

*IPCG*

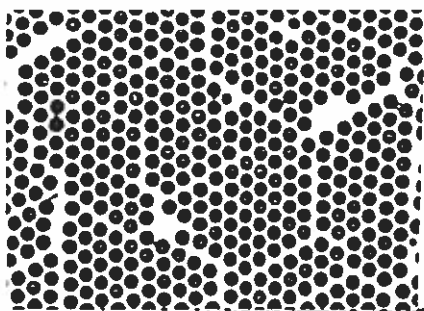
INTERNATIONAL POLYMER COLLOIDS GROUP

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MAY 1993

VOLUME 24

NUMBER 1



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## NEWSLETTER

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## FROM THE EDITOR'S DESK

### MEMBERSHIP

It is a pleasure to welcome the contributions to this Newsletter of three of our new members Drs Norio Ise, Martien Cohen Stuart and Peter Lovell. We look forward with pleasure to their continued contributions over the years.

Current membership lists are included later in this Newsletter. Please note that Bob Fitch, one of our founders, has two addresses and two FAX numbers: he is in residence in Racine from November to March and in New Mexico from April to October. Also note that Dr Ise has moved from Kyoto University to the Fukui Laboratory of Rengo Co.

A current list of FAX numbers is also attached. These numbers should be treated with caution since FAX numbers change frequently. Moreover, prefatory zeros are often dropped internationally but required locally.

### CONTRIBUTIONS

Several contributions arrived too late for the last Newsletter and were held over to this issue. Vivian Stannett also wants members to know that he has a good supply of his review chapter in *Progress in Polymer Processing on Emulsion Polymerization with High Energy Radiation* should they want a copy.

### ROLE OF THE NEWSLETTER

Finn Hansen has suggested that the Newsletter could usefully contain information on funding from grants and for industry projects so that interested students and researchers might contact the recipients. He also points out that in the EEC, cooperative grants for at least 3 research groups from European countries can be applied for under the new academic funding program called, appropriately enough, COST. Topic D is Design and Preparation of New Molecular Systems with Unconventional Electrical, Optical and Magnetic Properties and Topic E is Chemistry at Surfaces and Interfaces. Unless I am inundated with strong objections, I would be pleased to carry such information in future Newsletters.

### NEXT NEWSLETTER

Copy for the next Newsletter should reach me by 31 October, 1993

D H N

## CONFERENCES

CONFERENCE	LOCATION	DATE/CONTACT
<b>1993</b>		
206th ACS National Meeting	Chicago	22 – 27 August
Polymers at Interfaces	Bristol	8 – 10 September
Physical Aspects of Polymer Science	Reading	15 – 17 September
Phase Separation in Complex Colloidal Systems	Hull	20 – 21 September
1st World Conference on Emulsions	Paris	20 – 22 October
Neutron Studies of Colloidal Materials	London	27 October
Dynamics of Surfactant Monolayers	London	17 December
3rd Pacific Polymer Conference	Gold Coast Australia	13 – 17 December
<b>1994</b>		
8th International Conference on Colloid & Interface Science	Adelaide	11 – 19 February
207th ACS National Meeting	San Diego	13 – 18 March
Copolymerization in Dispersed Media	Lyon	18 – 22 April (Pichot)
68th Colloid & Surface Science Symposium	Stanford	19 – 22 June (Gast)
35th IUPAC Macromolecules Symposium	Akron	11 – 15 July
208th ACS National Meeting	Washington	21 – 26 August

# *Polymers at Interfaces Bristol 1993*

## *8-10th September*

*Wills Hall Conference Centre,  
University of Bristol*

In Association with the MACRO group of the Society for Chemical Industry and supported by the Colloid and Interface Groups of the SCI and the RSC and IACIS

*"An International Meeting on all aspects  
of the adsorption of polymers at interfaces"*

### **Registration Form**

The conference will take the form of a discussion meeting, based on the very successful Eindhoven meeting of 1987. The invited speakers will give a 20 minute presentation and this will be followed in each case by a 40 minute discussion. Short papers of 10 minutes will be fitted into the discussion slots where relevant. All contributions will be reprinted before the meeting and will appear in a special issue of *Colloids and Surfaces* together with all discussion remarks. There will also be an opportunity for posters to be displayed and reprinted in the conference proceedings. A provisional list of speakers is enclosed.

The accommodation and all lectures will be held in the new conference wing of Wills Hall situated on the edge of The Downs. Only *single* rooms are available but all have en-suite facilities. There are discounts for students, members and early registration. There is also a limited amount of bed & breakfast accommodation available before /after the conference.

#### *Organising Committee*

Bristol

Dr. T. Cosgrove (Chairman)

Dr. P. Griffiths

Mrs. P. Byrt (Secretary)

Imperial College

Dr. P. Luckham

Wageningen, The Netherlands

Dr. M. Cohen Stuart

## *Provisional*

*Wednesday 8th September*

9.00 - 10.45

Registration, coffee, welcome *T. Cosgrove*

### *Session I Dedicated to the Memory of Jan Scheutjens:*

- |                    |   |
|--------------------|---|
| <i>G. J. Fleer</i> | An appreciation of the work of Jan Scheutjens                       |
| <i>E. Zhulina</i>  | Structure of the polyelectrolyte brush                              |
| <i>O. Evers</i>    | Modelling of polymer aggregates in solution                         |
| <i>H. Ploehn</i>   | Molecular volume effects upon polymer adsorption and polymer forces |

### *Main speakers of the other sessions include:*

- |                         |   |
|-------------------------|---|
| <i>M. Tirrell</i>       | Self-assembled layers at surfaces   |
| <i>J. Klein</i>         | Shear of polymer brushes  |
| <i>M. Hair</i>          | Surface force measurements, SANS and Neutron reflection of adsorbed PEO-PS block copolymers     |
| <i>A. Balazs</i>        | Theoretical models for grafted homopolymers in poor solvents; observations of dimpling effects  |
| <i>J.F Joanny</i>       | Chain statistics in adsorbed polymer solutions  |
| <i>R. M. Richardson</i> | Neutron reflection studies of $\beta$ -casein adsorption.                                       |
| <i>R. Richards</i>      | Neutron reflectometry and surface QELS from polymers spread at the air/water interface          |
| <i>S. Granick</i>       | Dynamics of adsorbed polymer layers   |
| <i>G. Hadziianiou</i>   | Atomic Force Microscopy   |
| <i>T. van de Ven</i>    | Adsorption of PEO of polystyrene latex: effects of surface charge density and molecular weight. |
| <i>B. Vincent</i>       | Instabilities in dispersions of hairy balls.  |
| <i>M. Daoud</i>         | (Title to be confirmed)   |
| <i>J. Anderson</i>      | Effects of adsorbed polymers on viscous flow and molecular diffusion                            |
| <i>M. Cates</i>         | Hydrodynamics of adsorbed polymers; a new approach.   |

### *Other speakers include:*

- |                     |  |
|---------------------|--|
| <i>H. Sonntag</i>   | Forces between cross cylinders in the presence of macromolecules of different kinds and different molecular weights. |
| <i>J. Castaing</i>  | Stabilisation of particles by polymer grafting.  |
| <i>S. Satija</i>    | Neutron reflectivity studies of end-grafted polymer brushes in solution  |
| <i>M. Stamm</i>     | Adsorption and thin film formation of di- and tri-block copolymers   |
| <i>M. El-Aasser</i> | Adsorption/desorption studies of ABA water soluble polymers on planar and colloidal $\text{TiO}_2$ surfaces          |

- M. Ito** Atomistic simulations of short chain polymers at the liquid/liquid interface
- A. Zarbakhsh** Combined surface force and neutron reflectometry studies of adsorbed polymers
- D. Walsh** Reflection studies of segmental profiles and desorption kinetics of polymers at interfaces.
- R. Jones** Dynamics of polymer adsorption from the melt
- A. Silberberg** Polymer dynamics in the melt and near walls
- H. Arribart** AFM of polymers at interfaces.
- J. R. P. Webster** The use of polarised neutron reflection for the unique profile determination in thin films.
- J.P Cohen Addad** PDMS adsorption on silica particles
- R. Davis** Adsorption of non-ionic water soluble polymers on silica: effects of monomer structure and solvent on adsorption energetics.
- R. Varoqui** Conformations of weakly charged polyelectrolytes at the solid/liquid interface.
- J. Waters** Predicting the surface morphology of composite latex particles.
- P. Baglioni** Adsorption of surfactants at the polymer latex interface; ESR and photophysical studies.
- T. Birshtein** Polymer adsorption under constraint
- Per Linse** Adsorption of Pluronic copolymers
- B. Costello** Viscoelastic properties of adsorbed polymer layers
- K. Kawaguchi** Effects of polymer adsorption and desorption on rheological properties of silica suspensions
- H.D. Ou - Yang** Dynamics of chain transfer at interfaces
- L. Ödberg** Transfer of polymer from cellulosic fibres to filler particle
- A. Rennie** Adsorption of polymers to silica from cyclohexane solutions effects of temperature near the theta point.

v.l

# *Polymers at Interfaces Bristol 1993*

## *8-10th September*

*Wills Hall Conference Centre,  
University of Bristol*

*Terence Cosgrove, School of Chemistry, University of Bristol,  
Cantock's Close, Bristol, United Kingdom.*

Surname: ..... Initial: .....  
Affiliation: .....  
.....

Special dietary requirements: .....

Registration	Members (SCI, RSC, IACIS)*	@ £250	.....
	Non-members*	@ £300	.....
	Students	@ £100	.....
	Conference Dinner	@ £35	.....
	Extra residence	@ £34	.....

(please specify nights) .....

**Total** .....

\*Early Registration discount £20 (before 1st June)

Please make cheques (£ sterling) payable to "*University of Bristol*"  
Payment by credit card: Access / Visa / Mastercard (please delete)

Credit card No:

Expiry date:

I authorise payment of £ ..... in favour of the above account.

Signature .....  
Date .....



ROYAL SOCIETY OF CHEMISTRY  
COLLOID AND INTERFACE SCIENCE GROUP

**PHASE SEPARATION IN**  
**COMPLEX COLLOIDAL SYSTEMS**

University of Hull

Monday 20 and Tuesday 21 September 1993

This Meeting will commence at lunchtime on Monday 20 Sept. and continue until mid-afternoon on Tuesday 21 Sept. 1993. The aim of the Meeting is to bring together people concerned with phase changes in a wide range of diverse, complex colloidal systems. The main themes will include :

**Inorganic systems** including complex silicates (cements) and sol/gel processes.

**Organic systems** including polymer dispersions, surfactant systems (lyotropic liquid crystals and emulsions) and crystallisation of fats.

**Bubble formation and growth.**

**Effect of flow on phase behaviour.**

For further information please return the tear-off strip below to :

**Dr. Paul Fletcher, School of Chemistry, University of Hull, Hull HU6 7RX, U.K.**  
**(Tel 0482 465433 FAX 0482 466410)**

---

Please send me the second circular concerning "Phase Separation in Complex Colloidal Systems", 20 - 21 Sept. 1993 at the University of Hull.

Name : \_\_\_\_\_

Address : \_\_\_\_\_

\_\_\_\_\_

\_\_\_\_\_

\_\_\_\_\_

Tel. : \_\_\_\_\_ FAX : \_\_\_\_\_

**NEUTRON STUDIES OF COLLOIDAL MATERIALS**  
**- SURFACTANTS, INTERFACES AND DISPERSIONS**  
**ONE DAY MEETING TO BE HELD IN LONDON ON**  
**WEDNESDAY, 27 OCTOBER 1993**

The aim of this meeting is to introduce and present recent results from neutron studies of colloidal materials. The variety of information that can be obtained on colloidal systems will be emphasised. It is intended to cover both studies of bulk materials and surfaces with experimental techniques that include small angle scattering and neutron reflection. Contributions on dispersions, micelles, adsorbed layers and other materials will be included.

Please make offers of contributions or requests for further information to:-

Dr Adrian Rennie  
 Polymers and Colloids Group  
 Cavendish Laboratory  
 Madingley Road  
 Cambridge  
 CB3 0HE  
 UK

Telephone : 0223 337 012  
 Facsimile : 0223 337 000

Anyone interested in attending this meeting please forward the following to Dr Rennie.

Name .....

Address .....

.....

.....

.....

Telephone Number ..... Fax Number .....

ROYAL SOCIETY OF CHEMISTRY - FARADAY DIVISION  
COLLOID AND INTERFACE SCIENCE GROUP

**DYNAMICS OF SURFACTANT**  
**MONOLAYERS**

**Scientific Societies Lecture Theatre,  
New Burlington Place, off Savile Row, London W1.  
(Nearest tube station is Piccadilly Circus)  
Friday 17th December 1993.**

This one-day Meeting will consist of lectures on aspects of surfactant monolayer dynamics from invited experts in the field. The Meeting will review modern theoretical, instrumental and technique developments and will also deal with applications of the techniques in understanding technologically-relevant areas including foams and emulsions - **provisional Programme shown overleaf.**

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**REGISTRATION FORM (as soon as possible, last deadline 5th Nov.)**

The registration fee for the Meeting includes lunch, coffee and tea and is £40 for CISG Members, £60 for Non-Members and £20 for students. To register for the Meeting please complete the tear-off slip, attach the appropriate payment (either by cheque payable to : Colloid and Interface Science Group or by credit card using the appropriate form) and send to :

**Dr. Paul Fletcher, School of Chemistry, University of Hull, Hull HU6 7RX, U.K.  
Tel. 0482 465433    FAX 0482 466410**

Participants from overseas should make arrangements for payment to be made in £ sterling or by International Money Order. Please add £3 to cheques sent from overseas to allow for the cost of processing. Prices include VAT, but as the Group is a Charitable Trust, it does not have a VAT registered number.

Name : .....

Address : .....

.....

.....

.....

Tel. No. : ..... FAX : .....

Please state whether you are a CISG Member, Non-Member or bona-fide student (delete as appropriate).

Signed : ..... Date : .....

**DYNAMICS OF SURFACTANT MONOLAYERS**

**Payment by Credit Card :**

**PLEASE REMEMBER TO STATE THE EXPIRY DATE OF YOUR CARD,  
YOUR ACCOUNT ADDRESS FOR IDENTIFICATION AND TO ADD YOUR  
SIGNATURE.**

**I wish to pay by my Access/Mastercard/Visa/Eurocard\* Credit Card.  
\*Delete as appropriate**

**Card Number : .....**

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**Please charge to my account : £.....**

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**Signature :.....Date :.....**

**N.B. ALL SECTIONS MUST BE COMPLETED FOR REGISTRATION TO**

**DYNAMICS OF SURFACTANT**  
**MONOLAYERS**

**Friday 17th December 1993.**

**PROGRAMME**

- 10:30 - 11:00 Registration and Coffee
- 11:00 - 12:00 Prof. D. Langevin, Laboratoire de Physique Statistique de l'Ecole Normale Supérieure, Paris.  
"Experimental studies of the dynamics of surfactant monolayers".
- 12:00 - 12:40 Prof. J.C. Earnshaw, Dept. of Pure & Applied Physics, The Queen's University of Belfast.  
"Surface dynamics of surfactant solutions".
- 12:40 - 2:00 Lunch
- 2:00 - 2:30 Annual General Meeting of the Colloid and Interface Science Group
- 2:30 - 3:05 Dr. R. Miller (with Prof. G. Loglio, Florence and Prof. A.W. Neumann, Toronto), Max Planck Institute for Colloid and Interface Science, Berlin.  
"Relaxation studies of surfactant and protein adsorption layers".
- 3:05 - 3:40 Dr. J.H. Clint, B.P. Research Centre, Sunbury-on-Thames, Middlesex.  
"Monolayer dynamics in emulsion systems" (Provisional title)
- 3:40 - 4:00 Tea
- 4:00 - 4:30 Prof. B.H. Robinson, School of Chemical Sciences, University of East Anglia, Norwich.  
"Mechanism of inter-phase transport in Winsor II Microemulsions".
- 4:30 - 5:00 Dr. P.R. Garrett, Unilever Research, Port Sunlight Laboratory, Bebington, Wirral.  
"The relevance of dynamic surface tension for the study of foam behaviour".

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VI Eliseeva	7-95-230-2332	
RM Fitch	1-414-639-7510	(Wisconsin: Nov. - March)
RM Fitch	1-505-751-0175	(New Mexico: Apr. - Oct.)
AP Gast	1-415-725-7294	
AL German	31-40-46-3966	
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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.

**Reporter: José M. Asua**

### **MINIEMULSION POLYMERIZATION USING OIL-SOLUBLE INITIATORS**

(Juan A. Alduncin, Jacqueline Forcada and José M. Asua)

The ability of a series of initiators with different water solubilities (lauroyl peroxide, benzoyl peroxide and azobisisobutyronitrile) in stabilizing monomer droplets against degradation by molecular diffusion was investigated in the batch miniemulsion polymerization of styrene. Comparison of the evolution of the particle size distributions obtained in these experiments with those of a series of miniemulsion polymerizations where the stability of the monomer droplets was assured by using hexadecane in addition to the oil-soluble initiators, showed that only lauroyl peroxide was water-insoluble enough to stabilize the monomer droplets against degradation by molecular diffusion.

### **MONOMER PARTITION IN POLYDISPERSE EMULSION COPOLYMERIZATION SYSTEMS**

(Philip D. Armitage, José C. de la Cal and José M. Asua)

An algorithm for the calculation of monomer partition in emulsion copolymerization systems is presented. The outputs of the algorithm include the distribution of the volume fractions of the monomers according to the particle size distribution; the volume fractions of the monomers in the monomer droplets and aqueous phase and the total volumes of all the phases in the system. The algorithm can handle both Interval II and Interval III conditions using the same set of equations. Examples of applications are given.

**CALORIMETRIC MONITORING OF EMULSION COPOLYMERIZATION  
REACTIONS**

(Agustín Urretabizkaia, E. David Sudol<sup>1</sup>, Mohamed S. El-Aasser<sup>1</sup> and José M. Asua)

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An approach for monitoring both the overall conversion and the cumulative copolymer composition in emulsion copolymerization systems via calorimetric measurements was developed. The approach was checked by carrying out batch emulsion copolymerizations of methyl methacrylate/n-butyl acrylate, n-butyl acrylate/vinyl acetate, and methyl methacrylate/vinyl acetate and comparing calorimetric based estimations with off-line determinations of both the overall conversion and the cumulative copolymer composition. A good agreement was achieved for most of the cases studied.

# International Polymer Colloid Group Newsletter

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

by J.Barton.

The following papers will be presented at the 9th Bratislava International Conference on Polymers "Modification of Thermoplastic Polymers" to be held on June 14 - 18, 1993 in Tatranská Lomnica. The Conference is organized by the Polymer Institute at the occasion of the 30th anniversary of its foundation.

## CROSSLINKED POLY(ACRYLAMIDE-CO-N,N-METHYLENEBISACRYLAMIDE) REDISPERSABLE MICROGELS

(V. VAŠKOVÁ, J. BARTON)

Polymerization of water-soluble vinyl monomers in the presence of bifunctional vinyl monomers has been studied in many papers [1-3]. In these reaction systems, very high copolymerization rates have been observed and the polymer products obtained contain domains with microscopic as well as macroscopic inhomogeneities in gel networks[2,3].

In the present work, the copolymerization of acrylamide (AAM) and N,N-methylenebis-acrylamide (MBAAM) has been studied from the viewpoint of the process kinetics and of the products characterization.

### Experimental

Copolymerization of AAM and MBAAM has been performed in inverse microemulsion consisting of toluene and water using an emulsifier sodium bis(2-ethylhexylsulfosuccinate) (AOT). Initiators ammonium peroxydisulfate (APS) as well as dibenzoylperoxide (DBP) have been used. In the final dispersion, polymer particle sizes,  $d_p$ , have been measured in toluene. The polymer product of the final dispersion has been separated by precipitation in ethanol, following by repeated washing with ethanol and drying. The dry polymer product has been redispersed in water, and the swelled polymer particle diameters,  $d_w$ , have been measured.

## Results and Discussion

In the presence of MBAAM, the character of AAM inverse microemulsion polymerization [4-6] has been changed. This has especially been evident if oil-soluble initiator DBP has been used [6]. In these inverse microemulsion copolymerization systems, for example, no difference between percolating and non-percolating systems has been observed.

Using experimentally obtained  $d_T$  and  $d_W$  values, and assuming that the polymer particles number in the final dispersion does not change during the preparation of the water swelled redispersed microgel, the swelling index  $Q$  has been calculated.  $Q$  is defined as the ratio of the mass of water which swelled the crosslinked polymer in the redispersed polymer particle, and of the insoluble polymer gel maps in polymer particle.

The crosslinked polymer particle's sizes in the final dispersion,  $d_T$ , are influenced by the composition of the inverse microemulsion copolymerization system. The density of the polymer network is a function of the bi-unsaturated MBAAM concentration.

A comparison of the obtained  $Q$  values with the swelling indexes of the macro-crosslinked polymer particles obtained by AAM inverse microemulsion polymerization in the presence of divinylbenzene [1] shows that under similar reaction conditions (except of the kind of the bi-unsaturated monomer), the swelling index of crosslinked polymer particles formed in both types of inverse microemulsion copolymerization systems is comparable.

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# PREPARATION OF CROSSLINKED POLY(ACRYLAMIDE) NANOPARTICLES

(J. BARTON, M. STILLHAMMEROVÁ)

In previous papers the possibility of preparation of polyacrylamide particles of desirable particle diameter in inverse microemulsion was discussed<sup>[1,2]</sup>. It was shown, that the diameter of polymer particles of polyacrylamide inverse microemulsion depended on surfactant hydration degree  $w_o = [\text{Water}]/[\text{AOT}]$  (AOT: sodium bis (2-ethylhexyl)sulfosuccinate) and on the acrylamide/water weight ratio. It was also shown that the copolymerization of acrylamide with N,N-methylenebisacrylamide in inverse microemulsion enables preparation of crosslinked polyacrylamide particles<sup>[3]</sup>.

The extent of crosslinking of polymer particles can be regulated by the type and amount of bi-functional monomer. However, limited water solubility of bi-functional monomer in compartmentalized water droplets of inverse microemulsion can be, in some instances, a serious problem. In order to overcome this, hexamethylenetetramine, which is a compound highly soluble in water, was used as a component of acrylamide inverse microemulsion. The decomposition of hexamethylenetetramine yields formaldehyde and ammonia. Formaldehyde reacts with acrylamide and thus N-methylol derivatives of acrylamide and/or N,N-methylenebisacrylamide are formed. All these "in situ" formed functional monomers copolymerize with acrylamide and as a result a crosslinked polyacrylamide copolymer particle is formed. The decomposition rate of hexamethylenetetramine as well as the formation of N-methylolacrylamide and/or N,N-methylenebisacrylamide depend on pH of water in water droplet.

Typical course of conversion curves of inverse microemulsion polymerization of acrylamide in the presence of hexamethylenetetramine on pH of water used for preparation of microemulsion is given on Figure.

The information on the polymerization kinetics and the polymer particle properties of acrylamide polymerization in inverse microemulsion is shown in Table.

