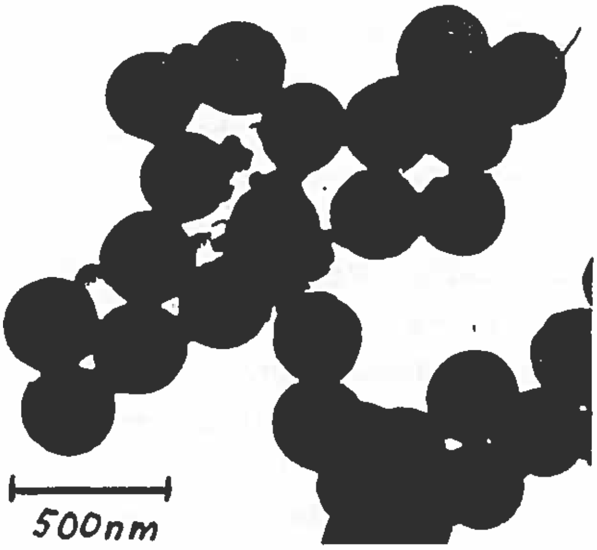


Fig.2 TEM of PS block copolymer particles (STY 130)

Fig.3 TEM of PMMA block copolymer particles (MMA 131)

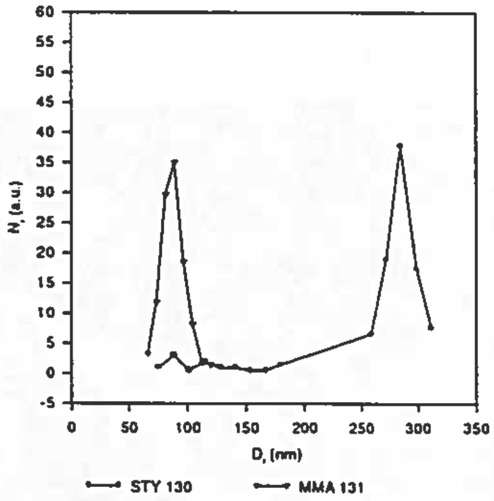


Fig.4 Particle size distri-bution of styrene and methyl methacrylate block copolymer particles, <u>Polymerisation:</u> 25°C; 9,25 g PEG 10.000; 2,855 g MMA or 3 g STY; 0,548 g Ce(IV)-ammonium nitrate; 0,126 g conc. HNO_3; 100g water

It may be supposed that the reason for the different behaviour of the STY- and MMA-block copolymers is their different chemical structure.

Another interesting fact with respect to the block copolymer particle structure is the following experimental observation. The STY block copolymer latexes have been dialysed to remove water soluble waste products. Surprisingly, the TEM as well as scanning (SEM) photographs show an enormous difference with respect to the particle structure before and after dialysis. Before dialysis the particles appear spherical with smooth surfaces and particle sizes in between ca. 70 nm and ca. 300 nm (cf. Fig.2, and Fig.4 sample STY 130, and Fig.5). After dialysis the shape as well as the size of the particles has been changed drastically. Fig.6 shows a TEM (Fig.6a) and a SEM (Fig.6b) photograph of the latex sample STY 130 after dialysis whereby the particles were deposited on the EM-grid by suspension preparation (this means a droplet of the latex sample was putted on the grid and the water was allowed to evaporate slowly).