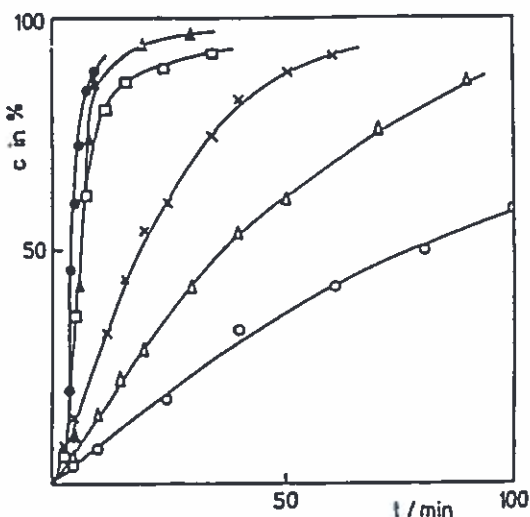


Figure: Time-Conversion curves of inverse microemulsion polymerization of acrylamide for different pH of the compartmentalized water droplets. Temperature: 60°C. pH: 2.0( $\Delta$ ), 3.2( $\blacktriangle$ ), 4.6( $\bullet$ ), 5.6( $\square$ ), 7.0( $\times$ ), 9.1( $\circ$ ). System: AAm(0.4g), Water(1.5g), AOT (3.6g), Toluene(15g), DBP(0.050g), hexamethylenetetramine (0.013g).

pH	$t_{50}^b)$ min	$d_T^c)$ nm	$d_W^d)$ nm	$N_p \times 10^{-15}^e)$ /cm <sup>3</sup>	$Q^f)$ g/g
2.0	38	41	163	2.30	293
3.2	8	31	120	5.32	264
4.6	6	29	101	6.50	192
5.6	7	27	106	8.07	277
7.0	20	35	195	3.71	800
9.1	78	68	-	0.51	-

Table: Polymerization kinetics and polymer particle characteristics for acrylamide polymerization in inverse microemulsion<sup>a)</sup>.

a) See Figure.

b) Polymerization time necessary for reaching 50% conversion of AAm.

c) Polyacrylamide particle diameter in toluene.

d) Polyacrylamide particle diameter in water (water swelled polyacrylamide particles).

e) Number of polymer particles per 1 cm<sup>3</sup> of inverse microemulsion, i.e.

$$N_p = (V_{AAm} + V_{H_2O}) / 0.5236 d_T^3 (V_{AAm} = 0.357 \text{ cm}^3; V_{H_2O} = 1.5 \text{ cm}^3).$$

f)  $Q = (V_{P,H_2O} - V_{P,T}) / G_{PAAm}$ , where  $V_{P,H_2O}$  and  $V_{P,T}$  are volumes (in cm<sup>3</sup>) of polyacrylamide particle in water and toluene,  $G_{PAAm}$  is the weight (grams) of dried polyacrylamide gel in polyacrylamide particle (all values related to 20°C).

The presented data on the inverse microemulsion polymerization of acrylamide illustrate that hexamethylenetetramine and its decomposition products influence the polymerization rate, polymer particle number and particle size, and crosslinking degree of polyacrylamide particles. The extent of the effect of hexamethylenetetramine depends on pH of dispersed phase of inverse microemulsion.

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# Microemulsion Polymerization of Butyl Acrylate.

(P. POTISK, I. CAPEK)

## Summary

The o/w microemulsion polymerization of butyl acrylate initiated by a water (ammonium peroxodisulfate, AP) - and oil (dibenzoyl peroxide, DBP) - soluble radical initiator was investigated by conventional gravimetric and dilatometric methods. Polymerizations with AP were faster than those with DBP. The size of particle decreased slightly with increasing temperature in both systems. As expected, the molecular weight decreased with temperature and the decrease was more pronounced with AP. The overall activation energy ( $E_0$ ) for the microemulsion polymerization initiated by AP and DBP was 109 kJ.mol<sup>-1</sup> and 86 kJ.mol<sup>-1</sup>, respectively. The  $E_0$  for the classical emulsion polymerization was estimated to be 42 kJ.mol<sup>-1</sup> and 44 kJ.mol<sup>-1</sup> with AP and DBP, respectively.

## Introduction

Generally, microemulsions are thermodynamically stable or transparent, and homogeneous systems with a particle size 10 - 50 nm. They are formed spontaneously and do not require vigorous agitation. However, the ratio of emulsifier to monomer concentration used in these systems is very high. Such high emulsifier concentrations are obviously undesirable in a polymerized latex.

Polymerization of an oil-in-water-type (o/w) microemulsion has not received up to now much attention. The microemulsion polymerizations of styrene were mostly investigated, less methacrylates and the least acrylates. A little has been done, however, on the kinetics of o/w microemulsion polymerizations. This may be in part due to the difficulties in directly obtaining kinetic, particle size and molecular weight data using most conventional analytical techniques, because of the relatively high polymerization rates, the high emulsifier concentration and the various complications associated with microemulsions.

Atik and Thomas<sup>1</sup> reported the polymerization of styrene microemulsion initiated AIBN and  $\gamma$ -radiation. The system contained more than 95% water and the situation is not much different from that of a micellar solution where the oil is completely solubilized. Such micellar solutions of monomers have been polymerized by Boxendale et al.<sup>2</sup> and was found to yield very small latex particles.

The controlled synthesis of well-defined polystyrene microemulsions with hydrodynamic radii between 10 and 60 nm using cationic emulsifiers were described by Antonietti et al.<sup>3</sup>

Jayakrishnan et al.<sup>4</sup> investigated styrene and methyl methacrylate (MMA) microemulsion polymerizations. They reported that the polymerization of their systems were slower than those in classical emulsion systems. The microemulsions were not transparent and stable as the polymerization advanced.

Stoffer et al.<sup>5</sup> observed the solution behavior for MMA microemulsion polymerizations initiated with water- and oil-soluble initiators. They reported that the effect of initiator on the particle size can be neglected and that an increase in initiator level results in a decrease in the molecular weight and an increase in the molecular weight distribution, as in the case of the classical emulsion systems.

Fcag and Ng<sup>6</sup> have investigated the microemulsion polymerization kinetics of styrene and MMA in SDS/pentanol/water microemulsion systems. Persulfate-initiated systems in general result in a higher initial rate, while the oil-soluble initiator systems show higher conversions. The initiator concentration is found to have very little effect on the polymerization process.

No studies on the effect of temperature and the type of initiator on the kinetics has been reported so far for these systems for which the polymerization mechanism is unknown. This article reports some of our data on the polymerization of butyl acrylate microemulsion (o/w) using a water- and oil-soluble initiator at different temperatures.

## Experimental Part

The batch polymerizations were run at different temperatures (40, 50, 60, 65 and 70°C). In all runs the recipe comprises 100 g water, 10 g BA, 0.025 g NaHCO<sub>3</sub> and 20 g SDS. In the emulsion polymerization of BA the seeded PBA latex (5wt%) was used. Here 0.5 g SDS was used. The type and concentration of initiator (ammonium peroxodisulfate, AP and dibenzoyl peroxide, DBP) varied as shown later. The polymerization technique and the measurements of particle size and molecular weights were the same as described earlier<sup>7,8</sup>. Conversion of monomer was determined by gravimetric and dilatometric measurements. Limiting viscosity numbers were measured in acetone at 30°C.

## Results and Discussion

Fig.1 shows conversion - time data of the radical microemulsion polymerization of butyl acrylate (BA) initiated by

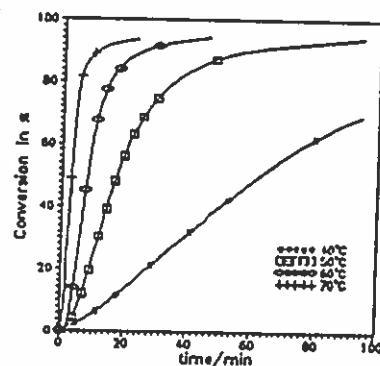


Fig. 1: Effect of temperature on conversion in the microemulsion polymerization of BA initiated by AP. Recipe: see Exptl. part.

ammonium peroxodisulfate (AP). Conversion curves have a "sigmoidal" shape typical for the conventional emulsion polymerization. Similar trends were observed in the BA/dibenzoyl peroxide (DBP) microemulsion and the AP/BA classical emulsion. The rate of polymerization (in the interval 2) was determined as the mean rate within the range of 30 - 50% conversion and equals the maximum rate and are for all systems expressed as a function of the initiator type and temperature in Table I. As expected, the rate of polymerization increased with increasing temperature. The overall activation energy ( $E_0$ ) estimated from the Arrhenius plot was 109 kJ.mol<sup>-1</sup> and 86 kJ.mol<sup>-1</sup>, and 42 kJ.mol<sup>-1</sup> and 44 kJ.mol<sup>-1</sup>, respectively, for the microemulsion polymerization and the classical emulsion polymerization of butyl acrylate initiated by AP and DBP.

The overall rate of emulsion ( $R_p$ ) and solution ( $R_p$ ) can be written as follows<sup>9,10</sup>

$$R_p = k_p [M]_m \cdot n \cdot N / N_A \quad (1)$$

and

$$R_p = k_p / k_t^{0.5} \cdot [M] \cdot (2fk_i I)^{0.5} \quad (2)$$

where  $k_p$  is the rate constant for propagation,  $k_t$  the rate constant for termination,  $k_i$  the rate constant for decomposition of initiator,  $f$  the initiator efficiency,  $[M]_m$  the equilibrium monomer concentration in particles,  $[M]$  the monomer concentration in the reaction solution,  $n$  the number of radicals per particle,  $N$  the number of particles in unit volume, and  $N_A$  the Avogadro's number.

The overall activation energy ( $E_0$ ) deduced from the equations 1 and 2 may be expressed as follows

$$E_p = E_p \quad \text{and} \quad E_0 = E_p - E_t/2 + E_i/2 \quad (3)$$

where  $E_p$  is the activation energy for propagation,  $E_t$  the activation energy for termination and  $E_d$  the activation energy for decomposition of initiator.

The  $E_m$  for solution polymerization of acrylates is ca. 80-90 kJ.mol<sup>-1</sup><sup>11</sup>. The observed  $E_a$  (= 86 kJ.mol<sup>-1</sup>) for the DBP/BA microemulsion system indicates that the polymerization process is governed by the kinetics of solution polymerization. Here the classical approach concerning of initiation and termination seems to be valid.

Table 1. Variation of kinetic, particle size and molecular weight parameters in the emulsion and microemulsion polymerization of butylacrylate with the type initiator and temperature<sup>a</sup>.

Initiator	Temp.	$R_p \cdot 10^3$		D		$M_v \cdot 10^{-4}$		R	
		(mol.dm <sup>-3</sup> )		(nm)		(a) (b)		(a) (b)	
		(a)	(b)	(a)	(b)	(a)	(b)	(a)	(b)
AP (1.10 <sup>-3</sup> )	40	0,14	-	52	-	2,5	-	-	-
	50	0,45	2,3	50	114	2	-	-	-
	60	1,3	3,9	47	100	1,6	-	-	-
	65	-	5,2	-	91	-	-	-	-
	70	4,2	6,1	40	87	1,2	-	-	-
DBP	50	0,18	0,8	63	-	2,7	-	0,4	0,33
	60	0,46	-	58	-	1,9	-	0,35	-
	65	-	1,5	-	-	-	-	-	-
	70	1,2	1,9	51	-	1,4	-	0,28	0,31

a) Cf. Exptl. part,  $R_p$ : Maximum rate of polymerization, D: Particle diameter,  $M_v$ : Viscosity-average molecular weight, R: ratio of rates with DBP and AP. (a) microemulsion, (b) classical emulsion

The decomposition of initiator and formation of initiating radicals proceed in the emulsified monomer droplets, the monomer swollen micelles and/or polymer particles. The high activation energy (109 kJ.mol<sup>-1</sup>) estimated in the AP/BA microemulsion system deviation cannot be explained by the increase of the particle number while the particle size - temperature dependence is the same in the both systems. The increase of the number of negatively charged AP fragments or the surface activation energy for termination is somewhat smaller. This may result from the dominant role of the chain transfer to monomer. Besides variations in the radical capture efficiency, however, with temperature is believed to play a role. The electrostatic repulsion between negatively charged radicals and the negatively charged surface of particles decreases with temperature due to a thermal disturbance of hydrogen bonds (degree of dissociation) or dehydration of surface emulsifier groups<sup>11</sup>.

In the case of the classical emulsion polymerization of butyl acrylate initiated by AP the  $E_a$  denotes the contribution of propagation. Here the classical approach concerning of initiation and termination is not valid. The initiation of emulsion polymerization is a two-step process. It starts in the aqueous phase by the primary free radicals from the water-soluble initiator. The second step occurs by the entry of radicals in particles is very restricted due to strong reduction of translation diffusion, the reaction with mobile radicals and the chain transfer to monomer with desorption of monomeric radical.

The same results were obtained in the emulsion polymerization of BA initiated by DBP. In this system the overall activation energy was found to be 44 kJ.mol<sup>-1</sup>. In this case two mechanism for the production of radicals are possible; 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. The latter seems to be unimportant while only traces of DBP are dissolved in water. The coexistence of growing (entangled) and mobile (primary) radicals at high conversion<sup>11</sup> (or in particles) is in support of the formation of radicals in particles.

Under such conditions termination of growing radicals proceeds by the reaction diffusion and the primary radicals are assumed to be formed via the cage effect mechanism<sup>10</sup>. The activation energy of the entangled radicals is expected to increase while that for the initiation to decrease and therefore they do not contribute to the overall activation energy of polymerization.

The rate of initiation (in water) was simulated to be the same. However, the rate of initiation in the monomer phase (with DBP) is by 1-order higher than that in the aqueous phase (with AP). Under such

conditions, the rate of polymerization should be higher with DBP. The experimental results show that the reverse is true. This may be discussed in terms of the strong primary radicals termination in the DBP/BA reaction medium and the cage effect mechanism.

The size of particles is nearly the same in both systems. This may be ascribed to the dominant role of the emulsifier due to its high concentration.

The molecular weights are slightly higher in system with DBP. Thus, the presence of DBP in polymer phase suppresses the number of radicals per polymer particles which may influence the lifetime of growing radical.

### Conclusion

From the foregoing discussion results that the rate of polymerization, the molecular weights and the overall activation energy ( $E_a$ ) are a function of the type of initiator and the reaction loci. The polymerizations in microemulsions are governed by the classical approach of the radical polymerization. Somewhat higher activation energy with AP is discussed in terms of the decreased termination contribution and/or variation in the radical capture efficiency. The value of  $E_a$  for the emulsion polymerization of BA initiated by AP and DBP deviates from that for the solution radical polymerization. In both systems propagation governs the  $E_a$  value.

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## Introduction

Alkali-soluble associative polymers are made by emulsion copolymerizing an acid-containing monomer, an associative "macromonomer" (i.e., a surfactant that has been capped with a polymerizable double bond), and a "non-associative" monomer [1]. The polymers are in the form of a latex following polymerization. At low pH, the carboxyl groups are uncharged, and the polymer is not water soluble; at higher pH (usually greater than 6), the carboxyl groups ionize, and the polymer becomes water soluble. These polymers thicken solutions by an associative mechanism, and by the expansion of the high molecular weight polymer backbone at high pH due to Coulombic repulsion between the neutralized carboxyls. Obviously, the technology can be generalized from the use of carboxyl (or other anionic groups) to cationic or amphoteric groups to control the pH of solubility.

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

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

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

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

IV) the molecular weight of the polymer backbone.

## Experimental Detail

Hydrophobes with labile hydrogens were ethoxylated to 20, 40, and 80 moles in a pressure autoclave. The number average molecular weights and molecular weight distributions of the surfactants were confirmed by end-group analysis (hydroxyl number), and gel permeation chromatography. Conversion of surfactant into macromonomer followed standard synthetic preparative techniques: reaction with unsaturated anhydrides to make esters, and with unsaturated isocyanates to make urethanes. Alkali-soluble associative emulsion copolymers were prepared by the conventional semi-batch emulsion polymerization of various weight fractions of methacrylic acid, associative macromonomer, and alkyl acrylates and methacrylates. To convert the resulting latexes into solutions, the latexes were diluted to the desired concentration and neutralized to a pH of 9 with 2-amino 2-methyl 1-propanol (AMP-95, Angus Chemical Company). Steady shear and linear viscoelastic properties of alkaline thickener solutions were measured on a Bohlin VOR rheometer (Bohlin Instruments, Cranbury, NJ) using two fixtures: cone and plate (30 mm diameter, 2.5° cone angle) for medium and high shear rates, and Mooney-Couette cup and bob for low shear rates, at a temperature controlled at 25 °C ± 0.5 °C.

## Results And Discussion

As described previously [2], the structure of the hydrophobe exerts a strong influence on thickening efficiency, and on interactions among associative polymers, surfactants, and colloidal surfaces (Figure 1). A future paper will describe the influence of hydrophobe structure on the rheology of alkali-soluble associative emulsion polymers more thoroughly. This paper describes the influence of macromonomer structure and polymer composition on alkaline solution rheology.

### Influence Of Macromonomer Concentration

The low shear viscosity (Figure 2) and shear storage modulus (Figure 3) of alkaline thickener solutions increase to a maximum and subsequently decrease as the concentration of a urethane-based associative macromonomer increases. Possible explanations for the maxima with respect to macromonomer concentration include the

macromonomer, and differences in the glass transition temperature and water solubility of the polymer backbone. NMR and light scattering studies are in progress.

At larger shear rates, the strongly shear-thinning steady shear viscosity profiles converge to a common asymptote (Figure 4). Technologically, this means we can independently adjust the low shear viscosity relative to the high shear viscosity by adjusting thickener composition. The physical chemistry producing shear-thinning in associative polymer solutions is still unknown, but at least two different mechanisms have been identified: the rupture of the network junction under shear, and the non-affine deformation of the network [2]. The strongly shear-thinning phenomenon is technologically useful in spray applied coatings, paper coatings, and the like. The large low shear viscosity of the thickener solutions suggests its use in textured paints, as a suspending aid for clay and other dispersions. The high thickening efficiency of the polymer containing the novel hydrophobe suggests its use as an economical thickener in contractor interior flat paints.

### Influence of Ethoxylation In the Macromonomer

As moles of ethoxylation increase to 80, the viscosity increase for a given weight fraction of macromonomer (Figure 2). Comparison based on constant weight fraction of macromonomer in the polymer are unfair perhaps, because the number of macromonomer units in a polymer decreases for a given weight fraction as the molecular weight of the macromonomer increases. Therefore, on a molar basis, polymers made with 40 and 80 mole ethoxylated macromonomers have half and quarter, respectively, of the active ingredient as those made with 20 mole ethoxylates. And yet the thickening efficiency increases as moles of ethoxylation increases.

The maximum in alkaline solution viscosity, as a function of the degree of ethoxylation between the thickener hydrophobe and backbone, results because the neutralized acid groups in the thickener backbone disrupt the hydrogen bonding among water molecules near the thickener backbone; this disruption in the structure of water reduces the entropic driving force for association. Increasing the moles of ethoxylation between the thickener backbone and the hydrophobe extends the hydrophobe beyond the range of Coulombic interaction among segments of the hydrated thickener backbone to allow the hydrophobes to sample a more structured solvent environment. Hence the hydrophobes associate more strongly, and solution viscosity increases, as the degree of ethoxylation increases. Still, increasing the degree of ethoxylation does dilute the concentration of hydrophobes in solution, and these two opposing effects produce a maximum in solution viscosity with respect to the degree of ethoxylation at about 80 moles.

### Influence Of Double Bond Structure In Macromonomer

Changing the structure of the double bond in the macromonomer should change the monomer sequence distribution (i.e., reactivity ratios), the degree of incorporation of the macromonomer, and possibly the molecular weight of the resulting polymer. The alkaline solution viscosities of polymers made with macromonomers based on acrylic esters are much larger than those based on crotonic esters, especially at large macromonomer concentration (Figure 5). By analogy with conventional acrylic monomers, macromonomers based on acrylic and methacrylic esters should have copolymerized and incorporated with acrylic monomers better than macromonomers based on crotonic esters. The structure of the double bond also affects rheological properties through polymer structure resulting from kinetics, imparting varying degrees of leveling at low shear rates in viscosity profiles of alkaline solutions and coatings (Figure omitted).

### Influence Of Water Solubility And Glass Transition Temperature

Figure 6 compares the influence of pH on the viscosities of polymers composed of 40% methacrylic acid, 30% ethyl acrylate, 10% associative monomer, and 20% of an "other" monomer by weight, where the "other" monomer is selected from the monomers listed in the Table below.

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

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



Decreasing the water solubility of the polymer backbone, holding all else (including glass transition temperature) constant, decreases thickener efficiency and delays solubilization of the latex polymer until a higher pH (compare styrene to methyl methacrylate). As the glass transition temperature of the polymer increases, thickening efficiency decreases (compare methyl methacrylate to ethyl methacrylate). These trends follow the expansion behavior of carbonic latexes studied previously [1,3]. From the perspective of maximizing thickener efficiency, ethyl acrylate exhibits an optimum water solubility and glass transition temperature. Although glass transition temperature and water solubility influence thickening efficiency, the magnitude of the viscosity and viscoelastic properties of alkaline solutions, they do not strongly alter the degree of shear-thinning in the viscosity profile.

### Summary And Conclusions

The large number of synthesis variables inherent with alkali-soluble associative emulsion polymers (both compositional and polymerization process variables) allow us to design polymers that can range widely in rheological response: from nearly Newtonian (useful in architectural coatings), to extremely shear-thinning (useful in spray coatings, paper coatings, and suspending fluids). The structure of the macromonomer (its unsaturation, linkage, ethoxylation, and hydrophobe), influences thickening efficiency and the qualitative nature of shear rheology and viscoelasticity. The glass transition temperature and water solubility of the polymer backbone also influences thickening efficiency, and governs the pH at which the polymer solubilizes.

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Figure 1: Influence Of Hydrophobe Structure On The Alkaline Solution Viscosity Of Alkali-Soluble Associative Emulsion Polymers.

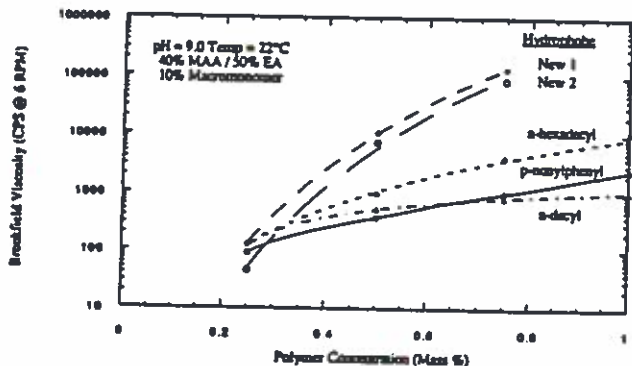


Figure 2: Influence Of Associative Macromonomer Concentration And Ethoxylation On Low Shear Alkaline Solution Viscosity.

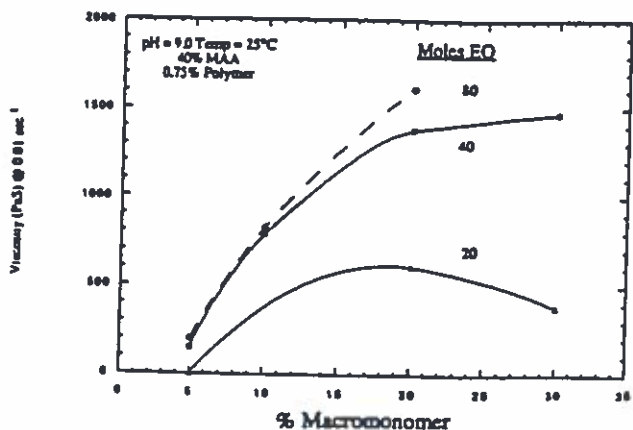


Figure 3: Influence Of Associative Macromonomer Concentration And Ethoxylation On Alkaline Solution Storage Modulus.

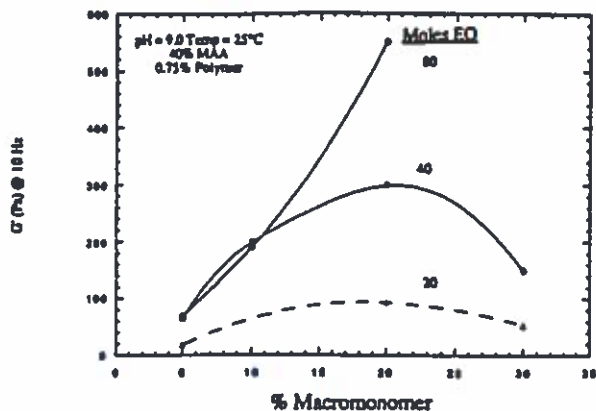


Figure 4: Influence Of Macromonomer Concentration On The Steady Shear Viscosity Profiles Of Alkaline Solutions.

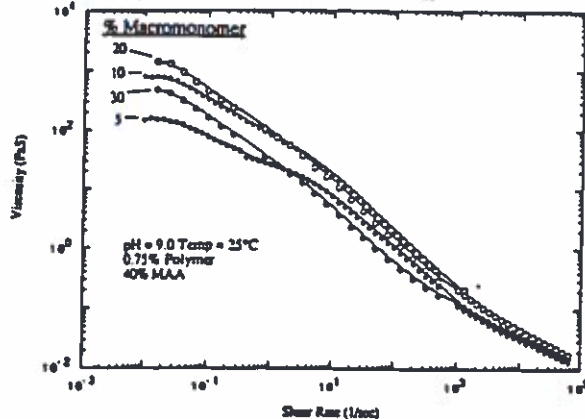


Figure 5: Influence Of Double Bond Structure In Ester Based Macromonomers On Alkaline Solution Viscosity.

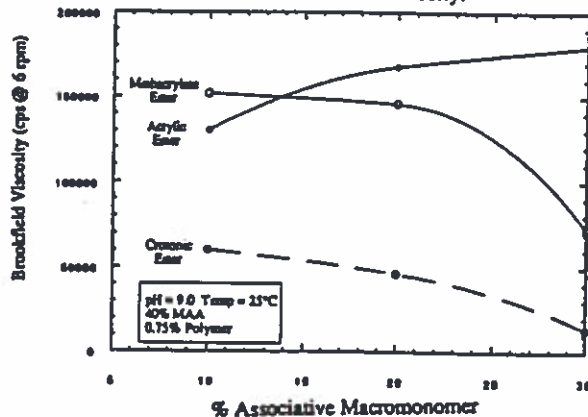
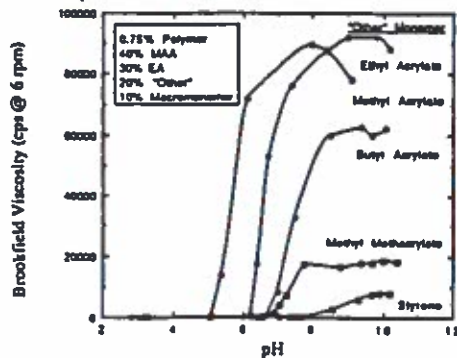


Figure 6: Influence Of Monomer Water Solubility And Glass Transition Temperature On pH Titration.



ZINC DESTABILISATION OF CARBOXYLATE-STABILISED LATICES (CONTINUED)

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This contribution continues 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, zinc oxide. The reasons for interest in this subject are given in our contribution to the previous number of the Polymer Colloids Group Newsletter. Reference was also made in that contribution 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 latices were prepared by seeded emulsion polymerisation. They were essentially monodisperse, with particle diameters ranging from ca. 90 nm to ca. 830 nm. In most cases, the latices were stabilised by adsorbed laurate anions, the effective surface potential in alkaline medium being ca. -19 mV. The results were interpreted using a value of  $4.3 \times 10^{-21}$  J for the effective Hamaker constant for polystyrene particles in water. The zinc ammine ions used to colloiddally destabilise the latices were pre-formed in aqueous solution by dissolving precipitated and washed zinc hydroxide in ammonium hydroxide solution. The kinetics of colloidal destabilisation were followed by measurement of turbidity as a function of time. For this purpose, the latices were diluted sufficiently to reduce the optical density to a value in the range 0.3 - 0.8. The volume fraction of polymer contained in the diluted latices was typically ca.  $1.5 \times 10^{-3}$ , and the particle concentration typically in the range  $10^{10}$  -  $10^{11}$  particles  $\text{cm}^{-3}$ . From measurements of the variation of turbidity with time elapsed after the addition of the destabilisative influence, it was possible to calculate values of  $k_{11}$ , the second-order rate coefficient for the reduction of particle number by binary encounters between primary particles. The coefficient  $k_{11}$  was taken as an inverse measure of the colloid stability as initially reduced by the addition of zinc ammine ions, and thus as a direct measure of the extent to which the latex had been initially colloiddally destabilised by the zinc ammine ions. In principle,  $k_{11}$  quantifies the overall effect of at least two quite distinct types of rate process upon the particle concentration:

- a) the normal process by which Brownian encounters reduce the particle concentration in a latex, the colloid stability of which has been reduced to a fixed extent; and
- b) additional processes by which the colloid stability of the latex is further reduced by continuing interaction between the latex particles and the added destabilisative influence.

It is probably reasonable to assume that the various chemical interactions which come into the second of these categories occur so rapidly that for practical purposes they are instantaneous. This is certainly the assumption which is usually made, and which was made by us in interpreting the results obtained in this investigation. Thus the coefficient  $k_{11}$  coefficient was taken as a direct measure of the extent to which the latex had been initially colloiddally destabilised by the zinc ammine ions.

The variables investigated were concentration of zinc ammine ions, concentration of ammonia, concentration of ammonium ions, pH, nature and concentration of colloid stabilisers, particle size of latex, concentration of polymer in latex, and temperature of colloidal destabilisation. Some of the conclusions reached from this investigation can be summarised as follows:

- i) Both "free" (i.e., un-aminated, but nevertheless hydrated) zinc ions and zinc tetraammine ions are able to destabilise laurate-stabilised polystyrene latices colloiddally, but "free" zinc ions are much more effective in this respect than are tetraammine ions.
- ii) In the case of polystyrene latex stabilised by adsorbed sodium dodecyl sulphate, colloidal destabilisation is brought about mainly by zinc tetraammine ions.
- iii) Results for the effect of pH (varied by addition of aqueous  $1.0 \text{ mol dm}^{-3}$  hydrochloric acid solution) at constant zinc concentration and constant ammonia + ammonium ion concentration upon the colloid stability of a laurate-stabilised latex are consistent with the primary destabilisative influence being ammonium ions, probably supplemented by zinc tetraammine ions. The effect of ammonium ions in compressing the electrical double layer surrounding the particles is probably enhanced by reduction of the inherent colloid stability of the latex as a consequence of reduction of the effective surface potential by interaction with zinc-containing ions. Results for the effect of pH upon  $k_1$ , show that colloid stability in this system falls very sharply as the pH is reduced. Furthermore, the decline in colloid stability with reducing pH is uniform, in that no catastrophic reduction occurs in the pH range over which one would expect the laurate stabiliser anions to be hydrolysed to acid anions and un-ionised carboxylic acid. When these results and others re-plotted as logarithm of  $k_1$ , against logarithm of calculated ammonium-ion concentration, a straight line of slope ca. 2 is obtained. Results for the effect of overall concentration of added zinc ions upon the effective surface potential of laurate-stabilised polystyrene latex obtained from this series of experiments are shown in section (a) of the table below.
- iv) These findings are confirmed by the results of a further series of experiments using a laurate-stabilised latex, in which the pH was varied by addition of ammonium ions to systems which contained fixed amounts of zinc ions and added ammonia. The results shown in section (b) of table below were obtained for the variation of the effective surface potential in these experiments. When effective surface potential is plotted against overall concentration of added zinc ions, the two sets of data shown in this table can be represented by a single curve, indicating satisfactory agreement between the two sets.

Effect of overall concentration of added zinc ions upon  
effective surface potential of laurate-stabilised polystyrene latex

overall concentration of zinc ions ( $\text{mol dm}^{-3}$ )	effective surface potential (mV)
(a) results from series of experiments in which pH varied by addition of acid to system containing constant $[\text{NH}_3] + [\text{NH}_4^+]$	
0	-18.9
$9.86 \times 10^{-3}$	-13.1
$1.38 \times 10^{-2}$	-12.3
$1.97 \times 10^{-2}$	-11.6
(b) results from series of experiments in which pH varied by addition of ammonium ions	
0	-18.9
$3.94 \times 10^{-3}$	-14.5
$7.88 \times 10^{-3}$	-13.5
$1.38 \times 10^{-2}$	-12.8



**POLYMER COLLOID GROUP NEWSLETTER**

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

**Françoise CANDAU**

**PROPERTIES OF HYDROPHOBICALLY ASSOCIATING  
POLYACRYLAMIDES : INFLUENCE OF THE METHOD OF SYNTHESIS.**

**Alain Hill, Françoise Candau and Joseph Selb (submitted to publication)**

**ABSTRACT :**

Hydrophobically modified water-soluble polymers have been prepared by radical polymerization of acrylamide and ethylphenylacrylamide as the hydrophobic comonomer. Three methods of synthesis in aqueous media have been investigated : (i) a "micellar" process in which the presence of a surfactant ensures the solubilization of the hydrophobic monomer ; (ii) a "homogeneous" process wherein a miscible cosolvent is used ; (iii) a "heterogeneous" process, without additive to solubilize the insoluble monomer. The properties of the copolymers in dilute and semi-dilute aqueous solutions strongly depend on the conditions of the synthesis. Copolymers prepared by the homogeneous and heterogeneous processes behave like homopolyacrylamide i.e. hydrophobic interactions do not occur significantly. Copolymers obtained by micellar copolymerization exhibit improved thickening properties due to intermolecular hydrophobic associations. These differences can be directly related to the copolymer microstructure i.e. to a random or blocky distribution of the hydrophobic units. The blockiness of the copolymer can be adjusted by varying the [hydrophobe]/[micelle] ratio at a constant hydrophobe level. Thus, it is possible to control the association degree and therefore the rheological properties. Fluorescence studies, using pyrene as a probe, reveal the formation of hydrophobic microdomains which corroborate the rheological results.

**COPOLYMERS OF ACRYLAMIDE/N-ALKYLACRYLAMIDE IN AQUEOUS SOLUTIONS : THE EFFECTS OF HYDROLYSIS ON HYDROPHOBIC INTERACTIONS.**

Simon Biggs, Françoise Candau and Joseph Selb. *Polymer*, **34**, 580 (1993)

**ABSTRACT :**

Two copolymers of acrylamide/N-4-ethylphenylacrylamide have been prepared by an aqueous micellar copolymerization technique with two different amounts of an anionic surfactant (sodium dodecyl sulphate). Such changes in the polymerization medium give copolymers with different microstructures. Samples of each copolymer were subsequently hydrolysed to 10, 20 and 40% completion. Hydrophobic interactions of all the samples in aqueous solution were then studied in the semi-dilute concentration range near to and above the chain overlap concentration,  $c^*$ , via rheological and fluorescence techniques. The samples were each studied as a function of concentration, salt concentration, surfactant concentration and temperature. In all cases, the rheological and the fluorescence data were consistent and directly related to the number of interchain liaisons in solution. The number of interchain liaisons increased with increase in the copolymer hydrophobicity and were hence related to the hydrolysis level and the blockiness of the copolymer.

**RECENT PUBLICATIONS :**

F. Candau, "*Polymerization in Microemulsions*" in "*Polymerization in Organized Media* (C.M. Paleos ed.), Gordon and Breach Sciences Publ., Philadelphia, 1992, pp 215-282.

D. Cochin, F. Candau, R. Zana, Y. Talmon, "*Direct Imaging of Microstructures Formed in Aqueous Solutions of Polyamphiphiles*", *Macromolecules*, **25**, 4220 (1992).

J.M. Corpart and F. Candau, "*Aqueous Solution Properties of Ampholytic Copolymers Prepared in Microemulsions*", *Macromolecules*, **26**, 1333 (1993).

## Newsletter 1993.

This is my first contribution to the International Polymer Colloids Group Newsletter and though I have met a number of members of the Group over the years on several occasions, many of you may not know me. Therefore I thought it appropriate to present myself briefly. I was trained as a polymer chemist at the State University of Groningen where I had to carry out emulsion polymerisations as part of the undergraduate labcourse. Later, I even supervised other students for that part of the curriculum. Latices have not become my main passtime, though. I went on to the University of Wageningen where I did my PhD under the supervision of Gerard Fleer, and it became an experience I'll never forget. That was also because Gerard's other PhD student happened to be Jan Scheutjens, who brilliantly developed a powerful (and now very well-known) theory for polymer adsorption right under my eyes. We became good friends and I learned a lot from him. I have ever since had a fascination for polymer physics, so most of my research deals with the intricacies of chains wandering about in force fields such as those provided by an adsorbing wall.

After my PhD I shared an assistant professorship with Jan for a while which, thanks to the Royal Academy of Science, was extended to a full-time position five years ago. I carried on doing experiments on all kinds of aspects of adsorbed polymer layers and a bit on wetting, foams and flocculation, and some of this work I had the pleasure to report on now and then for the Polymer Colloids community.

Last year was a very unhappy one since Jan died in a car accident. I miss his inspiration and companionship very much. Gerard Fleer and I, together with Terry Cosgrove and Brian Vincent from Bristol University, are now very busy finishing a book entitled "Polymers at Interfaces" to which Jan had already contributed an important part. As a tribute to his scientific work, a meeting on the same topic will take place at Bristol, where this book shall be on display. It is my hope that Jan's work will continue to inspire many colleagues, as it did me.

My present pet-subject is the kinetics of polymer adsorption. This is largely unknown territory, and therefore very exciting. Experimental data are sometimes explained referring to 'kinetic aspects' but most ideas are based on fiction rather than on fact, so I set out to do some experiments, and the first results are now coming out. Any group member who shares this interest is invited to contact me; perhaps we can exchange news and views!

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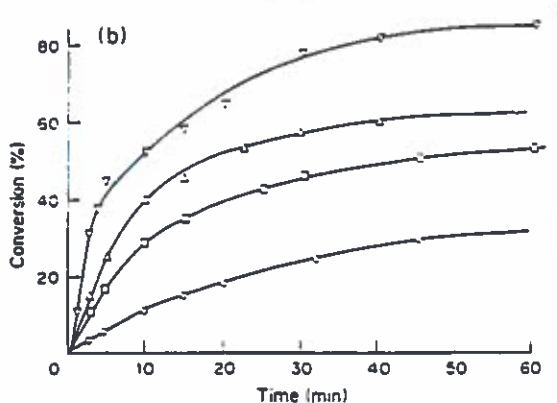
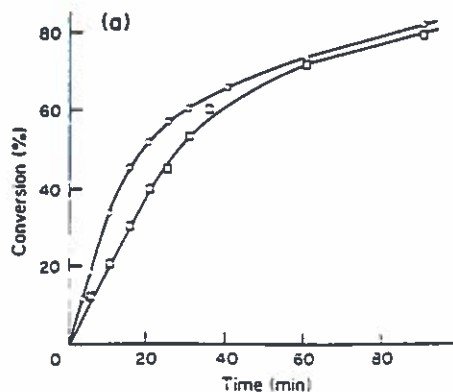


Fig. 1. (a) Polymerization of 2% styrene emulsion with 0.125% potassium persulphate at 50°C (□) 0.5%, (○) 1% sodium dodecyl sulphate [27]. Polystyrene  $T_g = 81^\circ$ . (b) Polymerization of a 2% *p*-tert-butyl styrene emulsion with 0.125% potassium persulphate at 50°C. Poly-*p*-tert-butyl-styrene  $T_g = 134^\circ$ . (○) 0.25%, (□) 0.50%, (△) 1.0%, (▽) 2.0% sodium dodecyl sulphate [27].

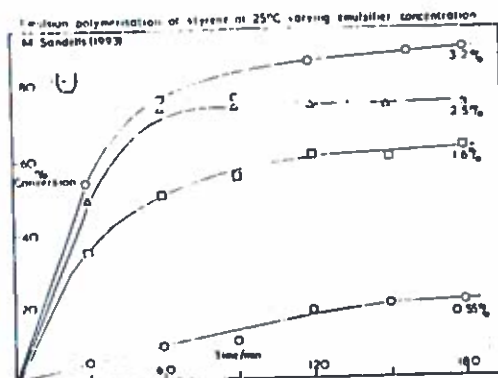


Fig. 2

From  
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### Emulsion Polymerisation of Styrene at Low Temperatures with varying Emulsifier Concentrations

A few years ago we observed a striking difference in the effect of varying the emulsifier concentration between styrene and *t*-butyl styrene (Fig. 1 from *Eur. Polym. J.* 25 (1989) 691-4 (7/8). Ref. 27 is U.S. Satpathy, unpublished work at UMIST). My surmise was that at 50°C poly(*t*-butyl styrene) latex particles were below their glass transition temperature even when swollen to equilibrium with monomer and that similar curves should be obtained with styrene at a sufficiently low temperature. This is indeed so (Fig. 2 which shows results obtained with styrene at 25°C using a redox initiator). Despite the fact that synthetic rubber is routinely prepared by polymerisation at 5°C, we found it difficult to locate a recipe which would give a convenient rate of polymerisation. The successful recipe was:

	Parts by weight
Styrene	100
Water	180
Sodium dodecyl sulfate	1.0, 2.9, 4.5, 5.8
Cumene hydroperoxide	0.8
Ferric sulfate EDTA complex	0.02
Lactose	0.5
Sodium pyrophosphate	1.5

When the latex particles are in a glassy state the total surface area cannot be reduced by coalescence thereby reducing the effectiveness of a fixed amount of emulsifier in stabilising them: consequently particles coagulate when the surface coverage becomes too low although no massive amounts of coagulum formed and the latices were all apparently stable for the duration of the experiment. On the assumption that the duration of Interval I was negligible, the interval II rates (calculated over the first 20-30 min.) at

## Contribution to the International Polymer Colloids Group Newsletter

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The titles of our current research projects are given in the Contents of our *Graduate Research Progress Reports*, No. 38, July 1992, which can be found at the end of this report. Summaries of progress in several research areas are presented here.

### 1. Miniemulsion Copolymerization of Vinyl Acetate and Vinyl 2-Ethylhexanoate Monomers (Ervin L. Kitzmiller)

Poly(vinyl acetate) (PVAC) and its copolymers currently find use in coatings and adhesives. However, PVAC has a relatively high glass transition temperature ( $T_g = 30^\circ\text{C}$ ) and it undergoes hydrolysis under aqueous acidic or alkaline conditions. Therefore, it finds limited applications in exterior coatings. It has been proposed that its copolymerization with certain vinyl esters may aid in film formation, yield greater film flexibility, and improve its resistance to hydrolysis. Requirements for this comonomer would include being resistant to hydrolysis, being able to interrupt the vinyl acetate sequences in the copolymer chain, and having a lower  $T_g$  thus giving the copolymer a glass transition in the desired temperature range.

Vinyl 2-ethylhexanoate (V2EH) was chosen as the comonomer for polymerization with vinyl acetate (VAc). Although V2EH has a  $T_g = -36^\circ\text{C}$ , it will only be of benefit for VAc property improvement if it readily copolymerizes, therefore dictating that the determination of the monomer reactivity ratios be the first requirement for this project. These were estimated for a bulk polymerization system at  $70^\circ\text{C}$  via several methods. The first set was calculated by the Q-e scheme. Three analytical techniques were employed to experimentally determine  $r_{\text{VAc}}$  and  $r_{\text{V2EH}}$ : gas chromatography, infrared spectroscopy, and nuclear magnetic resonance spectroscopy. The values are presented in Table 1. The necessity for determining the reactivity ratios for this system is due to the need for the V2EH comonomer to be sufficiently distributed along the copolymer chain. The range for  $r_{\text{VAc}}$  and  $r_{\text{V2EH}}$ , although varying somewhat by method of determination, indicates that the two comonomers do indeed copolymerize.

This study will focus on the VAc/V2EH miniemulsion polymerization system. Miniemulsions are stable oil-in-water emulsions with droplet diameters in the 50-500 nm range. A mixed emulsifier combination is used consisting of an ionic surfactant along with a co-surfactant, such as a fatty alcohol or a long chain alkane. The miniemulsion system was chosen for its differences from conventional emulsion polymerization systems. These differences include the locus of nucleation which affects the polymerization kinetics and perhaps the evolution of the copolymer composition.

The current work examines the homopolymerization reaction kinetics of V2EH obtained via dilatometry. Also miniemulsion stability is being examined using ultracentrifugation and shelf-life stability. The ionic surfactants chosen for this study are sodium dodecyl sulfate (SDS) and Trem LF-40 (Henkel). SDS is being used to provide a means of comparison to other monomer systems while Trem LF-40 was chosen since it was found to be a more efficient surfactant than SDS by interfacial tension measurements. Results indicating the effects of homogenization device and surfactant type on latex particle size are given in Table 2.

Future work will continue with examination of the reaction kinetics for select copolymer miniemulsion systems with investigation of surfactant/cosurfactant and initiator types and concentrations. Also, copolymer resistance to hydrolysis will be investigated.

**TABLE 1.** Summary of Reactivity Ratios for the Vinyl Acetate/ Vinyl 2-Ethylhexanoate System.

	$r_{VAc}$	$r_{V2EH}$
Q-e scheme	1.05	0.933
Gas Chromatography	$1.189 \pm 0.082$	$1.677 \pm 0.287$
Infrared Spectroscopy	$1.210 \pm 0.082$	$2.11 \pm 0.336$
Nuclear Magnetic Resonance Spectroscopy	$0.987 \pm 0.016$	$1.113 \pm 0.038$

**TABLE 2.** Effect of Surfactant and Homogenization Device on Latex Weight Average Particle Diameter (nm).

	Sodium Dodecyl Sulfate		Trem LF-40
conventional 10:0 <sup>†</sup>	87.4		125.4
Sonifier	hexadecane	cetyl alcohol	hexadecane
miniemulsion 10:10	487.1	255.6	302
miniemulsion 10:40	347.1	210.3	253
Microfluidizer			
miniemulsion 10:10	247.7	92.5	---
miniemulsion 10:40	228.5	77.9	---

<sup>†</sup> surfactant: cosurfactant (mM)

## 2. Emulsion Polymerization in an Automated Reaction Calorimeter (Luis Varela-de la Rosa)

Emulsion polymerization kinetic studies are traditionally carried out by employing gravimetry, dilatometry, and/or GC techniques. Using these methods, conversion-time curves are obtained from which slopes are used to determine the rates of polymerization; this can magnify any errors in the measurements and obscure details of the kinetic behavior. An automated reaction calorimeter (Mettler RCI) is being used to measure the heat evolved during emulsion polymerization and copolymerization experiments. This heat is proportional to the rate of polymerization which by integration can be used to obtain the corresponding conversion-time behavior; kinetic details are not lost in the process. The reactor is a one-liter jacketed glass vessel capable of operating in isothermal, adiabatic, and isoperibolic modes. An example illustrating the agreement obtained between calorimetric and gravimetric conversion-time behavior in an isothermal emulsion polymerization of styrene is given in Figure 1.