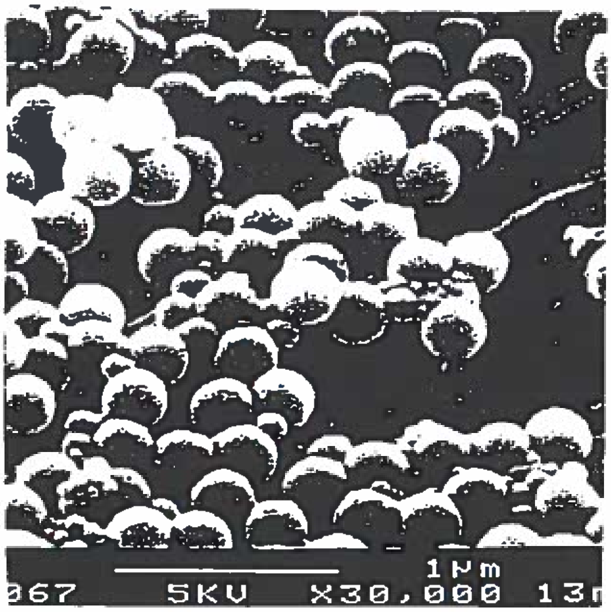


Fig.5 SEM photograph of PS block copolymer particles (STY 130)

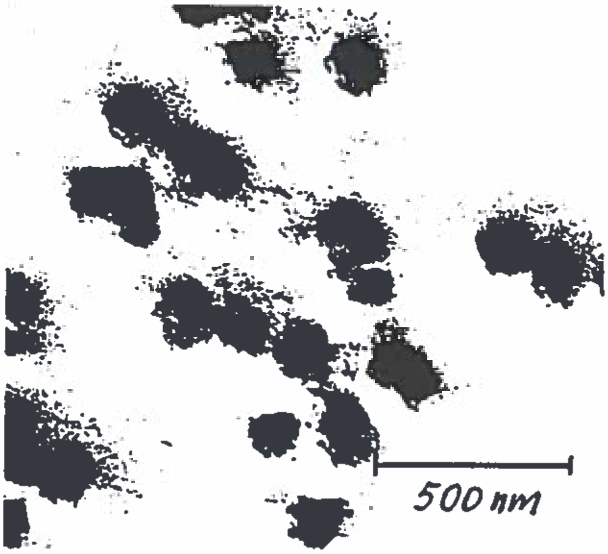


Fig.6a TEM photograph STY 130, dialysed sample

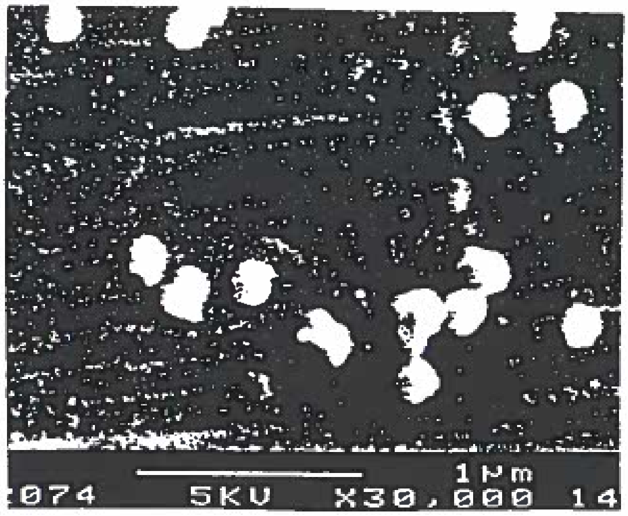


Fig.6b SEM photograph STY 130, dialysed sample

The particle surface is not any longer smooth and the shape not any longer spherical. Furthermore a bimodal size distribution is observed with small particles in the range of ca. 30 nm and large particles in the range of ca. 140 nm which seem to be aggregates of the smaller objects. Fig.7 shows a comparison of the PSD measured by TEM before and after dialysis. The difference is clearly to be seen.

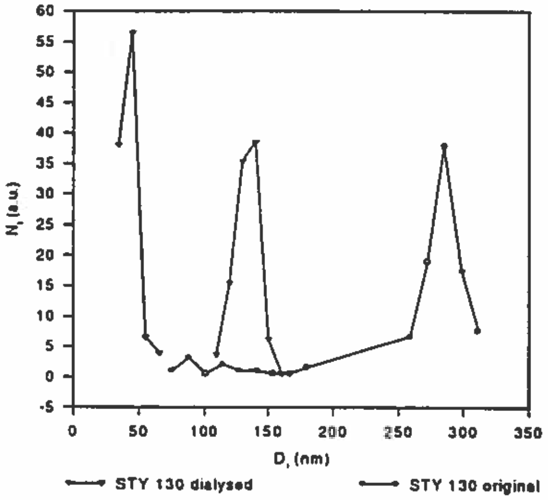


Fig.7 Comparison of the PSD between original and dialysed STY block copolymer latex particles,
<u>Polymerisation:</u> see Fig.6