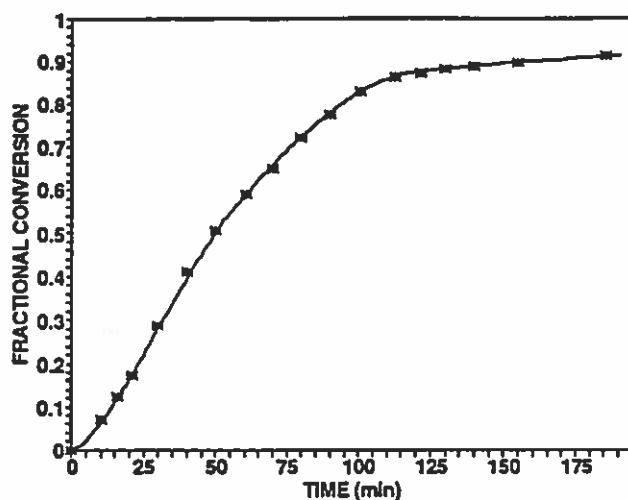


Figure 1. Comparison of conversion-time data for the emulsion polymerization of styrene obtained by gravimetric (points) and calorimetric (line) measurements; 87.6mM SDS, 50°C, 410 rpm.

In some initial work, designed to help gain familiarity with the reactor, a two factorial experimental design was implemented to study the effects of stirrer speed (300 and 500 rpm), emulsifier concentration (5mM and 10mM sodium docecyl sulfate, below and above the CMC, respectively), and reactor pressure (0.2 and 0.7 bars) on the rate of polymerization and the final latex particle size and number of particles. Some results are illustrated in Figure 2. At the same emulsifier concentration, the number of particles decreased when the stirrer speed and the pressure were decreased, as indicated by the increased particle size; the reactions were generally slower as expected. These effects were small when compared to the results obtained at the two emulsifier concentrations where the particle size decreased by more than half when the reactions

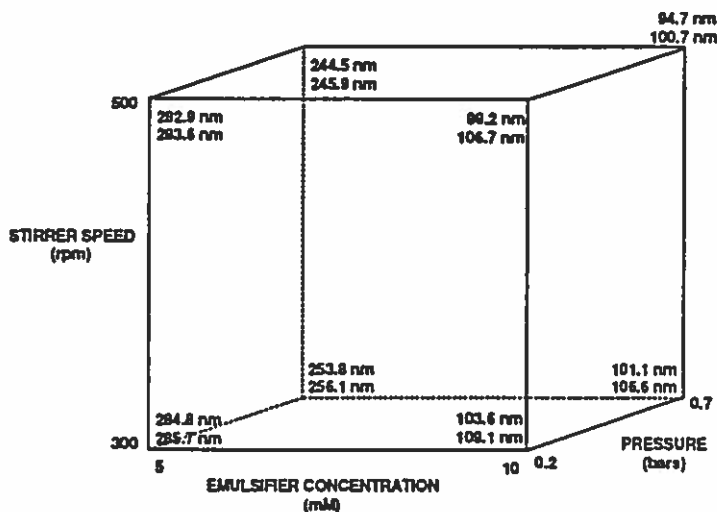


Figure 2. Effect of emulsifier concentration, pressure, and stirrer speed on the number average (upper) and weight average diameters of latex particles prepared by emulsion polymerization of styrene in the RC1; particle sizes determined by capillary hydrodynamic fractionation.



were conducted with 10mM SDS; this general behavior of course was expected. No constant rate period (Interval II) was observed in the faster reactions (10mM SDS) which had a relatively long nucleation period, as judged by the conversion recorded at the rate maximum (end of Interval I). These results contrast sharply with those experiments run at the lower emulsifier level (5mM) as shown in Figure 3. For these experiments, Interval I is relatively short and is followed by a long period characterized by a slow increase in the polymerization rate (Interval II). Both curves indicate significant gel effects toward the end of the reactions.

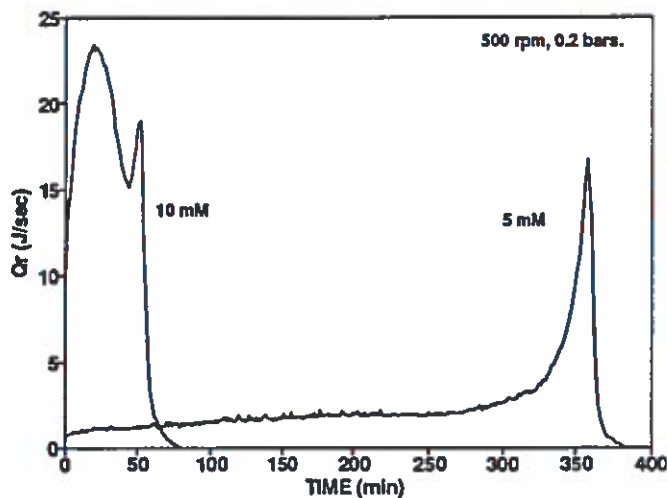


Figure 3. Comparison of the heat evolved during the emulsion polymerization of styrene at 70°C using 5 and 10mM SDS; 500rpm, 0.2bars.

To further illustrate the advantage gained using the RC1, Figure 4 (using the data of the experiment in Figure 1) shows the polymerization rates obtained by the two techniques. The gravimetric conversion-time data were fitted by a polynomial and differentiated to obtain the dotted line; the continuous curve represents the calorimetric data. Although the shapes may appear to be similar, the differences are significant. For example, the gel effect does not even appear in the curve derived from the gravimetric data and the original data is too "scattered" to be convinced of its presence.

### 3. The Structure and Breakup of Aggregated Latex Particles (Mehdi Durali)

Colloidal particles can form aggregates either through charge neutralization or by the formation of bridges among the particles by the long chain polymers. Although a useful process in some industries such as water treatment and purification of minerals, formation of aggregates in emulsion polymerization and latex technology is undesirable causing the waste of raw materials and variations in the final properties of the product. The study of the mechanism by which aggregates are formed and the effect of process parameters such as electrolyte concentration, pH, and agitation speed on the structure of aggregates can provide valuable information for application in industry.

Several experimental techniques have been used to investigate the kinetics of aggregate formation. These techniques are classified into those which focus on the average number of aggregates (light scattering and microscopy) and those which work on the separation of aggregates into singlets, doublets, triplets, and so on (sedimentation field flow fractionation and disk centrifuge). In this study, a capillary hydrodynamic fractionation (CHDF) unit was used to



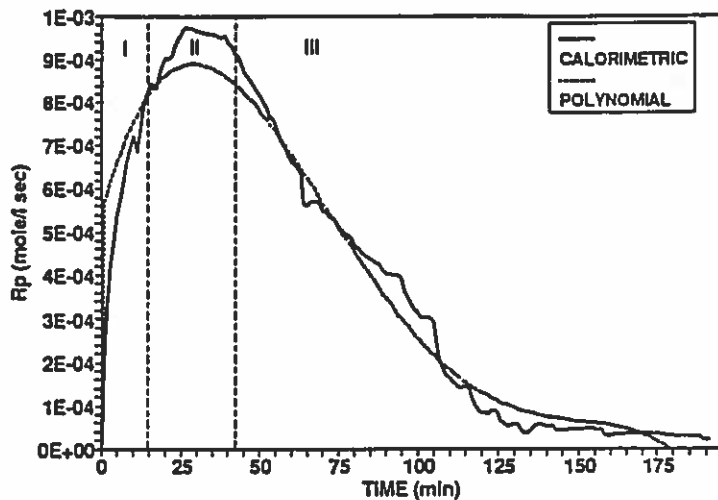


Figure 4. Comparison of the rates of polymerization obtained via calorimetry (solid line) and fitting of gravimetric data (dotted line) from the data in Figure 1.

study the kinetics of aggregate formation. This technique separates colloidal species flowing through a narrow bore capillary tube based on the difference in their size.

A 234 nm monodisperse latex was coagulated for different time periods using 0.2 M NaCl as electrolyte. Separation of aggregates was performed using the CHDF unit and species containing up to 5 particles were clearly fractionated (Figure 5). The system of differential equations describing the coagulation kinetics were solved using the Rosenbrock direct search method with Davies, Swann, and Campey modifications (D.M. Himmelblau, *Applied Nonlinear Programming*, McGraw-Hill, New York, 1972) and the LSODE initial value ordinary differential equation solver package (Alan C. Hinmarsh, *ACM-SIGNUM Newsletter*, Vol. 15, No. 4 (1980),

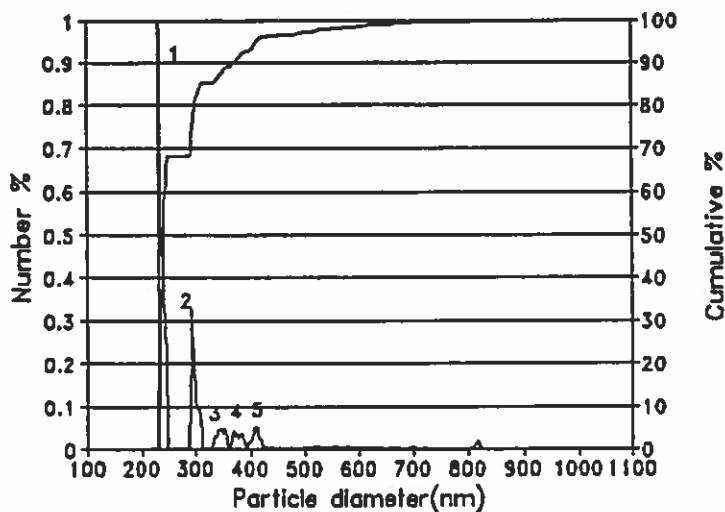


Figure 5. Fractionation of coagulated species consisting of 234nm monodisperse particles; coagulated for 15 sec. with 0.2M NaCl; number of particles/aggregate indicated at each peak.

pp. 10-11). The optimum coagulation rate constants were calculated for aggregates containing up to 3 particles. Figure 6 shows both experimental values (symbols) and theoretical simulation (lines) of the variation of the number density of the singlets and doublets as a function of coagulation time. A good agreement between the experimental results and the calculated values is observed.

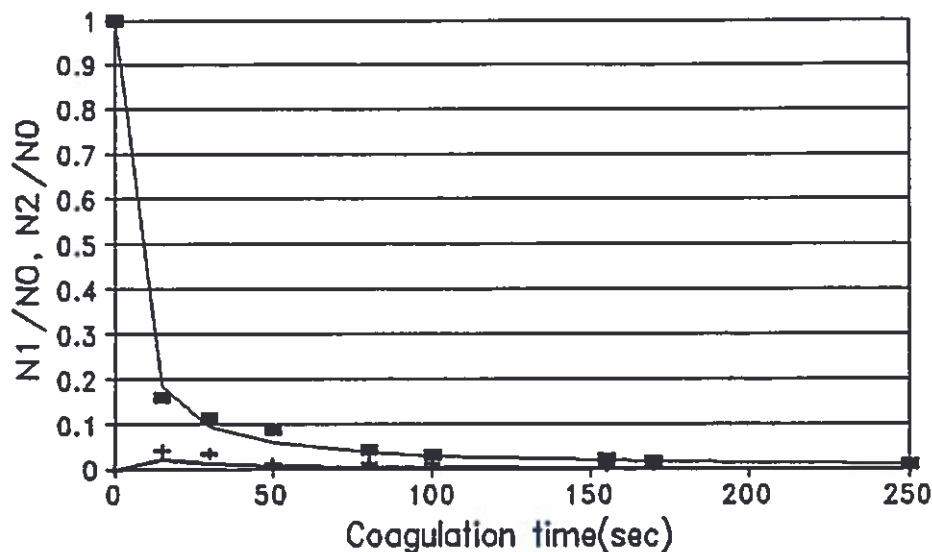


Figure 6. Variation in the number densities of singlets (■) and doublets (+) with coagulation time; 0.2M NaCl; points represent experimental data and lines the simulations.

The breakup of aggregates was studied using a sonication bath capable of creating 1200 watts at 28 kc. A 234 nm monodisperse latex was coagulated using 0.4 M NaCl (above the critical coagulation concentration) for two days. A 0.5% by wt. solution of Brij 35 (a nonionic surfactant) was added to stop the coagulation reaction and stabilize the phase separated solution. The coagulated sample was then sonicated for different periods of time and immediately analyzed using the CHDF. The addition of the nonionic surfactant to the coagulated sample also had the benefit of preventing the formation of larger aggregates upon collision between smaller aggregates during the sonication. It was found that the sonication force was enough to break the aggregates down to single particles in less than 30 minutes. Sonication of the sample for more than 30 minutes caused reaggregation of broken species. It was believed that the extensive heat generated by the sonication process was responsible for the desorption of the nonionic surfactant from the surface of the particles, leading to the formation of new aggregates.

#### 4. Film Formation from Miniemulsion Latex Systems (Yoshimi Inaba)

Water-based, low energy, curable materials such as low temperature curable resins and latexes are becoming more important for meeting stringent environmental regulations in coatings, inks, and adhesives applications. The basic objective of this work is to study the film formation process and final film properties of water-based low temperature curable latexes which are formulated using miniemulsification techniques.

Hydrophobic (i.e., n-butyl acrylate/styrene copolymer) miniemulsion latexes and conventional latexes were prepared as model systems. The n-butyl acrylate monomer was used to lower the glass transition temperature of the resulting copolymers such that continuous latex films are formed at room temperature. Dimethyl meta-isopropenyl benzyl isocyanate (TMI) (American Cyanamid Co.) monomer was incorporated into the formulations as a crosslinking agent. A small

amount of carboxylic acid monomer (methacrylic acid, MAA) was also introduced to enhance the crosslinking reactions. A redox initiator system was employed to polymerize the comonomer miniemulsions at a low temperature in order to reduce premature crosslinking at the polymerization temperature. The combination of ionic surfactant (sodium dodecyl sulfate, SDS) and a co-surfactant (hexadecane, HD) were used as the mixed emulsifier system. Hexadecane was dissolved in the organic phase, and the mixture was then added to the aqueous emulsifier solution. The crude emulsion was then subjected to ultrasonification and polymerized after introduction of initiator. Conventional control latexes were prepared using sodium dodecyl sulfate alone at the same overall surfactant concentration. The degree of crosslinking was evaluated from swelling experiments using air-dried latex films.

Figure 7 shows the relationship between the swelling ratio ( $W/W_0$ ) of dried conventional latex films and the MAA/TMI weight ratio used in a formulation. This result indicates that a small amount of MAA is effective in enhancing the crosslinking reaction. A lower swelling ratio indicates a higher degree of crosslinking. Figure 8 shows the relationship between the swelling ratio (as determined from the change in film length after swelling) of dried miniemulsion latex films and emulsifier (SDS) concentration. In this case, the films prepared with the miniemulsion latexes also cured at room temperature with only a slight influence of the emulsifier concentration.

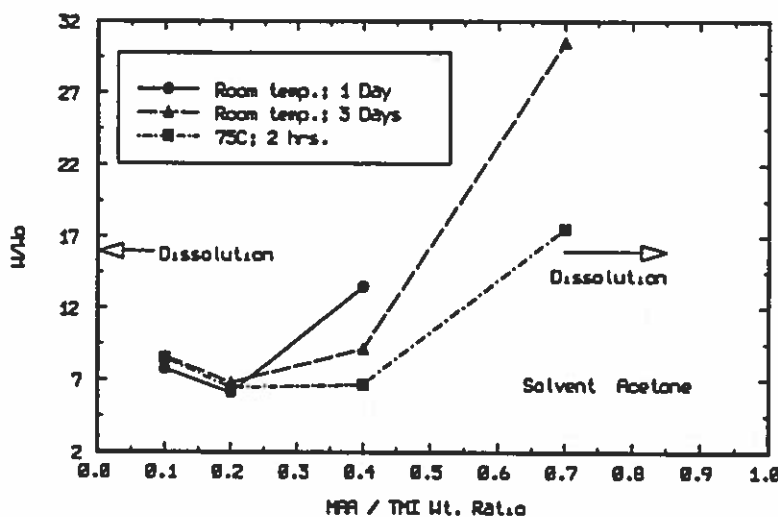
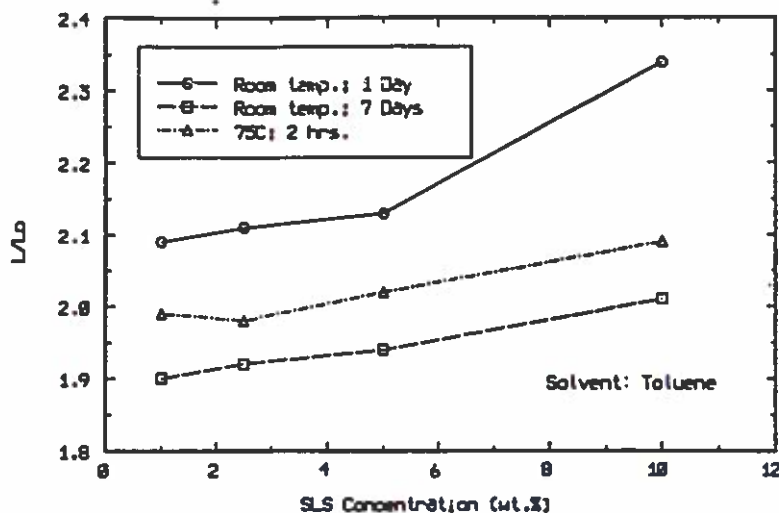


Figure 7: Relationship between the swelling ratio ( $W/W_0$ ) of dried conventional latex films and the MAA/TMI weight ratio used in a formulation (as determined by a change in sample weight). The experimental conditions are: SDS = 3wt% based on monomers; TMI+MAA = 3wt% based on monomers, St/n-BA=1/1(weight ratio); where  $W$  is the swollen sample weight, and  $W_0$  is the initial sample weight.



**Figure 8:** Relationship between the swelling ratio (as determined by dimensional changes in the swollen sample) of dried miniemulsion latex films and emulsifier (SDS) concentration. The experimental conditions are: SDS/HD=1/4 (molar ratio); MAA / TMI=1/2 (weight ratio); 3wt% based on monomers.; where  $L$  is the swollen sample length, and  $L_0$  is the initial sample length.

### Recent Publications

"Synthesis and Characterization of Monodisperse Porous Polymer Particles", C.M. Cheng, J.W. Vanderhoff, F.J. Micale, and M.S. El-Aasser, *J. Polym. Sci.: Part A: Polym. Chem.*, **30**, 235-244 (1992).

"Monodisperse Porous Polymer Particles: Formation of the Porous Structure", C.M. Cheng, J.W. Vanderhoff, and M.S. El-Aasser, *J. Polym. Sci.: Part A: Polym. Chem.*, **30**, 245-256 (1992).

"Pore Structural Studies of Monodisperse Porous Polymer Particles", C.M. Cheng, F.J. Micale, J.W. Vanderhoff, and M.S. El-Aasser, *J. Colloid & Interface Sci.*, **150**(2), 549-558 (1992).

"Effects of Dispersion Concentration on the Electroacoustic Potentials of O/W Miniemulsions", R.J. Goetz and M.S. El-Aasser, *J. Colloid & Interface Sci.*, **150**(2), 436-452 (1992).

"Partitioning Behavior and Thermodynamic Model for Styrene O/W Microemulsions", J.S. Guo, E.D. Sudol, J.W. Vanderhoff, H.J. Yue, and M.S. El-Aasser, *J. Colloid & Interface Sci.*, **149**(1), 184-196 (1992).

"Particle Nucleation and Monomer Partitioning in Styrene O/W Microemulsion Polymerization", J.S. Guo, E.D. Sudol, J.W. Vanderhoff, and M.S. El-Aasser, *J. Polym. Sci.: Part A: Polym. Chem.*, **30**, 691-702 (1992).

"Modeling of the Styrene Microemulsion Polymerization", J.S. Guo, E.D. Sudol, J.W. Vanderhoff, and M.S. El-Aasser, *J. Polym. Sci.: Part A: Polym. Chem.*, **30**, 703-712 (1992).

"Role of Surfactant in Composite Latex Particle Morphology", Y.C. Chen, V.L. Dimonie, M.S. El-Aasser, *J. Appl. Polym. Sci.*, **45**, 487-499 (1992).

"The Topochemistry of Acrylamide Polymerization in Inverse Suspension", M. Dimonie, N. Marinescu, D.S. Vasilescu, O. Shaffer, H. Caldararu, A. Caragheorgheopol, and J. Languri, *J.M.S.- Pure Appl. Chem.*, A29(3), 277-296 (1992).

The following papers can be found in *Polymer Latexes: Preparation, Characterization, and Applications*, ACS Symposium Series, Vol. 492, E.S. Daniels, E.D. Sudol, and M.S. El-Aasser, Eds., American Chemical Society, Washington, D.C., 1992:

"Overview of Emulsion Polymerization: Stepping Toward Prediction", E.D. Sudol, E.S. Daniels, and M.S. El-Aasser, pp 1-11.

"Miniemulsion Polymerization", P.L. Tang, E.D. Sudol, M.E. Adams, C.A. Silebi, and M.S. El-Aasser, pp 72-98.

"Kinetics and Mechanism of Styrene Microemulsion Polymerization", J.S. Guo, E.D. Sudol, J.W. Vanderhoff, and M.S. El-Aasser.

"Emulsion Copolymerization of Small-Particle-Size, High-Molecular-Weight Poly(alkylaminoalkyl methacrylate-co-alkyl methacrylate) Latexes", J.W. Vanderhoff, S.H. Hong, M.R. Hu, J.M. Park, I. Segall, S. Wang, and H.J. Yue, pp 216-233.

"Preparation of Particles for Microvoid Coatings by Seeded Emulsion Polymerization: Soft Hydrophilic Polymer Core-Hard Hydrophobic Polymer Shell", J.W. Vanderhoff, J.M. Park, and M.S. El-Aasser, pp 272-281.

#### Recent Ph.D. Dissertations

"The Role of Polymerizable Surfactants in Emulsion Polymerization" by M. Belen Urquiola.

"Interfacial Mass Transfer of Monomer into the Latex Particles Stabilized with Mixed Surfactants and Water Soluble Polymers" by Joong-In Kim.

#### Recent M.S. Reports

"Grafting Reactions in the Emulsion Polymerization of Vinyl Acetate Using Poly(Vinyl Alcohol) as Emulsifier" by Guadalupe Del Socorro Magallanes Gonzalez.