A completely different picture (Fig.8, SEM photograph) of the same dialysed samples is obtained if the particles were deposited on the EM-grid by an ultra sonification of the dispersion. This deposition technique leads to a much faster drying of the sample on the grid.

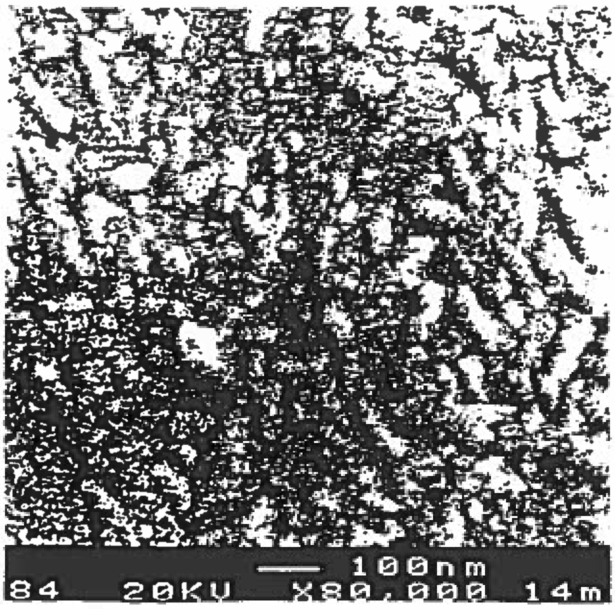


Fig.8 SEM photograph STY 130, dialysed, ultra sonic deposition

In this case we see rice corn-like structures which are again consist of smaller objects. A "mean" rice corn is composed of ca. 5 smaller objects with a size of ca. 20-30 nm.
A satisfactory explanation of these experimental results isn't not yet possible. However, it is very likely that the solution and/or aggregation behaviour of the block

copolymers has an influence on the particle appearance. There are still other questions waiting for an answer in connection with this special kind of latex particles. Exemplary, two questions are mentioned making clear the complexity of the scientific problems. Firstly, the properties of the shell: its size as well as the PEG chain conformation in dependence on the type of the dispersing medium. The electrolyte influence on the shell properties is of special interest in the case of water as dispersing agent. Secondly, what is the mechanism of particle formation ?. Is it a micellar aggregation mechanism (?), since the polymerisation starts with the formation of an amphiphilic block copolymer.

A. VRIJ

Contribution of the van 't Hoff Laboratory for the Polymer Colloid Group Newsletter.

MAGNETIC SILICA DISPERSIONS; PREPARATION AND STABILITY OF SURFACE-MODIFIED SILICA PARTICLES WITH A MAGNETIC CORE

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Running title: Magnetic silica

ABSTRACT

Preparation and properties are discussed of a novel magnetic dispersion, containing surface-modified silica colloids with a core of single-domain magnetite particles. The underlying idea is to taylor the silica shell thickness and surface properties such that the colloids are stable spheres with isotropic interactions, whereas an external magnetic field produces weak dipolar attractions and consequently reversible anisotropic structures. The influence of the shell thickness is analyzed in terms of a dipolar-sphere potential. Preparation of magnetite cores, silica growth and surface modifications with an alcohol and a silane are described in detail. Particle properties are investigated, among other things, with SAXS, light scattering and electron microscopy. The major conclusion is that the preparation route yields stable, non-aggregated magnetic silica particles with a shape and internal structure which is mainly determined by small magnetite clusters in the starting ferrofluid.