"The Role of Water-Soluble Oligomers in Emulsion Polymerization" by Claudia E. Kokkeler.

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- The Preparation of Highly Crosslinked Polymer Particles by Dispersion Polymerization (M. Hattori)
- Dispersion Polymerization of Styrene in Ethanol Using Poly(vinyl pyrrolidone) as Stabilizer (J.A. Anyumba)
- Anionic Dispersion Polymerization of Styrene (M.A. Awan)
- Structured Latex Particles for Modification of Polycarbonate (I. Segall)
- Synthesis and Characterization of Core-Shell Ionomeric Latexes (A. Arora)
- The Role of Compatibilizing Agents in the Development of Latex Particle Morphology (P. Rajatapiu)
- Droplet/Particle Interactions in Miniemulsion Polymerization (C.M. Miller)
- Miniemulsion Copolymerization of Vinyl Acetate and Vinyl 2-Ethylhexanoate Monomers (E.L. Kitzmiller)
- Miniemulsion Polymerization of Divinylbenzene-HP: A Facile Route to Highly Crosslinked Particles (S. Mohammed)
- Phase Behavior of Lamellar Surfactant Systems (J.F. Hessel)
- Emulsion Polymerization of Vinyl Acetate Using a Polymerizable Surfactant (M.B. Urquiola)
- Grafting Reactions in the Emulsion Polymerization of Vinyl Acetate using Poly(vinyl alcohol) as Emulsifier (G. Magallanes)
- The Use of Ethoxylated Tetramethyl Decyldiol Surfactants as Emulsifiers for the Emulsion Polymerization of Vinyl Acetate and Styrene (W.R. Dougherty)
- Interfacial Mass Transport of Monomers into Latex Particles Stabilized with Mixed Surfactants and Water-Soluble Polymers (J.I. Kim)
- Characterization of Latex Particle Surfaces: The Effect of Polyoxyethylene Chains (R. Hu)
- The Role of Water-soluble Oligomers in Emulsion Polymerization (C. Kokkeler)
- Emulsion Polymerization in an Automated Reaction Calorimeter (L. Varela-de la Rosa)
- Preparation of Large-Particle-Size Monodisperse Latexes in Simulated Microgravity Conditions Using a Rotating-Cylinder Reactor (V. Mishra)
- Modeling of Latex Particle Size Distribution in Emulsion Polymerization (A. Sood)
- Absolute Particle Size Analysis by Combining Capillary Hydrodynamic Fractionation and Turbidimetry (J. Venkatesan)
- An Investigation into the Structure and Breakup of Aggregated Latex Particles (M. Durali)
- Separation of Colloidal Particles Using Capillary Electrophoresis (A.B. Hlathwayo)
- Rheology of Mixed Associative Polymer Solutions (L. Zhuo)
- Role of the Interphase Region in the Transport of Small Molecules in Heterogeneous Polymeric Systems (C.R. Correa-Cely)
- Film Formation from Miniemulsion Latex Systems (Y. Inaba)
- Elastomeric Films from Structured Latexes (Y. He)
- Mechanical Behavior of Polystyrene Latex Films (M. Sambasivam)
- Telechelic Polybutadiene Terminated with Amino, Carboxyl, and Hydroxyl Functional Groups (J. Xu)
- Preparation of Latex Particles Containing Laser-Excitable Dyes (J.H. Chen)

## Dynamics in Crystallizing Colloidal Systems

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An understanding of crystallization and the nature of the solid-liquid interface is crucial to a wide variety of fields including separation processes, solidification of ceramics and polymeric materials, and protein purification and characterization. Unfortunately, the complexity of these systems precludes their use in experimental studies to elucidate the fundamental interplay between interactions, structure and dynamics. In our work, we use aqueous dispersions of highly charged, monodisperse, polystyrene particles as a model system; the purely repulsive, Coulombic interactions are well understood and easily controlled via solution ionic strength. These systems are known to undergo a disorder to order transition with the resulting crystals exhibiting a rich variety of structures including body-centered cubic and face-centered cubic crystals as well as finger-like growth instabilities. Our current work is aimed at understanding the dynamics in these systems and how the interparticle interactions influence crystal growth and the motion of individual particles within the crystal. To study these highly turbid systems, we are using static and dynamic light scattering techniques which we interpret using the novel theoretical framework of *diffusing wave spectroscopy*. This treatment models the transmission of multiply scattered light as a diffusive process characterized by the distance a photon must travel before its direction of propagation is completely randomized. In our static scattering experiments, we exploit the fact that the disordered and ordered regions scatter light differently. By monitoring the time averaged intensity transmitted through a sample, we directly monitor the nucleation and growth of bulk crystallites in a metastable suspension. In our dynamic light scattering experiments we monitor the short time intensity fluctuations of the multiply scattered light and record an intensity autocorrelation function. Since the total phase shift of the scattered light is due to the contribution of many scattering events, the decay of the intensity autocorrelation function characterizes particle motion on length scales much smaller than the wavelength of light. We will use this technique to probe the particle motion in single crystals as well as in crystallizing suspensions.

## ENZYMES ON INSOLUBLE SUBSTRATE SURFACES: REACTION AND DIFFUSION

Pamela B. Gaspers, Channing R. Robertson, Alice P. Gast

Many biotechnological applications depend on the function of proteins near or on an interface. Much previous work has been aimed at the macroscopic events in protein adsorption such as isotherms and kinetics, but molecular scale studies on conformation, orientation, and lateral mobility have been limited. An interesting question arises when reactive proteins or enzymes are adsorbed onto surfaces that contain the enzyme's substrate. We have previously shown that proteins move on polymer surfaces and now we want to examine the interplay between reaction and diffusion. The goal of this project is to study proteins on surfaces at the molecular scale by probing the lateral diffusion of the adsorbed protein. To further probe the mobility of enzymes at interfaces, we study a reactive protein on a surface that contains the enzyme's substrate. We use a model system of collagenase on an insoluble substrate surface. Collagenase cleaves the synthetic peptide covalently attached to the surface. We study the surface mobility of both an active and inactive collagenase enzyme. By measuring both lateral diffusion and reaction rate, we can characterize the reactivity and mobility of the enzyme adsorbed on a surface. We measure lateral diffusion by a combined technique of total internal reflection fluorescence (TIRF) and fluorescence recovery after pattern photobleaching (FRAPP) and reactivity through radiolabeling experiments.



## On the solid-fluid interface of adhesive spheres

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*To appear in the Journal of Chemical Physics*

The adhesive-sphere interaction potential provides a good model system to study the influence of the attractive well depth on phase behavior and interfacial phenomena. We investigate the solid-fluid phase behavior of adhesive spheres with the modified weighted density approximation (MWDA) of Denton and Ashcroft. We then apply a planar-averaged density functional approach (PWDA) to determine interfacial properties. We find both a narrowing of the interface between fluid and coexisting fcc solid and an increase in the interfacial energy with increasing attractive interaction strength in accord with the empirical relation  $\gamma \approx 0.47\Delta H\rho_s^{2/3}$ . In addition, we investigate metastable solid nucleation through calculation of metastable bcc solid-fluid interfacial tensions and find results suggesting the possibility of such a route to stable solid formation.

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

The following papers (with abstracts) are recent publications from various members of the SUPC, summarizing current research directions.

**Diffusion of oligomeric species in polymer solutions.** M.C. Piton, R.G. Gilbert, B. Chapman and P.W. Kuchel. *Macromolecules*, in press.

*Abstract*

Self-diffusion coefficients ( $D_S$ ) for analogs of polystyrene (PS) oligomers were measured using pulsed field gradient (PFG)  $^1\text{H}$  NMR as a function of the weight fraction ( $w_p$ ) of high molecular weight PS (125,00 - 250,000 Daltons) in solution over the range  $0 \leq w_p \leq 0.6$ . The studies were performed at 25 °C using benzene as solvent. Model compounds used were benzene, 1,3-diphenyl-1-butanol, and a commercially-available, monodisperse sample of PS (so-called M5) of a peak-average molecular weight of  $M_p = 580$  as determined by gel permeation chromatography (GPC). GPC data and PFG NMR data were used to determine a new average molecular weight for M5 of 500. The scaling law dependence of the  $D_S$  values on the molecular weight of the model compounds were determined and a simple scaling dependence was observed with the scaling law changing linearly with  $w_p$  over the range studied. This is discussed in light of current models.  $D_S$  data are also presented for the diffusion of toluene in toluene/PS solutions over the range  $0 \leq w_p \leq 0.7$  and are 20% - 30% smaller than identical experiments reported by S. Pickup and F. Blum (*Macromolecules* 1989, 22, 3961).

**The role of aqueous-phase kinetics in emulsion polymerizations.** B S Casey, B R Morrison and R G Gilbert. *Progress in Polymer Science*, in press.

*Abstract*

The kinetics of species in the aqueous phase control many events in emulsion polymerization: the rate of entry of free radicals into particles (equivalent to initiator efficiency), the rate of exit (desorption) of free radicals from particles, the fate of desorbed free radicals and of free-radical species derived directly from aqueous-phase initiator. Aqueous-phase kinetics also dominate particle nucleation and re-seeding (secondary nucleation), and the *in situ* formation of surfactant. The mechanisms of each of these events are discussed, showing how general methods can be constructed to deduce the rate-determining events for each of these. The methodology is then applied extensively to styrene, which leads to the following conclusions. (a) The aqueous-phase events which govern entry (initiator efficiency) are propagation and termination, with entry occurring irreversibly when a critical degree of propagation  $z$  is reached so that the resulting species (a di- or tri-styrenesulfonate species in the case of styrene with persulfate initiator) is sufficiently surface-active that, once adsorbed onto the particle it does not desorb before it propagates; the actual adsorption event is sufficiently rapid so as not to be rate-determining except during nucleation. (b) Exit of free radicals is governed by transfer inside the particle to form a monomeric radical which may desorb and diffuse irreversibly away from the parent particle before it propagates therein. (c) The fate of desorbed free radicals in the wide range of styrene systems examined is to re-enter another particle and remain therein, rather than the other possible fates (aqueous-phase termination or re-exit until intra-particle termination eventually occurs). (d) Below the cmc, nucleation is by the homogeneous-coagulative mechanism, while above the cmc, nucleation is through a process which combines the essential features of both homogeneous-coagulative and micellar-entry models. (e) Analysis of the aqueous-phase products produced in an emulsion polymerization shows that the species involved in termination, entry and exit also undergo subsequent reactions: hydrolysis and reaction with persulfate.

**Solvent effects on the propagation rate coefficient for free-radical polymerization.** B.R. Morrison, M.C. Piton, M.A. Winnik, R.G. Gilbert and D.H. Napper. *Macromolecules*, in press.

*Abstract*

The effect of solvent on the propagation rate coefficient ( $k_p$ ) for styrene and methyl methacrylate was examined using pulsed laser polymerization. Solvents used were ethanol and methanol over the range 25-50°C. Solvent : monomer ratios were increased until phase separation of the polymer was observed during the polymerization. A block copolymer was also used to stabilize the formed particle phase, thereby simulating the early-time nucleation behavior of dispersion polymerization systems. There were no observable solvent effects on  $k_p$ . This can be rationalized in terms of the transition state for propagation, where the reaction coordinate comprises the incipient bond in a configuration such that solvent molecules can play no direct role in the reaction dynamics.

**Free-radical exit in emulsion polymerization: I. Theoretical model.** B.S. Casey, B.R. Morrison, I.A. Maxwell, R.G. Gilbert and D.H. Napper. *J. Polym. Sci., Polym. Chem. Edn.*, submitted.

*Abstract*

The exit or desorption of free radicals from latex particles is an important kinetic process in an emulsion polymerisation. This paper unites a successful theory of radical absorption (i.e. initiator efficiency), based on propagation in the aqueous phase being the rate determining step for entry of charged free radicals, with a detailed model of radical desorption. The result is a kinetic scheme of wide-ranging utility and yet, with a number of generally applicable assumptions, relative simplicity. Indeed, in many physically reasonable limits, the kinetic representation reduces to a single rate equation. Specific experimental techniques of particular significance and methods of analysis of kinetic data are detailed and discussed. A methodology for both assessing the applicability of the model and its more probable limits, via use of known rate coefficients and theoretical predictions, is outlined and then applied to the representative monomers, styrene and methyl methacrylate. A detailed application of the theory and illustration of the methodology of model discrimination via experiment is contained in the second paper of this series.

**Free-radical exit in emulsion polymerization: II. Model discrimination via experiment.** B.R. Morrison, B.S. Casey, I. Lack, G.L. Leslie, D.F. Sangster, R.G. Gilbert and D.H. Napper. *J. Polym. Sci., Polym. Chem. Edn.*, submitted.

*Abstract*

In emulsion polymerizations, desorption (exit) from latex particles of monomeric radical species that arise from transfer can be an important determinant of the overall kinetics. An examination of various methodologies for the testing of postulated free radical exit mechanisms is made. These utilize the model descriptions for the exit process presented in the accompanying paper of Casey et al., employing data consisting of conversion as a function of time for the approach to steady state polymerization conditions. Experimental data are presented on the exit rate coefficients as a function of such experimental parameters as: particle size, monomer concentration, and aqueous-phase free-radical concentration for a series of styrene polymerizations at 50 °C where the average number of free radicals per particle ( $\bar{n}$ ) never exceeds 0.5. It is demonstrated for these systems that while the conversion/time dependence from a single run, under conditions sensitive to exit, is insensitive to mechanistic assumptions as to the fate of desorbed free radicals, the variation of the exit rate coefficient with particle size so obtained suggests a second order dependence on  $\bar{n}$ , implying complete re-entry of desorbed free radicals under all conditions studied. Once the monomeric radicals have re-entered, they are more likely to remain inside the particle where they will either propagate or undergo termination rather than re-escape. The paper also presents an estimate for the rate coefficient at 50 °C of the first propagation step of the monomeric radical subsequent to transfer. The conclusions drawn here for seeded

systems should prove useful for study of particle nucleation mechanisms, when exit is particularly likely in small, newly formed, particles.

**Pulsed laser study of the propagation kinetics of acrylamide and its derivatives in water.** P. Pascal, M.A. Winnik, D.H. Napper and R.G. Gilbert. *Macromolecules*, in press.

*Abstract*

The pulsed laser polymerization method has been applied to aqueous acrylamide (AAM) in the absence and presence of 3 mol dm<sup>-3</sup> propionamide to obtain the propagation rate coefficient ( $k_p$ ) as a function of temperature. Below *ca.* 50°C in the absence of propionamide,  $k_p$  decreases with increasing temperature. It is proposed that this is due to the existence of an H-bonded intermediate complex along the reaction coordinate which at low temperatures enhances propagation but which breaks down at higher temperatures. In the presence of propionamide or above 50°C in the absence of propionamide, the temperature dependence of  $k_p$  behaves normally, supporting the proposition. Assuming that the high-temperature rate represents "normal" propagation in the absence of the formation of complex,  $k_p = 7 \times 10^6 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1} \exp[-(21 \pm 2 \text{ kJ mol}^{-1})/RT]$ . Analysis of these results suggests that the driving force behind the proposed intermediate complex could be H-bonding in nature. Studies of  $k_p$  for  $\alpha$ -methyl and N-methyl substituted AAM derivatives indicate that the former imposes greater constraints upon the propagation pathway than the latter.

**Chain-length dependent termination rate processes in free-radical polymerizations: II - Modeling methodology and application to methyl methacrylate emulsion polymerizations.** G.T. Russell, R.G. Gilbert and D.H. Napper. *Macromolecules*, in press.

*Abstract*

Results are presented from modeling of extensive methyl methacrylate seeded emulsion polymerization data. Both chemically initiated and  $\gamma$  radiolysis initiated experiments were modeled; in the latter type of experiments the system is removed from the  $\gamma$ -source, thereby providing kinetic data which are particularly sensitive to termination processes. While the data cannot be fitted consistently and meaningfully with conventional termination models, all are fitted in a unified way using the description of Russell *et al.* (*Macromolecules* 1992, 25, 2459). Fitting completely without adjustable parameters gives quite acceptable agreement with these sensitive experimental data, and exact accord is obtained with minor, and physically reasonable, parameter changes. The model description is applicable to free-radical polymerizations at intermediate and high conversion (i.e., above  $c^{**}$ ). Its main feature is that it takes full account of the dependence of termination rate coefficients on radical chain length, while still requiring only modest computational resources. The most important model parameters are therefore experimental diffusion coefficients for monomer as a function of weight fraction polymer, and exponents for the scaling of oligomeric and polymeric diffusion coefficients with degree of polymerization. For emulsion systems, desorption (exit) kinetics are included, and the theory of Maxwell *et al.* (*Macromolecules* 1991 24, 1629) for the rate of chemical initiation is found to be accurate. The modeling indicates that the predominant mode of termination above  $c^{**}$  and prior to the glass transition involves a short free radical, usually one formed by transfer, and a long entangled macroradical; above the glass transition, this dominant mode involves two long entangled macroradicals encountering as a result of propagation ("reaction-diffusion"). The origin of the Trommsdorff effect is the slowing with conversion of the termination rates of shorter chains, this being brought about by the increase with conversion of viscosity and of tendency to become entangled.

**Small angle neutron scattering studies of inhomogeneities in latex particles from emulsion homopolymerizations.** M.F. Mills, R.G. Gilbert, D.H. Napper, A. R. Rennie and R.H. Ottewill. *Macromolecules*, in press.

*Abstract*

Small-angle neutron scattering experiments were carried out to examine the extent of monomer/polymer spatial inhomogeneities in latex particles formed in an emulsion homopolymerization, using contrast variation and isotopic labelling systems to look at the morphology of swollen and 2-stage latices. Samples covered a range of molecular weights including systems where the radius of gyration of the polymer chains was both comparable to and smaller than the particle size. The experiments were designed to test separately inhomogeneities arising from two different effects: (1) The "repulsive wall" (thermodynamic) effect arising from the decrease in entropy of a polymer chain confined near the surface of a particle; the experiments here examined polymer distribution in polystyrene particles swollen with toluene. (2) "Surface anchoring" (largely kinetic) arising mainly because, with a water-soluble initiator, free radicals enter latex particles at the surface; here experiments examined the distribution of newly formed polymer in seeded growth; related to this are inhomogeneities arising from finite rates of diffusion of monomer and of polymer. Results support the conclusion that repulsive wall effects do not give rise to significant non-uniformities but that inhomogeneities may arise in the final product where the polymer chain dimensions are substantially less than the particle radius. The latter conclusion is consistent with predictions of the surface anchoring model.

**Spatial inhomogeneities in emulsion polymerizations: Repulsive wall calculations.** C.A. Croxton, M.F. Mills, R.G. Gilbert and D.H. Napper. *Macromolecules*, in press.

*Abstract*

The extent of the spatially inhomogeneous distribution of polymer particles in a latex formed by emulsion polymerization, dictated by thermodynamic considerations, is investigated computationally. Polymer chains suffer a loss of freedom near the particle surface, causing an entropic repulsion away from the surface and so favoring enhanced monomer concentration near the surface and thus polymerization by encapsulation. Thermodynamic calculations of the equilibrium polymer segment density distribution within a swollen latex particle show that while substantial entropic repulsions do occur, these are countered at higher polymer concentrations by polymer crowding effects. These calculations are performed using the iterative convolution technique to evaluate the segment-segment and segment-boundary correlations, corroborated where practicable with Monte-Carlo calculations. This technique represents an advance over previous work which neglected polymer excluded volume effects. Although the calculations were for low polymer fraction, trends from the results show that repulsive wall effects are highly unlikely to give rise to any significant inhomogeneities in latex particles formed from emulsion homopolymerization in conventional systems.

**EPR investigation of the nature of the propagating species in MMA polymerization.** M.P. Tonge, R.J. Pace, R.G. Gilbert, *Macromolecules*, submitted.

*Abstract*

The EPR spectrum of methyl methacrylate in a range of systems can be successfully simulated using a consistent set of parameters for a single type of free radical. The 9-line spectrum observed in bulk and emulsion polymerizations corresponds to a somewhat hindered, non-rotating macroradical; the 13-line spectrum observed at low conversion with very high free-radical flux is the same radical (with a more relaxed geometry) which is now part of a very short chain undergoing free rotation in a low-viscosity medium. This refutes earlier suggestions that there might be two types of free radicals ("trapped" and "untrapped") in these systems. The existence of an enormous proportion of very short free radicals under such conditions is supported by quantitative calculations of the radical chain-length distribution.



**Pulsed laser study of the propagation kinetics of *t*-butyl methacrylate.** P. Pascal, M. A. Winnik, D. H Napper and R. G. Gilbert. *Makromol. Chem., Rapid Commun.*, in press.

**Abstract**

This article presents the temperature dependence of the propagation rate coefficient,  $k_p$ , for the free-radical polymerization of bulk *tert*-butyl methacrylate (*t*-BMA) at low conversion. The motivation for this work was to provide reliable data which could be used for kinetic modelling of more complex polymerization systems such as emulsion polymerization, as well as to provide data for future testing of models for the transition states for the propagation process. The  $k_p$  values found over a temperature range of 25-70°C were found to have Arrhenius parameters of:  $A=10^{7.4\pm 0.4} \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$  and activation energy  $E_p=27.7\pm 2.5 \text{ kJ mol}^{-1}$ . This is in agreement with earlier data obtained at 25°C by the SIP technique.

\* The following publications have appeared in press during 1992 and 1993 from various members of the SUPC (with their publication details):

Polymer-fraction dependence of entry rate coefficients in emulsion polymerization. G. L. Leslie, D. H. Napper and Robert G. Gilbert, *Aust. J. Chem.*, 45, 2057-60 (1992).

The effects of diffusion control on the propagation and transfer rate coefficients in free radical polymerization. B S Casey, M F Mills, D F Sangster, R G Gilbert and D H Napper, *Macromolecules*, 25, 7063-5 (1992).

The seeded emulsion polymerization of butadiene. I: The propagation rate coefficient. E.M. Verdurmen, E.H. Dohmen, J.M. Versteegen, I.A. Maxwell, A.L. German and R.G. Gilbert. *Macromolecules*, 26, 268-275 (1993).

Characterization of water-soluble oligomers formed during the emulsion polymerization of styrene by means of isotachopheresis. B.R. Morrison, I.A. Maxwell, D.H. Napper, R.G. Gilbert, J.L. Ammerdorffer and A.L. German, *J. Polym. Sci., Polym. Chem. Ed.*, 31, 467-483 (1993).

Kinetics of particle growth in emulsion polymerization systems with surface-active initiators. J. M.H. Kusters, D. H. Napper, R. G. Gilbert and A. L. German, *Macromolecules*, 25, 7043-50 (1992).

Desorbed free radicals in emulsion polymerizations: effect of aqueous-phase spin trap. I. Lacík, B. S. Casey, D. F. Sangster, R. G. Gilbert and D. H. Napper. *Macromolecules*, 25, 4065-4072 (1992).

Chain-length dependent termination rate processes in free-radical polymerizations: I - Theory. G. T. Russell, R.G. Gilbert and D. H. Napper. *Macromolecules*, 25, 2459-69 (1992).

Consistent values of rate parameters in free radical polymerization systems. Part II: Outstanding dilemmas and recommendations. M Buback, R G Gilbert, G T Russell, D J T Hill, G Moad, K F O'Driscoll, J. Shen and M. A. Winnik. *J. Polym. Sci., Polym. Chem. Edn.*, 30, 851-63 (1992).

Testing nucleation models for emulsion polymerization systems. B.R. Morrison, I.A. Maxwell, R.G. Gilbert and D.H. Napper. *ACS Symposium Series 492*, pps 28-44: *Polymer Latexes - Preparation, Characterization and Applications*. American Chemical Society, Washington DC, 1992.

Contribution to the International Polymer Colloid Group Newsletter  
April 1993

from

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In the last few years, we have started work on the physical properties of associative thickeners. Especially, we want to use the combined information from different techniques in order to describe these systems in a more fundamental way. We are especially using PGSE-FT NMR, Dynamic Light Scattering and different Rheologic methods. Now some of this effort is paying off, several publications are submitted, and some are published. I gave a lecture on some of the methods and results at the Gordon Conferene at Irsee last year. Here I give a short summary of 2 papers that are submitted to J.Phys.Chem. The work is continuing on multi-component systems.

**Dynamic Crossover Effects Observed in Solutions of a Hydrophobically Associating Water Soluble Polymer.**

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The dynamics of aqueous solutions of a hydrophobically associating polymer is studied by means of Pulse Gradient-Fourier Transfer NMR (PGSA-FT NMR) and dynamic light scattering (DLS). The results from the NMR measurements at higher concentrations reveal an anomalous diffusion behavior. However, when the observed time is increased the classical Fickian diffusion is recovered. These features are discussed in terms of effects of fractal structure and in the light of a coupling model. The concentration dependence of the self-diffusion coefficient is well described by a stretched exponential function. These results constitute the basis for the evaluation of the concentration dependent coupling parameter.

The time correlation function data obtained from the DLS experiments are analyzed, at all concentrations, with the aid of a model, where the initial decay is described by a single exponential followed by a non-exponential relaxation function, which is characterized by a fractional exponential of the Korasch-Williams-Watts type. In the initial stage an uncoupled relaxation time  $\tau_f$  is recognized, which decreases slowly with concentration. The wavevector ( $q$ ) dependence of  $\tau_f$  indicates a crossover from diffusive to Zimm-like behavior as the concentration increases. At longer times the analysis yields a mean relaxation time  $\tau_s$ , associated with the release of coupled clusters. The width of the distribution of relaxation times is given by a parameter  $\beta$ . This quantity, which is independent of  $q$ , decreases from 0.97 at low concentrations to about 0.4 at high concentrations. The parameter  $\tau_s$  increases dramatically (several decades) in the studied concentration range. The  $q$  dependence of  $\tau_s$  is considerably stronger, at higher concentrations, than that of  $\tau_f$ . All these features can be rationalized in the framework of the coupling model.

### Associative Thickeners.

#### NMR Self-Diffusion and Rheology Studies of Aqueous Solutions of Hydrophobically Modified Poly(oxyethylene) Polymers.

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Nonionic associative thickeners are produced by hydrophobically modifying poly(oxyethylene) with hydrophobic end group straight hydrocarbon chain length varying from 8 to 18 carbon atoms. Solutions of these polymers in water have been studied by Pulsed Gradient Spin Echo - Fourier Transform NMR diffusion measurements (PGSE-FT NMR) and rheology measurements.

The NMR results reveal a distribution of self-diffusion coefficients that broadens continuously with increasing concentration. The distribution is described by a stretched exponential of the same mathematical form as the classical Kolrausch-Williams-Watts function, yielding a parameter  $\beta$  to describe this distribution. From a fit of the echo attenuation (i.e. signal intensity) raw data to this stretched exponential a mean diffusion coefficient,  $D_S$ , is calculated for each concentration for all systems. These representative self-diffusion coefficients are found to scale with concentration in the dilute and semi-dilute concentration regimes according to a (different) stretched exponential as suggested by Phillies,  $D_S/D_0 = \exp(-\alpha c^\gamma)$ , where  $D_S$  denotes the mean diffusion coefficient at a concentration  $c$ ,  $D_0$  is the extrapolated zero-concentration diffusion coefficient, and  $\alpha$  and  $\gamma$  are two parameters.  $\gamma$  is found to increase with increasing chain length of the hydrophobic end groups. The two parameters,  $\alpha$  and  $\gamma$ , are used to calculate coupling parameters at arbitrary concentrations in the semidilute concentration regime within a model developed of Ngai and coworkers for molecular transport in polymer solutions. The coupling parameters are found to increase with both concentration and length of the hydrophobic end group. The extrapolated zero-concentration diffusion coefficients,  $D_0$ , are used to estimate cluster sizes, i.e. the number of polymer molecules per cluster, at low concentrations. These clusters are very small, of 2-5 polymer molecules, depending on and increasing with hydrocarbon end group chain length.

The rheology data on the same systems give partly complementary information on the aggregation state of the polymers in the semidilute concentration range. Average numbers of polymer molecules between association units have been calculated, and these decrease with increasing concentration from a value of 15-30 at  $c/c^* \approx 2$  to a value close to 1 at  $c/c^* \approx 10$  ( $c^*$  is the overlap concentration). These findings parallel the Ngai coupling parameters in that as the network gets denser the coupling parameters increase.

An observation during the study of these systems is that at concentrations above ca 0.03 g/ml (except for the  $C_8$  and  $C_{10}$  systems) we observe an apparent increase in self-diffusion coefficients with concentration. At 0.05 g/ml the self-diffusion coefficient is ca.  $10^{-11}$  m<sup>2</sup>/s. We note that no phase transition has been observed at these concentrations, although there is presently a lack of knowledge of phase behaviour in systems like these. Similar effects have been observed by others for PEO PPO block-copolymers.



## INTERNATIONAL POLYMER COLLOIDS GROUP NEWSLETTER

Contribution from Norio Ise, Fukui Research Laboratory, Rengo Co. Ltd., 10-8-1 Jiyūgaoka, Kanazu-cho, Sakai-gun, Fukui 919-06, Hideki Matsuoka, Department of Polymer Chemistry, Kyoto University, Kyoto 606-01, and Kensaku Ito, Department of Chemical and Biochemical Engineering, Toyama University, Toyama 930, Japan

Reporter: Norio Ise

Monodisperse latex particles form ordered structures even in dilute dispersions at very low salt concentrations. These ordered structures become less and less stable with increasing salt concentration and finally disappear in the presence of  $10^{-4}$ M 1-1 type salt. This change of the stability of the ordered structure with salt concentration is in clear contradiction to the traditional DLVO theory. In addition, there are several experimental findings, which cannot be accounted for in terms of the theory. Our main interest was and is to find the true nature of the interparticle interaction, in other words, to estimate the role of an electrostatic attraction between latex particles in dispersions or macroions in solutions, which has been largely ignored or claimed to be unimportant in most of recent works in this field. Our activity along this line can be divided into the following areas.

## Sedimentation Equilibrium

Perrin carried out sedimentation experiments using gamboge particles in 1908 [1]. He found that the following relation was obeyed,

$$N = N_0 \exp[-4\pi N_A g a^3 (\rho - \rho_0) H / 3RT] \quad (1)$$

where  $N$  and  $N_0$  are the particle numbers at a height  $H$  and at the reference height, respectively,  $N_A$  is the Avogadro number,  $\rho$  and  $\rho_0$  are the densities of the particle and the medium, respectively, and  $g$ ,  $R$  and  $T$  are the acceleration of gravity, gas constant, and temperature, respectively. By measuring the radius  $a$  by microscopic method, he determined  $N_A$  to be  $6 \sim 7 \times 10^{23}$ . It is reminded that the radius  $a$  used here was the hard sphere radius.

On the other hand, it has been often claimed that various colloidal phenomena can be satisfactorily accounted for by invoking "effective" radius of particles, for example, the hard sphere radius plus Debye length ( $1/\kappa$ ). This is not in line with Perrin's treatment. We questioned this interpretation but it was not possible to demonstrate its imperfection by using his data since he did not provide the number of electric charges of the gamboge particles so that the  $1/\kappa$  could not be determined. Thus we used well-defined polymer latex particles. Furthermore, a confocal laser scanning microscope (LSM) was employed, which enabled us to observe particles in a more interior part ( $200 \sim 700 \mu\text{m}$ ) of dispersions than in Perrin's case ( $5 \sim 35 \mu\text{m}$ ). Our study [2] showed that Eq. (1) is valid. Furthermore, from Eq. (1) by adopting  $N_A = 6.02 \times 10^{23}$  the particle radius  $a$  was found to be in good agreement with that determined by electron micrographs. This implies that, if the effective radius was introduced into Eq. (1),  $N_A$  values different from the accepted one would be resulted. The Avogadro number thus estimated showed a good agreement with  $6.02 \times 10^{23}$  in the presence of  $10^{-3}$ M NaCl, and decreased with decreas-

ing salt concentration. In the absence of salt, it was  $2 \times 10^{23}$ , which is highly paradoxical.

Another apparent paradox in using the "radius plus Debye length" will be realized as follows: As the latex concentration is decreased, the Debye length increases at a rate faster than the interparticle distance increases. This means that more ordered structure of latex particles should result upon dilution with the "radius plus Debye length" interpretation. This is in complete disagreement with observation.

Thus, although it seems convenient to think of an effective radius to interpret data, we would not gain any insight as to the physics of colloidal systems with the "radius plus Debye length" model.

### Void Structure

By using a metallurgical microscope, Hachisu et al. reported the presence of void structures in latex dispersions [3]. This was confirmed by us later [4]. It was however feared that the voids observed were artifacts due to the dispersion-glass interface (wall) effect, since we could see only (polystyrene-based) latex particles in the vicinity of the glass wall (usually 2~3 and at most 10  $\mu\text{m}$  away from the wall in the case of water as dispersant). Thus we took the advantage of the laser scanning microscope.

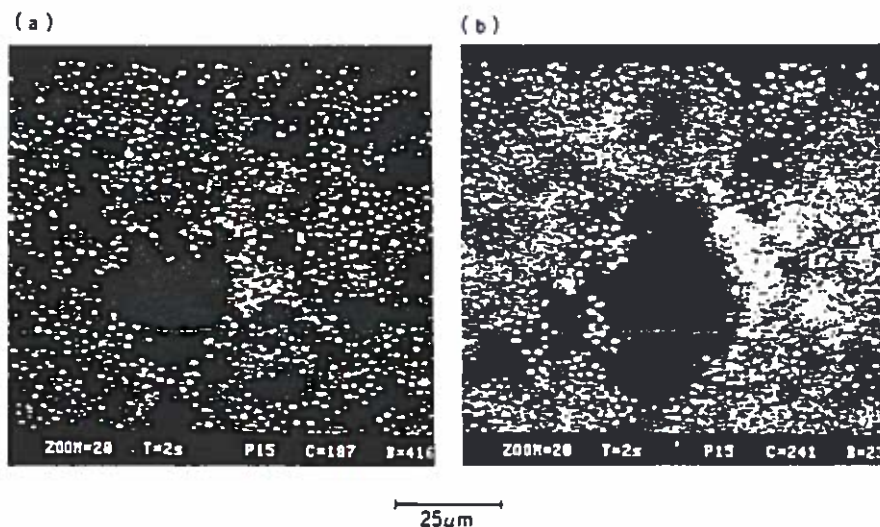


Fig. 1 Void structures as observed by a confocal laser scanning microscope on the horizontal focus planes 10 (a) and 20  $\mu\text{m}$  (b) away from the top of the dispersion. Latex:N1000, diam.:0.96  $\mu\text{m}$ , charge density: 12.4  $\mu\text{C}/\text{cm}^2$ ) [latex]:3 %, solvent:  $\text{H}_2\text{O}-\text{D}_2\text{O}$  for density matching. Temperature was kept constant by placing the dispersion cell in a thermostated air bath.

Dispersions were first extensively purified and then latex particles were confirmed by microscope to form ordered arrangement or distribute uniformly. After the dispersions were kept standing on the microscope bench for 24 hrs, the LSM observation was initiated. By this technique, very stable and huge void structures could be observed [5,6]. An example is demonstrated in Figure 1, which shows the cross section of a three-dimensional void.

In light of the scale given, the cross section was as large

as 20 x 25  $\mu\text{m}$ . Although the pictures are not given here, we could observe a void as large as 60 x 150 x 50  $\mu\text{m}$  [6]. Interesting is the fact that, at a given time after the dispersion cell was placed on the microscope bench, it was more difficult to find the void structures near the dispersion-glass interface than at larger depths. (Compare the picture taken at 6  $\mu\text{m}$  and others at 10, 20, 30, and 40  $\mu\text{m}$  in Figure 6 of Ref. [6].) Furthermore, at a given depth, the longer the dispersion was kept standing, the more easily large voids could be observed.

It should be mentioned that the voids observed above were far larger than the spacings that can be studied by the conventional scattering techniques. Thus, to our knowledge, no one has suggested or concluded the existence of such a structural inhomogeneity in solutions or dispersions in general. Although detailed study of the time evolution of the void structure is under way, this bizarre phenomenon must be taken into consideration in evaluation of the interparticle interaction. In other words, the voids most graphically support the interparticle attractive interaction.

### Scattering Study at Very Low Angles

#### SANS Study of Polystyrenesulfonate (PSS) Solutions in Heavy Water

In collaboration with Dr. D. Schwahn, Jülich, Germany, neutron scattering at low angles was conducted [7]. As is shown in Figure 2, a single broad peak was observed at higher angles and a steep upturn was found below  $0.01 \text{ \AA}^{-1}$ . We note that the peak was observed at the same position as in previous small-angle X-ray scattering in  $\text{H}_2\text{O}$ . This might exclude the possibility of the presence of impurities in  $\text{D}_2\text{O}$ . The upturn indicates a large scale density fluctuation in the apparently homogeneous solutions. Our interpretation is that the fluctuation is due to the localized ordered structure of the macroions. By applying the Guinier plot, the size of the domain (radius of gyration,  $R_g$ ) could be obtained, though approximately. The results are shown in Table I.

Table I SANS Data of NaPSS- $\text{D}_2\text{O}$  Solutions

[NaPSS] (g/ml)	[NaCl] (M)	$R_g$ ( $\text{\AA}$ )	$2D_{\text{exp}}$ ( $\text{\AA}$ )	$2D_0$ ( $\text{\AA}$ )	N
0.01	0	407	166	255	130
0.02	0	516	103	202	1100
0.04	0	686	85	160	4700
0.08	0	(630)	64	128	8600
0.04	0.05	664	94	160	3200
0.04	0.1	683	(132)	160	(1250)
0.04	0.3	---	---		

The brackets imply that a large uncertainty is contained.

From the  $R_g$  value, the radius of spherical ordered structure was estimated and, when combined with the intermacroion Bragg spacing ( $2D_{\text{exp}}$ ), we could obtain the number of macroions (N) in an ordered structure. The N value is seen to increase with increasing PSS concentration and seems to decrease with increasing salt concentration. We note that the size of the structure under the salt-free condition was estimated by dynamic light scattering (DLS) by Sedlak and Amis [8]. The results from these

two groups were in good agreement.

By the Babine principle, void structure might have caused the upturn, to which brief consideration was recently given [7]. Anyway, apparently homogeneous solutions are microscopically inhomogeneous. This fact has to be carefully taken into consideration in efforts to understand the true nature of the interparticle or intermacroion interaction. It is also remembered that the "smooth" extrapolation of the scattering intensity (observed in the conventional scattering experiments) to zero scattering vector is not warranted in light of the upturn.

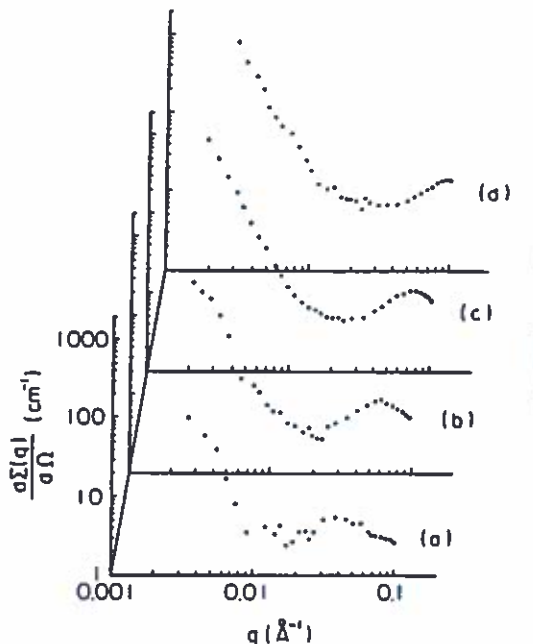


Fig. 2 Small-angle neutron scattering curves of a NaPSS-D<sub>2</sub>O solution at different polymer concentrations without salt. [polymer]: (a) 0.01, (b) 0.02, (c) 0.04, (d) 0.08 g/ml.

#### Ultra-small-angle X-ray Scattering

We constructed an ultra-small-angle x-ray scattering (USAXS) apparatus [9] using the principle proposed by Bonse and Hart [10]. The rocking curve had a width at the half maximum of 4 sec, which implies that an electron density fluctuation of about 8  $\mu\text{m}$  is in principle detectable. The calibration of the apparatus was satisfactorily carried out using monodisperse latex particles, as shown in Figure 3. The colloidal crystal growth in latex dispersions was followed by the USAXS apparatus, which showed eventually scattering maxima characteristic to face-centered-cubic structures for a 3.7 % ethanol/water dispersion of polystyrene-based latex particles and for a 8.8 % water dispersion of polymethylmethacrylate-based latex particles [11].

Another advantage of the USAXS apparatus was that the particle size in dispersion could be determined *in situ* from scattering maxima; from Figure 3, the particle radius of a latex was estimated to be 0.28  $\mu\text{m}$  when the measurement was made in powder state, whereas a value of 0.3  $\mu\text{m}$  was found in an ethanol dispersion. The difference seems to be due to swelling of the particle in ethanol. Important is that the USAXS method has a decisive advantage over electron microscopy, which provides information

only in solidified samples. Needless to say, the USAXS technique can be used even for turbid samples, to which light microscopy cannot be applied.

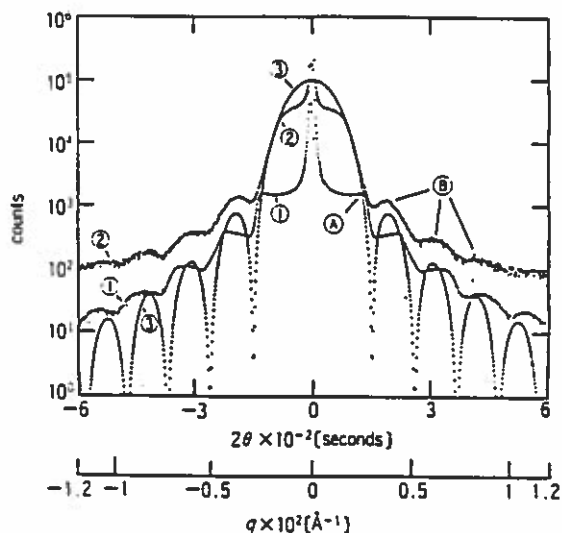


Fig. 3 USAXS curves for latex powder and dispersion. The latex has a diameter of  $0.29\mu\text{m}$ . Curve 1: powder, Curve 2: ethanol dispersion (latex conc.: 12 %), Curve 3: the theoretical scattering function for isolated sphere of a diameter of  $0.3\mu\text{m}$ .

In previous scattering experiments on ionic polymers and microscopic study of latex dispersions [See for example Ref. 6], we found that, at lower concentrations such as 1 %, the observed interparticle spacing ( $2D_{\text{exp}}$ ) is smaller than the average interparticle spacing ( $2D_0$ ) calculated from the concentration, which led us to the recognition of the two-state structure. Now this relation was confirmed by applying the USAXS measurements for polymethylmethacrylate-based latex particles (diam.:  $0.3\mu\text{m}$ ). At higher concentrations above 6 %,  $2D_{\text{exp}}$  was found to be equal to  $2D_0$  [11]. At lower concentrations such as 1 %, we recently observed  $2D_{\text{exp}} < 2D_0$ .

The applications of the USAXS method to structural studies of polymer films, polymer mixtures, metal alloys, fibers, silica dispersions, etc., were described elsewhere [12].

#### Recent Development in Controversy over the Interparticle Interaction

It has been widely believed that colloidal phenomena can be satisfactorily described by the (purely repulsive) DLVO or Yukawa potential. As mentioned above, there have been discovered various facts which are incompatible to these potentials and testify to the contribution of an electrostatic attractive interaction in addition to the widely accepted repulsive interaction. Recently Sogami proposed an interionic theory for colloidal or macroionic systems, which reveals the simultaneous contribution of the electrostatic attraction and repulsion [13]. Sood et al. calculated the structure factor and radial distribution function of a latex dispersion by using the Yukawa potential and Sogami potential [14]. Interestingly, the two calculated values were in good agreement with the observed value. This means that the DLVO or

Yukawa potential cannot be claimed to be the only correct potential for colloidal systems, in contrast to the widely accepted view.

Similarly, we demonstrated that the elastic modulus of latex dispersions could be reproduced in a likewise satisfactory manner both by the DLVO potential and Sogami potential [15]. Thus, the frequent statements such as "colloidal crystals are stabilized from purely repulsive Coulombic interactions" is not justified.

Overbeek claimed that the attractive part exactly disappears from the Sogami potential if the contribution of solvent is duly taken into account [16]. This criticism is a grave mistake, judging from the very basis of thermodynamics, since his argument violates the Gibbs-Duhem relation, which reads

$$N_{\text{solv}}d\mu_{\text{solv}}^{\text{el}} + \sum N_i d\mu_i^{\text{el}} + N_{\text{part}}d\mu_{\text{part}}^{\text{el}} = 0 \quad (2)$$

where part implies the particles or macroions,  $i$  denotes small ionic species (counterions and salt ions) and solv the solvent,  $N$  the concentration,  $\mu$  the chemical potential, and  $\text{el}$  the electrostatic contribution. In his argument, he contended that

$$(N_{\text{solv}}d\mu_{\text{solv}}^{\text{el}} + \sum N_i d\mu_i^{\text{el}})_{p,T} = 0 \quad (3)$$

so that the attraction was canceled. Obviously the contribution of the particles was ignored, in other words, the Gibbs-Duhem relation was violated. Since the particles are much more highly charged than the simple ions and they are expected to exert incomparably striking influences on the chemical potential of the system, the disregard of the particle contribution led Overbeek to the incorrect conclusion.

**Concluding Remark: "Fair is foul, and foul is fair".**

From the above comparison of the Yukawa potential and Sogami potential, it is seen that most of previous arguments in favor of the Yukawa potential or the repulsion-only assumption contain a logical flaw. In other words, the role of the attraction has not been tested. Without demonstrating that the attraction results in a paradox or disagreements with observation, the attraction has been claimed to be unimportant or negligible.

It was pointed out above that the repulsion-only assumption led us to quite a paradoxical result. The fact, that the DLVO theory and/or Yukawa potential provided agreement with experimental observation, does not necessarily justify them, but is consequent probably on the very shallow potential minimum in colloidal systems.