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International Polymer Colloids Group Newsletter

Contribution from the Pulp and Paper Research Centre, McGill University
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COLLOIDAL PARTICLE SCATTERING
A New Method to Measure Surface Forces

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ABSTRACT

A new method for determining the forces between colloidal particles is presented, based on observing the changes in two-particle collision trajectories in a linear shear flow and inverting the trajectory equations describing such collisions. In the absence of colloidal forces and under low Reynolds number conditions, collisions are symmetric and reversible. When colloidal forces are acting between the particles, this symmetry is broken and the degree of asymmetry is a measure of the magnitude of colloidal forces.

From a sufficiently large number of experimentally observed collision trajectories we can determine the colloidal forces by a minimization method, assuming some relationship between the interaction force and interparticle distance. This relationship can either be taken from theory, e.g., classical DLVO theory, or be represented by a general function of interparticle distance with adjustable parameters which can be determined from the best fit between theory and experiment. From Monte Carlo simulations it has been found that the number of collisions required for a reliable determination of the colloidal force-distance relationship is about 25.

Some experiments have been done with a "surface collision apparatus" which we describe in detail. The results for latex particles in mixtures of glycerol-water and D_2O-water show that the method is capable of detecting forces that are 3-4 orders of magnitude smaller than those measured by a conventional surface force apparatus or by atomic force microscopy. A minimization analysis of data obtained previously with the traveling microtube apparatus is also presented.

ELECTROSTATIC AND STERIC INTERACTIONS IN PARTICLE DEPOSITION STUDIED BY EVANESCENT WAVE LIGHT SCATTERING

Marco Polverari and Theo G.M. van de Ven

ABSTRACT

The kinetics of deposition of bare latex particles onto bare collector surfaces and poly(ethylene oxide) (PEO) coated latex particles onto PEO coated collector surfaces was studied by evanescent wave light scattering. This allowed for the study of the effects of electrostatic and steric interactions affecting particle deposition. The experiments were done as a function of colloid particle surface morphology, solution salt concentration, and hydrodynamic layer thickness of the adsorbed polymer (PEO) on both the colloidal particles, measured by photon correlation spectroscopy, and collector surface, measured by evanescent wave spectroscopy. From the data it was found that bare and smooth latex particles adsorb much more strongly onto collector surfaces than "hairy" latex particles which have long copolymer chains, such as itachonic acid, grafted onto their surfaces. The rate of deposition of uncoated latex particles onto collectors was found to be about 10 times larger than that of the analogous PEO coated latex particles. This difference became more pronounced as the polymer molecular weight was increased. These results indicated that the thicker the adsorbed polymer layer, the stronger the steric force preventing deposition of the polymer coated colloidal particles onto the collector surface. When the combined ellipsometric layer thickness of the particles and the collector surface exceeded a critical value, found to be about 15 nm, no particle deposition onto the collector surface was possible. The depth of the energy minimum required to cause deposition was calculated to be about half a kT unit.

International Polymer Colloid Group Newsletter

Contribution from the Polymer and Colloid Chemistry Group, Department of Chemistry, University of Toronto, TORONTO, M5S 1A1 - CANADA

Reporter : **Mitchell A. Winnik**

FLUORESCENCE ENERGY TRANSFER FROM FLUORESCEIN TO TETRAMETHYLRHODAMINE COVALENTLY BOUND TO THE SURFACE OF POLYSTYRENE LATEX PARTICLES

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Summary

Steady-state fluorescence energy transfer experiments have been carried out with fluorescein (FL, donor) and tetramethylrhodamine (TMR, acceptor) covalently bound onto the surface of amino functionalized polystyrene latex microspheres. Some changes in the spectroscopic characteristics of the dyes after their covalent binding onto the PS latex were observed. A theoretical model describing a random distribution of dyes onto the surface of a sphere corroborates well the experimental energy transfer results.

Introduction

Fluorescence energy transfer experiments with the dye couple fluorescein/ tetramethylrhodamine have been applied extensively in biology. The direct nonradiative energy transfer [DET] process gives information about the distribution or proximity of species over distances in the range of 15 - 100 Å.