On the other hand, there are new observations that cannot be accounted for or are not explainable without introducing additional ad hoc parameter(s) in terms of the DLVO theory. First the fact, that the ordered structure is stabilized at low salt concentrations and disappears when the salt concentration is increased, is in qualitative contradiction with the DLVO prediction. The localized ordered structure and hence the sharp upturn of scattering intensity at low angles are inconsistent with the repulsion-only assumption, since the solute distribution would become homogeneous if only repulsion is in action. Though not discussed here, the Ostwald ripening mechanism found in colloidal crystal growth testifies to the presence of the attraction. The void structure appears to support positively the presence of the attraction.



Matsumoto and Kataoka carried out a computer simulation by using the Sogami potential and found out that the "order-disorder transition" took place at a low volume fraction of 0.02 under low salt condition in agreement with the experimental observation [17]. We note the dramatic improvement over the hard sphere potential adopted in the Alder simulation [18], which led to a very high volume fraction for the transition point (above 0.5). Arora et al. [19] observed the re-entrant phase separation in latex dispersion for a restricted range of salt and latex concentrations and demonstrated that this phenomenon can be accounted for in term of the Sogami potential, not by the DLVO potential.

Thus, in light of the recent experimental findings that are not compatible to the Yukawa (or DLVO) potential but to the Sogami potential, the DLVO potential cannot be claimed to be correct. A variety of experimental data have been and will be reported to be satisfactorily reproducible by the DLVO potential but the agreement between the theory and experiments would be due to numerical accidents and be only superficial, as was pointed out above for the structure factor by Sood and for elastic modulus by us.

In this respect, it is indispensable to recall the statement by Debye and Hückel[20] that, "considering any one ion, we shall find on an average more dissimilar than similar ions in its surroundings, an immediate consequence of the electrostatic forces effective the ions". Naturally, we have to take into consideration the asymmetric nature of colloidal and macroion systems. Even then we realize that the repulsion between the low-valent counterions is overwhelmed by the electrostatic attraction between the high-valent colloidal particles and counterions, which in turn surpasses the purely repulsive interaction between the particles. The DLVO theory is judged not to satisfy this axiomatic situation.

Acknowledgments. Sincere thanks go to the coworkers, whose efforts made the work possible. Financial support from the Ministry of Education, Science and Culture is gratefully acknowledged.

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**PARTICLE SIZE DISTRIBUTION OF BIMODALS : A  
COMPARATIVE STUDY OF SUBMICRON SIZING  
INSTRUMENTATION.**

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During the preparation of polymer colloids the formation of bi- and multimodal populations can be observed. In order to control processes and applications one should be able to monitor the phenomena underlying the formation of multimodals. Therefore the capability of different particle sizing instruments to resolve bimodals in the submicron range, has been investigated. The selected techniques were : Photon Correlation Spectroscopy (PCS), Static Light Scattering (SLS), Sedimentation Field Flow Fractionation (SFFF), Disk Photocentrifuge (DPC) and Electron Microscopy (EM). For PCS the comparative study has been broadened towards different commercial instruments and software packages located in a university as well in an industrial environment.

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

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

## Particle Sizing by Photon Correlation Spectroscopy

### Part III: Mono and Bimodal Distributions and Data Analysis

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#### Abstract

The possibilities and limitations of photon correlation spectroscopy (PCS) as a practical tool for particle sizing are reviewed. In this part the most frequently used methods of data analysis are briefly surveyed. The practical performances for the determination of particle size distributions were evaluated by a comparative study with different kinds of users (industrial and academic research groups and manufacturers). The PCS results were also compared with electron microscopy (EM) and static

light scattering (SLS) results. Thereby it was confirmed that the amount of reliable information that can be obtained by PCS about particle size distributions with measuring times of the order of minutes is limited by the ill-conditioning of the data inversion procedure, among other factors. Nevertheless, the information obtained from the PCS measurements agrees essentially with the EM and SLS results.

## Data Analysis of Multi-Angle Photon Correlation Measurements Without and With Prior Knowledge

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#### Abstract

The application of the singular value analysis and reconstruction method (SVR) and of the Contin method for the collective analysis of multi-angle noisy photon correlation data sets was investigated. Provided the data are sampled equidistant in time and by proper tuning of the sampling time to the scattering angle, a collective multi-angle SVR analysis is feasible. For homogeneous spherical particles such an analysis does not require any prior knowledge of the angular dependence of particle scattering power (e.g. Mie scattering). SVR allows the information content to be separated from noisy intensity auto-

correlation data. It is illustrated that the multi-angle SVR analysis enhances the recovery of the information content. Moreover, SVR can be used as a fast and accurate preprocessor for extracting the field autocorrelation function for a subsequent Contin analysis whereby prior knowledge of particle scattering power as a function of scattering angle is used as a constraint. Compared with the data analysis of multi-angle time-averaged scattered intensity measurements, the information that can be extracted from multi-angle PCS data in comparable accumulation times is poorer.

## The influence of organic cosolvents on the lipase catalyzed hydrolysis of decylchloroacetate

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### Abstract

The hydrolysis of decylchloroacetate by *Pseudomonas fluorescens* lipase was studied in a two-phase organic solvent-aqueous buffer system using toluene, dibutylether and isooctane as cosolvents. The experiments were analyzed by on-line determination of the interfacial area and activity. Using low amounts of substrate the activity in the presence of toluene and dibutylether was low compared with the activity in the presence of isooctane. This phenomenon is not caused by a limitation of the interfacial area nor is a reduced affinity to the interface responsible for this effect. The effect of the various cosolvents can partially be explained by the log P and the interfacial tension of the pertinent organic solvent.

### LIPASES : BIOTRANSFORMATIONS, ACTIVE SITE MODELS AND KINETICS.

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### SUMMARY

Lipases can be used to obtain various (chiral) intermediates. To select a suitable hydrolytic enzyme from the increasing number of commercially available lipases application of active-site models may be very useful. Since the hydrolysis takes place at the interface, the kinetics of lipase catalyzed reactions are strongly dependent upon the quantity and quality of the interface. A newly developed dynamic method, based on measuring the droplet-size distribution by light scattering (Fraunhofer diffraction), has proven to be very useful to measure the total interfacial area of a non-stabilized emulsion. In an alternative approach lipase kinetics could be determined by using a hollow fiber membrane reactor. Both approaches indicate that there is a linear relationship between the rate of lipolysis and the interfacial area. The effect of the quality of the interface on the enzymic hydrolysis reaction is currently being studied to optimize both the rate as well as the (stereo)selectivity of the hydrolysis.

## POLYMER COLLOID NEWSLETTER

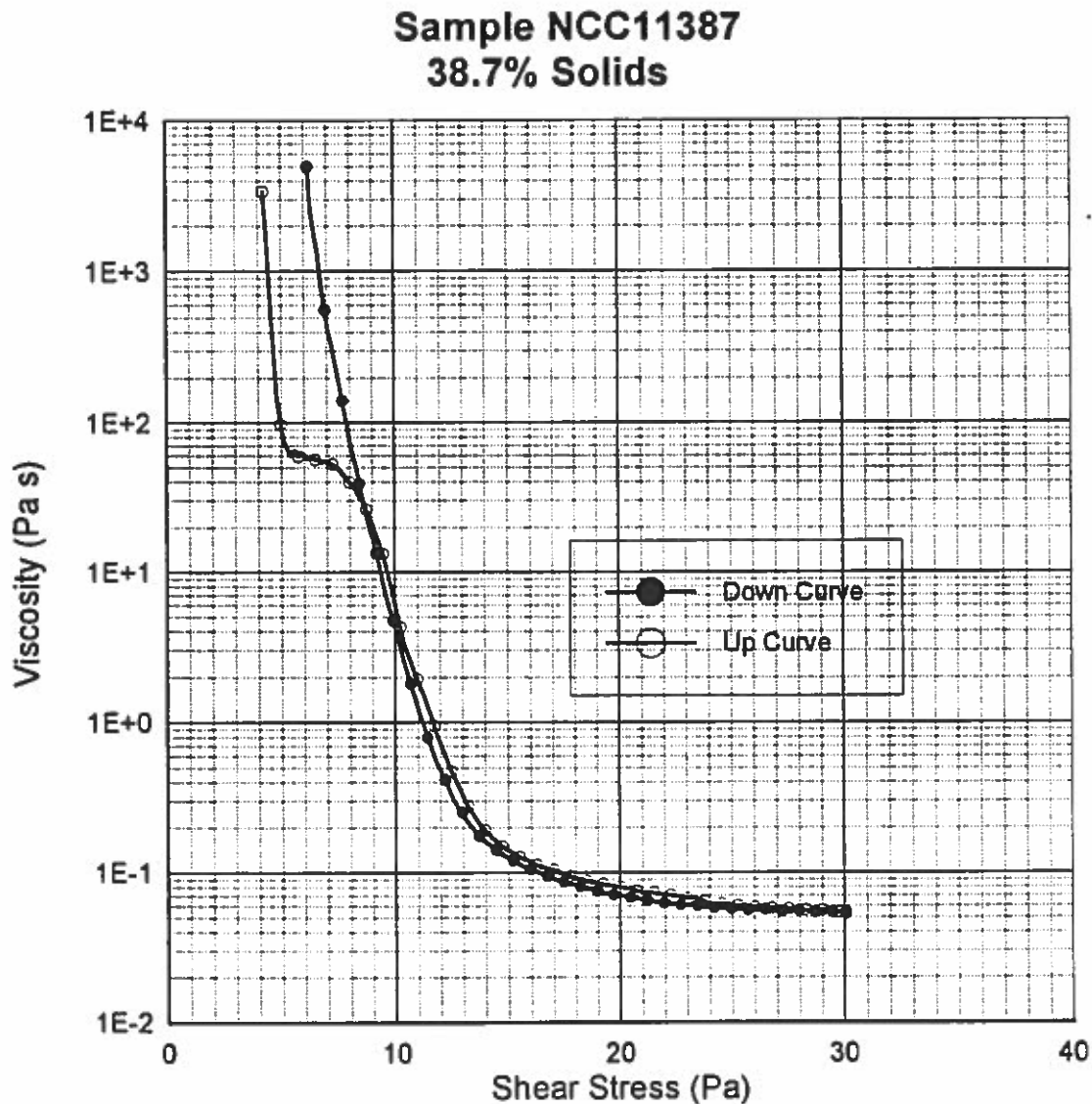
Contribution from I. M. Krieger

I have not contributed to the Newsletter for several years now, ever since I retired from teaching in 1988 and closed my laboratory at Case Western Reserve University. At that time, the main focus of my research shifted from the rheology of polymer colloids to the science of rheometry, *i.e.*, to the measurement of rheological properties. I spent most of 1989 in Strasbourg, working with Jean Candau at the CNRS which he heads there. He had just equipped a new rheology laboratory, to supplement his optical and ultrasonic techniques for studying complex fluids, and brought me in to help inaugurate the laboratory and train his research associates. The paper on inertial effects in controlled-stress rheometry (*J. Rheology* 34, 471-483 (1990)) was written there.

We subsequently inaugurated a collaborative project between the Strasbourg group and Alain Guyot's group at Lyon, to prepare and study small-particle uniform lattices (diameters less than 100 nm). This research is still under way; a NATO travel grant allows me to consult with them occasionally. They have observed some dramatic examples of shear melting in their small-particle lattices, which Dr. Guyot may be able to report in the near future. The enclosed figure, showing measurements by Dr. F. Kern (Strasbourg) on a small-particle latex prepared by C. Graillat (LMO, Lyon) is a good example. Shear stress was increased from 0 to 30 Pa and then decreased back to 0. The break in the up-curve, at *ca.* 5 Pa, is thought to be due to "shear melting" of a solid-like lattice, which does not reform when the stress is reduced at the same rate.

After my return to the U.S., I consulted for two years with Rheometrics, Inc. on the development of two new rheological instruments. This work resulted in three papers, which were presented at meetings of The Society of Rheology, and are now being submitted to the *Journal of Rheology*. The first two concern annular flow, which is used in the high-shear attachment to the Rheometrics RFX extensional rheometer. One of these deals with the kinetic energy correction, which plays an important role in high-shear rheometry, and the other analyzes the effects of centering and alignment errors in annular flow. The third paper describes real-time implementation of an inertial correction in a controlled-stress rheometer. With the real-time inertia correction in place, it becomes possible for the first time to use controlled-stress rheometry to characterize rapid thixotropic transitions.

The 12-man panel of experts which conducted the study included Jim Goodwin and Theo van de Ven. Our final report has been submitted, and will soon be available from the U.S. Printing Office. We found that the critical need is to develop a stable, ecologically acceptable ERF which will produce a high yield stress upon the application of a strong electric field (of several kilovolts per millimeter). Nonaqueous dispersions sterically stabilized by carefully tailored moieties bound or adsorbed to their surfaces are prime candidates.



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As a new member of the group, for my first contribution to the newsletter I have elected to give an overview of my activities in the area of polymer colloids in order to introduce myself to those of you who are not familiar with my research interests.

Most of my research has the underlying theme of controlling polymer structure and morphology in order to establish structure-property relationships, especially with regard to the mechanical properties of multiphase polymeric materials. In view of this, my research programmes usually begin with polymer synthesis. Studies of correlations between polymerisation process-conditions and the structure and molecular properties of the polymers produced are of fundamental importance in underpinning my research objectives.

About half of my research work is related to polymer colloids. In this area, a major focus of attention has been, and continues to be, studies of the formation and properties of multi-layer particles produced by sequential "seed-and-grow" semi-continuous emulsion polymerisations. With help from Dr. Frank Heatley (Chemistry Department, University of Manchester) techniques of Fourier-transform nuclear magnetic resonance spectroscopy (FT-NMR) are being used to help determine correlations between the synthesis, molecular structure and bulk properties of acrylate-based emulsion polymers. In terms of bulk polymer properties, most of the work is in the areas of rubber-toughening brittle polymers and water-borne, pressure-sensitive adhesives.

### *Rubber-Toughening Brittle Polymers*

*Sponsors:* Science & Engineering Research Council, ICI Acrylics

*Collaborators:* Professor Robert J. Young, Dr. Richard J. Day, Dr. Anthony J. Ryan

*Past research workers:* Adrian C. Archer, John McDonald, David E.J. Saunders

*Current research workers:* M. Onesmus Munyati, Dorian Pierre, Matthew N. Sherratt

A large research programme into the rubber-toughening of poly(methyl methacrylate), PMMA, using multi-layer toughening particles was initiated about six years ago. The research is multidisciplinary, involving: synthesis of the particles; their isolation by latex coagulation followed by blending with PMMA by extrusion; morphological and physical characterisation of the materials; and studies of the deformation micromechanics.

Studies of factors affecting the seed stage and the controlled growth of the seed particles to produce multi-layer particles using processes with up to five growth stages have been



made and have led to a high degree of control of particle size and morphology. Secondary particle nucleation is limited by use of high seed particle numbers and low surfactant levels during the growth stages. A low level of crosslinking of the polymers forming the layers is essential for the use and performance of the particles, and has the additional benefit of providing a kinetic barrier to phase rearrangement, thereby enabling good control of particle morphology.

A range of nine types of toughening particles have been prepared with controlled differences in overall particle diameter, the number (two to four) of layers of glassy and rubbery polymer, the individual layer thicknesses, the extent of interfacial grafting, and the chemistry of crosslinking. The chemical compositions of the individual layers has been selected so that they have refractive indices which match that of PMMA, hence eliminating light scattering in the blends with PMMA and giving rise to optically-transparent, rubber-toughened PMMA materials.

For each type of particle, four blends with PMMA have been produced at particle weight fractions ranging from 0.1-0.4. Important correlations have been established between rubber-toughened PMMA mechanical properties, deformation mechanisms and the diameter, layer structure and chemistry of the toughening particles. The optimum particle structure consists of an outer layer and inner core of PMMA, both of which are chemically-grafted to a styrene-acrylic rubber inter-layer. Through control of the various layer thicknesses, it has been possible to increase mechanical properties such as modulus whilst simultaneously increasing the energy required to fracture the material. In the past year, optical microscopy, transmission electron microscopy and small-angle X-ray scattering studies into the micromechanics of deformation in these materials have revealed detail of the mechanisms by which the particles induce toughness and have shown differences in the mode of action of the particles depending upon the particular particle size/morphology/chemistry and the type of deformation applied.

The knowledge gained from the work on toughening PMMA now is being adapted in new research programmes on the toughening of epoxy resins and polyester resins. These systems are particularly interesting because the resins form the matrices in many high volume-fraction, fibre-composites and the sub-micron size toughening particles offer the potential for retaining resin toughness in the composites.

### *Studies of Water-Borne Pressure-Sensitive Adhesives*

*Sponsors:* Science & Engineering Research Council, Rhone-Poulenc Chemicals Ltd.

*Past research worker:* Tahir H. Shah

*Current research worker:* Roger D. Viney

The initial research project in this area focused on correlations between emulsion polymerisation process-conditions, and the molecular structure and bulk properties of the n-butyl acrylate based polymers formed.

The present research project is exploring the potential, as pressure-sensitive adhesives, of latexes with structured particles. Most of the work is concerned with latexes comprising



two-layer particles that have rigid crosslinked PMMA cores and outer layers of poly[(n-butyl acrylate)-co-(acrylic acid)]. A range of such latexes have been prepared, each having an overall particle diameter of 300 nm, but with differences in the diameter of the PMMA core (0-250 nm). The diameter of the PMMA core has a strong effect on the peel adhesion and the shear resistance of coatings prepared from the latexes. These effects are being compared to those for latexes with particles in which there is a graduated radial composition change and to those for simple blends of "hard" and "soft" latexes.

### *Experimental and Theoretical Studies of Chain Transfer to Polymer and Crosslinking*

*Sponsors:* Science & Engineering Research Council, ICI Acrylics, Rhone-Poulenc Chemicals Ltd.

*Collaborator:* Dr. Frank Heatley

*Past research workers:* John McDonald, Tahir H. Shah

*Current research workers:* Maria M. Tellez-Rosas, Roger D. Viney

By combining kinetics analysis, molar mass distribution measurements and determinations of copolymer fine-structure using FT-NMR, subtle correlations between the synthesis, structure and properties of acrylic emulsion polymers have been established. The key role of chain transfer to polymer in the evolution of molar mass distribution with reaction time has been revealed. Further experimental and theoretical studies of branching and crosslinking in acrylic polymerisations are planned.

Work on the chemistry of polymerisation of allyl methacrylate (ALMA) has been carried out in support of the research into toughening brittle polymers. This work has so far focused on two areas: (i) experimental studies, employing FT-NMR to probe polymer fine-structure; and (ii) derivation of theoretical models to simulate ALMA polymerisation. The results have clearly shown how the contributions from the allylic and methacrylic C=C bonds change with overall C=C bond conversion and have revealed that cyclopolymerisation is insignificant. The work is at present being extended to investigate copolymerisations involving ALMA.

### *Phase Behaviour of Aqueous Poly(vinyl alcohol) Solutions in Relation to Coacervation-Coating of Microemulsion Oil Droplets*

*Sponsors:* Science & Engineering Research Council, Unilever plc

*Collaborator:* Professor Robert F.T. Stepto

*Research worker:* Kevin Frobisher

This project has been concerned with the coacervation-coating of oil-in-water microemulsion droplets by poly(vinyl alcohol), with the overall objective of studying slow release of encapsulated chemicals, such as perfumes. As part of the work, microemulsions with droplet diameters in the range 10-20 nm have been prepared that are stable with aqueous phase concentrations of sodium chloride in the range 80-100 g dm<sup>-3</sup> and that show only a small dependence of droplet diameter upon temperature in the range 23-30 °C.

In order to establish conditions for controlled coating of the microemulsion droplets, the phase separation behaviour of aqueous poly(vinyl alcohol) solutions has been characterised in relation to: percentage hydrolysis, molar mass, sodium chloride concentration and temperature. The lower critical solution temperatures for poly(vinyl alcohol) samples of 12% acetate content have been accurately correlated with molar mass and sodium chloride concentration using the Flory-Huggins equation, modified to take account of the reduction in chain expansion arising from screening by salt of long-range interactions between dipoles present in the polymer chains.

*Publications related to Polymer Colloids (September 1992 - March 1993):*

1. "Correlation of the Extent of Chain Transfer to Polymer with Reaction Conditions for Emulsion Polymerisation of n-Butyl Acrylate", P.A. Lovell, T.H. Shah and F. Heatley, *American Chemical Society Symposium Series*, 492, 188-202 (1992)
2. "Structure-Property Relationships in the Toughening of Poly(methyl methacrylate) by Sub-Micron Size, Multiple-Layer Particles", P.A. Lovell, J. McDonald, D.E.J. Saunders, M.N. Sherratt and R.J. Young, *Materials Research Society Symposium Proceedings*, 274, 17-23 (1992)
3. "NMR Studies of the Polymerisation of Allyl Groups in Monomers and Polymers", F. Heatley, P.A. Lovell and J. McDonald, *European Polymer Journal*, 29, 255-268 (1993)
4. "Studies of Rubber-Toughened Poly(methyl methacrylate): Part 1. Preparation and Thermal Properties of Blends of Poly(methyl methacrylate) with Multiple-Layer Toughening Particles", P.A. Lovell, J. McDonald, D.E.J. Saunders and R.J. Young, *Polymer*, 34, 61-69 (1993)

## CONTRIBUTION TO POLYMER COLLOID GROUP NEWSLETTER

From Laboratoire de Chimie et des Procédés de Polymérisation  
(L CPP-CNRS)-Solaize and UMR/CNRS-bioMérieux-Lyon- FRANCE  
(submitted by C. Pichot)

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### **EMULSION POLYMERIZATION IN THE PRESENCE OF NON IONIC SURFACE ACTIVE MONOMERS. A. Fillet, J. Gullot, A. Guyot. (L CPP)**

The behaviour of polymerizable surfactants in emulsion polymerization is being studied. These products have a vinyl polymerizable function, an hydrophobic part (6 or 12 alkyl chains) and an hydrophilic one (24,35 or 42 polyethylene oxide chains). At first, purified products have been characterized (CMC, cloud point...). Then emulsion copolymerization with these monomers are currently studied in batch. Three different comonomers have been tried : styrene, butyl acrylate and methyl methacrylate, with a nonionic initiator. Stable latexes are obtained, with a particle size around 300 nm. As a function of the monomer nature, the stability against salt and freeze/thaw cycles is more or less satisfying but excellent with styrene and styrene/butyle acrylate. The kinetics are also being studied; in each case a fast homopolymerization of surfactants was observed at the beginning of the reaction. This could, probably, explain the important production of water soluble oligomers or polymers

### **EMULSION POLYMERIZATION IN THE PRESENCE OF A NON IONIC SURFACE ACTIVE INITIATOR. F. Vidal, J. Gullot, A. Guyot. (L CPP)**

An initiator was synthesized: the diester of 4,4' azobis (4 cyanopentanoic acid) and polyethylene glycol methyl ether (2000). The diester was prepared according to the method of J.M.H. KUSTER (Laboratory of Polymer Technology and Chemistry, A. GERMAN). This initiator was found to initiate the emulsion polymerization of styrene and make stable latex with a solid content around 10%. Particle size ranges around 340 nm with a narrow particle size distribution. Stability is good after three centrifugations. Steric stabilisation was controlled by determination of the critical flocculation concentration. No flocculation occurs with a water solution at 0,33 mol/l of sulfate magnesium at room temperature. In these conditions, the critical flocculation temperature is about 38°C.