Latex particles also represent a kind of system in which information on these length scales is needed and can be studied by DET[1,2]. We present a steady-state analysis of fluorescence energy transfer from FL to TMR, with both dyes covalently attached to the surface of an amino functionalized polystyrene latex[3]. We are unaware of any previous efforts to study energy transfer in two dimensions by steady-state methods, and we derive the appropriate equations to describe the efficiency of DET as a function of acceptor concentration.

Results and discussion

Donor labeled particles, acceptor labeled particles and donor-acceptor labeled particles were prepared with a binding yield of 40% to 88 %. A substantial red shift occurs in the excitation and emission spectra of FL and TMR when the dyes are transferred from the aqueous phase to the latex surface. This shift may be due to loss of mobility of the bound dyes accompanied by a more planar conformation.

Fluorescence spectra of a series of donor-acceptor labeled particles (with constant donor concentration and increasing acceptor concentration) were obtained. Increase in the acceptor concentration leads to a decrease in the FL emission and an increase in the TRM emission. Donor quenching occurs via energy transfer. The ratio of the FL fluorescence quantum efficiencies Q_{DA}/Q_D in the presence and absence of acceptor, respectively, is obtained from the areas under the FL emission peak, after correcting for the small amount of light absorbed directly by the acceptor. The efficiency of energy transfer can be calculated from the expression: $E = 1 - Q_{DA}/Q_D$. In the case of the particles bearing the highest concentrations of acceptors, the efficiency of energy transfer is close to 100 % (Figure 1).

Comparison with a theoretical model

The fluorescence decay profile for donors and acceptors distributed randomly on a two dimensional surface is well known[4]. For latex and other microspheres, the surface will appear locally flat if the particle radius R is much larger than the critical Förster distance R_o. Under these circumstances[5], the fluorescence decay rate can be described by the expression :

$$I(t) = Io \exp\left[-\frac{t}{\tau_D} - <n> \frac{\Gamma(\frac{2}{3})}{4} \left(\frac{R_o}{R}\right)^2 \left(\frac{t}{\tau_D}\right)^{1/3}\right] \qquad (1)$$

Here <n> is the average number of acceptors per particle, τ_D is the unquenched donor decay time, and $\Gamma(x)$ is the Gamma function.

The quantum yield corresponds to the integral of I(t). Derivation leads to a power series which can be evaluated numerically :

$$\frac{Q_{DA}}{Q_D} = \sum_{n=0}^{\infty} (-1)^n \frac{p^n}{n!} \int_0^{\infty} \exp(-X)\,(X)^{\frac{n}{3}}\,dX \quad \text{with } X = t/\tau_D \text{ and } p = <n>\,\Gamma(2/3)\,(R_o/R)^2/4 \qquad (2)$$

Note that p depends on R_o. Because of the spectral shifts which occur when FL and TMR bind to the particles, the exact value of R_o is unknown. One strategy for data analysis would be fit the data in Figure 1 to equation 2 with R_0 as the fitting parameter.

In calculating the efficiency of energy transfer, the value of p is determined for each sample, using the measured number of TMR groups per particle. We test the assumption that R_0 maintains its value of 5.4 nm^6. The ratio Q_{DA}/Q_D is calculated numerically from equation 2, until the last term becomes smaller than 0.005. Energy transfer efficiencies obtained in this way are also plotted in Figure 1. The concordance between the theoretical and experimental values gives strong support to the model of energy transfer in two dimensions, and also to the assumption that R_0 remains equal to 54 Å.

Conclusions

Polystyrene latex particles were prepared with fluorescein and tetramethylrhodamine groups covalently attached to the surface. Energy transfer from fluorescein to tetramethylrhodamine could be followed by steady state fluorescence spectroscopy. A deeper analysis of the system was possible in terms of two-dimensional energy transfer between groups on the surface of a sphere.

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Figure 1