### **FUNCTIONALIZED NANO PARTICLES OF SILICA ENCAPSULATED IN LATEX PARTICLES. REINFORCED FILMS FROM THE LATEXES. A. Guyot, Ph. Esplard and E. Bourgeat-Lami (L CPP)**

Nucleation of emulsion polymerization onto nanosized silica particles is carried out. Hydrophilic Ludox silica from Du Pont with an average particle diameter of 22 nm and trimethoxysilylpropylmethacrylate (MPS) grafted Degussa silica are involved in this emulsion polymerization leading to the formation of polymer-encapsulated silica particles. Concerning the MPS functionalized silica, it appears that the MPS grafting ratio influences its aqueous dispersion. Particles of 37 nm are obtained in water for a MPS surface coverage of 90% of the silanols which is close to the maximum

coverage: This dispersion step is one of the determining factors for reaching silica encapsulation.

Nucleation of emulsion polymerization on these silica particles is successful thanks to the adsorption of nonionic emulsifier under the form of admicelles. The critical admicelle concentration being lower than the critical micellar concentration, no latex particle nucleates beside silica. It is also required to choose the appropriate emulsifier for a given monomer: for example a high HLB emulsifier is necessary for water soluble monomers whereas low HLB emulsifier is required for hydrophobic monomers. When Ludox silica is involved, an adsorbed polymer layer can be extracted. In the case of MPS-grafted Degussa silica, an adsorbed polymer layer is first extracted in addition of which a chemically bounded polymer is isolated.

Films obtained by coalescence of the encapsulating latexes are fully transparent. Some aggregates can be detected by SAXS in the films prepared from encapsulated Ludox silica. The dispersion of MPS functionalized silica is better. In addition, the mechanical properties of the latter films are quite different being close to that of reinforced elastomers instead of that of reinforced plastics. A model explaining these behaviours will be presented.

#### **MODELLING AND SIMULATION OF GRAFTING ONTO FUNCTIONALIZED SILICA- INVESTIGATION OF MOLECULAR WEIGHT DISTRIBUTION - J. Guillet, D. Leroux (LCP)**

The objective of this paper is the modelling of the molecular weight distribution (MWD) and the polydispersity index (IP) of polystyrene grafted on porous silica beads prefunctionalized by a thiosilane molecule. This grafting occurs by a transfer reaction to the fixed mercaptogroups. We have especially analysed the MWD of the grafted and ungrafted polymer by the GPC technique. A good agreement between the experimental GPC diagrams and those calculated from the reaction rate constants is obtained with the following hypothesis:

1) the medium is a two phases system constituted of an interparticular phase and a porous intraparticular phase with a high local mercaptogroups concentration in the pores; 2) a higher transfer efficiency of the transfer agent in the pores; 3) a lower termination rate in the pores, which results in a higher rate of polymerisation than in the interparticular phase. Those assumptions have been done to account for the polymerisation medium heterogeneity.

(to be published in Die Makromol. Chem., Theory and Simulation)

#### **CONTROL OF MOLECULAR WEIGHT DISTRIBUTION AND GLASS TRANSITION TEMPERATURE IN SOLUTION COPOLYMERIZATION - J. Guillet, C. Graillat (LCP)**

Experimental and theoretical works are in progress to control molecular weight distribution and glass transition phenomenon in vinyl acetate copolymers and polystyrene homopolymers. Parameters as copolymerization process, temperature, rate of reagents addition (monomers, initiators, transfer agents, . . .) on MWD and Tg's are investigated.

Modelling and computer simulation programmes have been developed and revealed a powerful tool to optimize and control such solution polymerizations. In particular, the accurate simulation of Size Exclusion Chromatograms (GPC) in correlation with the kinetics and the glass transition behaviour is interesting for both practical and theoretical studies.

## ADSORPTION OF OLIGONUCLEOTIDES ONTO LATEX PARTICLES (A. Elaissari, C. Pichot, Ph. Cros - UMR CNRS-bioMérieux)

As a part of a systematic investigation on the adsorption behaviour of nucleic probes onto polymer interfaces, a preliminary study has been performed on the adsorption of various well-defined oligonucleotides in the presence of polystyrene-based particles. Due to the presence of surface charges onto the particles and the polyelectrolyte character of the particles, it was observed that the electrostatic forces play a major role in the adsorption process. For instance, with negatively-charged latex adsorption was slight with a poor affinity; on the contrary with cationic-charged latex, strong adsorption was clearly evidenced together with a high affinity. A decrease in the adsorption was observed upon raising the pH since above the pKa of quaternary ammonium groups, anionic charges are originated. The contribution of hydrophilic forces was estimated using the various adsorption isotherms at various pH and extrapolated to  $\zeta = 0$ . More works is currently investigated in order to study the influence of ionic strength and to get more information on the conformation state of these oligonucleotides under adsorbed form.

## SYNTHESIS AND CHARACTERIZATION OF FUNCTIONAL MONOMERS AND STUDIES OF THEIR POLYMERIZATION ONTO LATEX PARTICLES ( UMR CNRS/BioMérieux)

1. Styrene-terminated polyvinylalcohol macromonomers :  
II - Free radical (co)polymerisation studies and application to the functionalisation of latex particles B. CHARLEUX, Ch. PICHOT, MF. LLAURO, in press, Polymer

### ABSTRACT

Kinetics of radical-initiated solution homopolymerization of a styrene-terminated polyvinylalcohol (PVA) macromonomer with  $DP_n = 7-9$  (A), and copolymerization with styrene (S) have been investigated at 60°C in deuterated DMSO solution using AIBN as initiator and  $^1H$  NMR as analytical technique. It was found that the macromonomer exhibits a slighter reactivity than styrene or that of a model monomer with  $n=0$ , which is confirmed by copolymerization with styrene, ( $r_a = 0.9 \pm 0.1$  and  $r_s = 1.3 \pm 0.1$ ). Such hydrophilic macromonomer was then copolymerized onto seed polystyrene latex particles, by a shot growth process, the more efficient surface yield being ensured with using polar comonomers like methyl methacrylate and acrylonitrile.

2. Preparation and characterisazion of polystyrene latexes bearing disaccharide surface groups. MT. CHARREYRE, P. BOULLANGER, Th. DELAIR, B. MANDRAND, Ch. PICHOT. In press, Colloid Polymer Sci.

## ABSTRACT

Emulsifier - free polystyrene latexes covered with disaccharide species have been prepared by a seed (co)polymerisation method in the presence of an hexylmethacrylate-terminated oligosaccharide 6-(2-methylpropenyloxy)hexyl  $\beta$ -D-cellobioside (CHMA). First, the surface activity of this macromonomer was studied using ring and drop volume methods, respectively. Then, its polymerization onto polystyrene seed latexes was carried out upon varying experimental conditions : particle size, solid contents of the seed and type of comonomer. Analysis of the macromonomer distribution between aqueous and polymer phases suggested that an optimal surface yield can be reached upon increasing the overall surface area of particle and or using methylmethacrylate as comonomer. Finally the presence of the disaccharide residues at the particle surface was shown either directly using NMR and ESCA analysis or undirectly through the comparison of the electrophoretic mobility behavior of the seed polystyrene and functionalized latexes.

3. Synthesis of surface active monomers and application to the preparation of bioactive latex particles. Ch. PICHOT, M.T. CHARREYRE, J. REVILLA, Th. DELAIR, P. BOULLANGER, B. GALLOT. Abstract Paper Symposium "Polymeric surface active materials" ACS Meeting, Denver, April 1993.

Surface active (macro)monomers bearing hydrophilic moities have been designed with a view to produce polystyrene based latex particles with biocompatible spacer arms. Two main families of monomers have been prepared : the first one, a hexylmethacrylate-terminated disaccharide was obtained according to a five-step procedure starting from cellobiose ; the second one, a styrene-terminated lipopeptide was synthesized from vinylbenzylamine and N-protected aminoacid compounds. At first, the surface activity of the monomers was examined as well as their kinetic behavior in radical-initiated solution homo and copolymerization. Then, they were (co)polymerized, using a shot-growth process, onto polystyrene seed latexes, upon changing the experimental conditions so as to optimize the surface functionalization yield. Finally, the location of the hydrophilic moities was carefully investigated, either directly through their colloidal and surface properties or undirectly from the interactions of the polymer particles with biological molecules.

### Recent thesis:

- . M.T. CHARREYRE : "Synthesis of functionalised saccharide monomers-radical-initiated copolymerisation studies in solution and covalent fixation onto latex particles. Oct. 92, Univ. Lyon I.
- . M. LEPAIS : "Preparation of acrylic acid quaternarized dimethylaminoethyl acrylate copolymers in solution and in inverse emulsion. Characterisation of the polymers and hydrogels. Dec. 92, Univ. Lyon I





NEWLETTER CONTRIBUTION FROM THE UNIVERSITY OF AKRON  
submitted by H.M. Cheung

Our recent work has involved using acrylamide modified anionic and cationic polymerizable surfactants based on  $C_{12}$  hydrophobic moieties. The two projects have focused on the formation of microlatex particles and porous polymeric solids. The anionic surfactant is the salt of acrylamidostearate with the acrylamide moiety in the tail. The cationic surfactant is a quarternary ammonium halide with the acrylamide moiety in the head. Our future plans are to synthesize a corresponding nonionic polymerizable surfactant.

POLYMERIC MICROLATICES FORMED USING POLYMERIZABLE SURFACTANTS  
W.R. Palani Raj & H.M. Cheung

The use of both anionic and cationic polymerizable surfactants to form microlatices which are free of monomeric surfactants was been under study recently here. Polymerization of emulsions formed using the polymerizable surfactants resulted in the incorporation of the surfactant in the latex particles. The presence of free monomeric surfactant after polymerization was thus avoided. In addition, functionalization of the latex particles could be achieved by using suitable polymerizable surfactants. The effects of the polymerizable surfactant concentration on the stability, particle size, and functionalization of the microlatex was evaluated and the polymerization kinetics were investigated.

POROUS POLYMERIC SOLIDS BY HETEROPHASE POLYMERIZATION USING  
POLYMERIZABLE SURFACTANTS W.R. Palani Raj & H.M. Cheung

The formation of porous polymeric solids by polymerizing heterophase systems having a bicontinuous structure stabilized by polymerizable surfactants has been investigated. The porous morphology of the polymeric solid obtained was found to be significantly dependent on the structure of the heterophase precursor. Control of the pore morphology was achieved by varying the composition of the precursor and hence its structure. The heterophase systems were characterized by phase behavior studies, conductivity, viscosity and light scattering. The morphology of the polymeric solids was studied with scanning electron microscopy and thermal techniques. The results indicate the potential advantages in using this technique to form porous polymeric solids.



# Characterization of the interphase in the poly(butyl acrylate) (PBUA) - poly(methyl methacrylate) (PMMA) core-shell latexes by high resolution solid state NMR

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## 1. INTRODUCTION

Core-shell latexes have interesting applications possibilities as impact modifiers in polymer blends and as processing aids (1, 2).

For these types of additives, the interphase between the different layers of a core-shell latex appeared to have a dramatic influence on the final properties.

Recently we have shown that the combination of solid state NMR and DSC technics are a powerful tool to investigate the interphase of core-shell latexes having a core of polybutadiene (PBut) and a shell of poly(methyl methacrylate) (PMMA), polystyrene (PS) or a styrene-acrylonitrile copolymer (PSAN) (3-7).

We extended our study to acrylic/acrylic systems like poly(butyl acrylate) (PBUA)-poly(methyl methacrylate) (PMMA) core-shell latexes as well as to mechanical blends of PBUA and PMMA homopolymer latexes.

The characteristics of the interphase in the PBUA-PMMA core-shell latexes have been examined by magic-angle cross-polarization solid state NMR technique .

The evolution of the spectroscopic characteristic ( $T_{1\rho}(H)$  relaxation time in the rotating frame) of polymers forming the core and the shell in the core-shell, led to interesting informations about the molecular motions and the interphase of latex particles.

## 2. EXPERIMENTAL

### 2.1. Synthesis and characterization of latexes by classical methods

PBUA latex stabilized by anionic surfactant (SDS), as a starting material, has been prepared by a batch process at 60°C. It has an average particle size of 85 nm and a solid content of 17 weight%. The latex of PMMA homopolymer, with an average particle size of 77 nm, was also obtained by emulsion polymerization in a batch process at 60°C. Different samples of core-shell latexes have been prepared either by a batch or by a "semi-continuous" emulsion polymerization at 60°C by adding MMA monomer to the seed latex at an addition rate of 2.9 ml/h which is lower than the polymerization rate of MMA monomer under the present reaction condition. In case of the batch technique, the polymerization was started immediately after the addition of

MMA. The concentration of the initiator,  $K_2S_2O_8$ , was in all cases 0.40 weight% (with respect to PABu solid content).

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

The average size of latex particles ( $D_w$ ), determined by photon correlation spectroscopy (Coulter N4) and the particle number ( $N_p$ ) are given in table 1.

PMMA content (in weight%)		15	30	40	57	75
<u>semi-continuous</u>	Dw (nm)	87±2	93±2	95±2	99±1	102±2
	$N_p \cdot 10^{-18}$	1.22±0.08	1.35±0.10	1.28±0.09	2.09±0.04	2.07±0.14
<u>batch</u>	Dw (nm)	88±1	90±1	96±1	101±2	106±1
	$N_p \cdot 10^{-18}$	1.28±0.02	1.43±0.06	1.35±0.07	1.85±0.09	1.80±0.06

PBuA seed latex:  $D_w = 85 \pm 1$  nm ;  $N_p = (1.15 \pm 0.04) 10^{18}$

**Table 1:** Particle size ( $D_w$ ) and particle number in one litre of core-shell latexes with various compositions and prepared by the semi-continuous and by the batch process.

## 2.2 NMR measurements

Solid-state  $^{13}C$ -NMR experiments using cross-polarization, dipolar decoupling, and magic angle spinning (CP/DD/MAS) were run on the samples with a  $^{13}C$  frequency of 75.47 MHz on a Bruker MSL300 spectrometer. The cross-polarization experiments (27-29) with variable contact times were used to determine  $T_{1\rho}(H)$ . The relaxation time of the proton spin is observed from its effect on the carbon nucleus to which the proton is bonded. Magnetic field strengths of 54KHz and 50 KHz were used for the matched spin-lock cross-polarization transfers, respectively for core-shell latexes and the mechanical blends of latexes. Contact times from 2 ms to 24 ms were used with delays of 2.5 s between scans (recycle time). About 80 mg of powder were packed in 4 mm zirconia spinners with Kelf-F caps and were spun at the magic angle at 6 KHz. Depending on the composition, 200-800 scans were necessary per contact time value for a satisfactory signal-to-noise ratio. All spectra were obtained at a temperature of 20°C.

## 3. RESULTS AND DISCUSSION

### 3.1 CORE-SHELL LATEX : Influence of the core-shell latex composition and synthesis process on the relaxation time $T_{1\rho}(H)$

The  $T_{1\rho}(H)$  relaxation time values of PMMA in the PBuA-PMMA core-shell latexes prepared by the batch and semi-continuous process are listed in table 2. Figure 1 shows the variation of  $T_{1\rho}(H)$  as a function of the PMMA content in the core-shell latex. The evolution of the weight fraction of the interfacial PMMA (with respect to the PBuA solid content) is shown in figure 2

as a function of the PMMA content in the core-shell latex. The experimental details of the NMR measurements and the calculation methods have been given previously (3, 6).

PMMA content (in weight%)		15	30	40	57	75
<u>semi-continuous</u>	methoxy carbon C5	6.5	9.5	10.2	11.4	12.8
	quaternary carbon C6	6.7	10.2	10.4	11.0	13.3
<u>batch</u>	methoxy carbon C5	7.3	11.4	12.4	14.7	15.6
	quaternary carbon C6	7.5	11.2	12.9	14.9	15.6

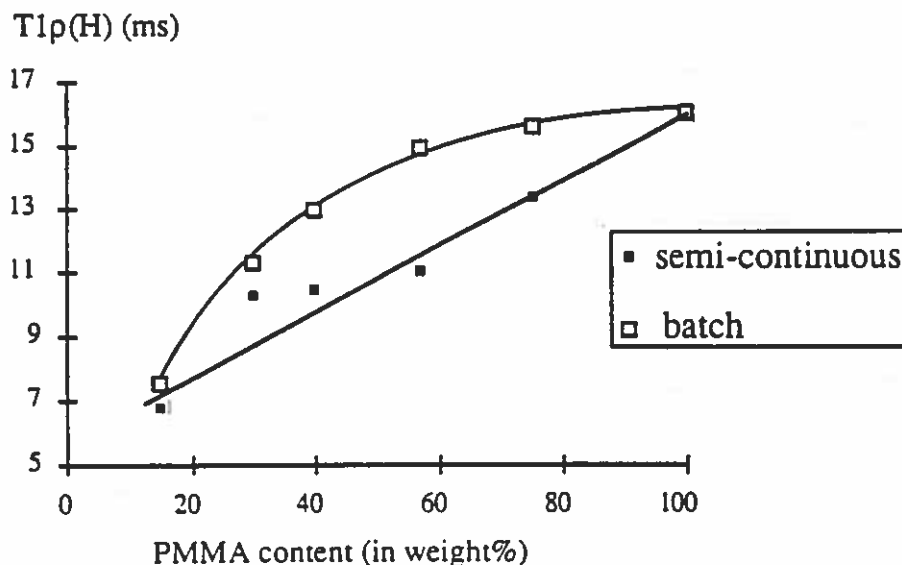
$T_{1\rho}(H)$  of homopolymer PMMA:

methoxy carbon C5 : 15.9 ms; quaternary carbon C6 : 16.0 ms

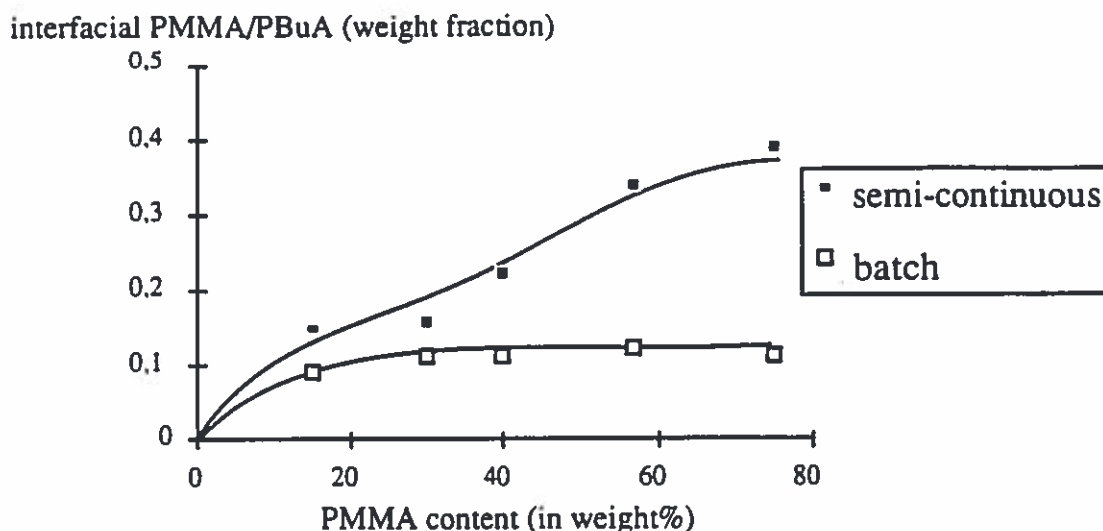
**Table 2:** Relaxation time of PMMA in the core-shell latexes with various compositions and prepared by the semi-continuous and by the batch process.

As we have previously shown with the PBut-PMMA system, the relaxation time values of PMMA in the PBuA-PMMA core-shell latexes are perturbed with respect to the homopolymer PMMA values because of the existence of an interphase. These relaxation time values are also lower than the one of the pure PMMA indicating an increasing mobility of PMMA in the core-shell latex. In fact the PMMA is plasticized in contact with PBuA phase.

It is interesting to note that the relaxation time values of the PMMA in the core-shell latexes prepared by the semi-continuous process are lower than the values of samples synthesized with the batch method. This situation is due to the formation of a higher amount of interphase in the samples obtained by the semi-continuous method as we can see in the figure 2. The weight fraction of the interfacial PMMA increases with the increase of the PMMA content in the core-shell latex and becomes constant at a given PMMA content which is 57% in the semi-continuous process and 30% in the batch method.



**Figure 1:** Relaxation time of PMMA in the core-shell latexes prepared by the semi-continuous and by batch process versus the PMMA content.



**Figure 2:** weight fraction of the interfacial PMMA in the core-shell latexes prepared by the semi-continuous and by batch process versus the PMMA content.

### **3.2 BLENDS OF LATEX : influence of the preparation temperature and the composition**

The blend of latexes is prepared by mixing the PMMA latex (Particle size 77 nm) with the PBuA latex (particle size 85 nm). At 65°C the two latexes are in contact for 4 hours before their coagulation with a concentrated solution of sodium chloride at room temperature. The latex blend prepared at 20°C is coagulated immediately after mixing.

The relaxation time of PMMA of the latex blends have been determined and the values are listed in table 3.

PMMA content in weight%	30	40	57
preparation temperature 20°C	11.0	12.2	12.4
preparation temperature 65°C	10.0	10.3	10.8

Homopolymer PMMA T1ρ(H) value (carbon C5) : 13.9 ms \*

**Table 3 \* :** Relaxation time of PMMA in the blends of PBuA and PMMA homopolymer latexes prepared at 20°C and 65°C.

\* These values are not determined with the same experimental NMR conditions as those of the table 2. In fact T1ρ(H) value depends on the magnetic field as previously shown (3).

In contrast to the PBut-PMMA system (3, 4), the relaxation time values of PMMA in a PBuA-PMMA blend of latexes are perturbed with respect to

pure PMMA. This perturbation increases when the two latexes are mixed at the temperature of 65°C.

These results lead to the conclusion that there might be a partial miscibility between these two polymers due to a possible exchange between the short chains of PMMA particles and those of the PBuA particles.

#### 4. CONCLUSION

This study confirms that solid state NMR is a powerful method to investigate the structure of a core-shell latex particle and that PBuA-PMMA systems have a similar behavior concerning the interphase as previously shown for PBut-PMMA.

Concerning the interaction in the blends of different latexes, further studies might be useful in order to establish the mechanism and the kinetics of this phenomena.

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Contribution for the Polymer Colloids Group Newsletter

Enclosed are short contributions for the upcoming newsletter. I have enclosed the abstract of a paper comparing experiment with theory from the December issue of *Langmuir*. Also, I have enclosed the abstract and reference information to a chapter on electrophoretic fingerprinting prepared for Ted Provder's book.

From April 10 through May 8th of this year I plan to be in Japan as a Visiting Lecturer where I will spend three weeks at the Science University of Tokyo hosted by Prof. Ueno and one week at Kyoto University hosted by Prof. Ise.

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*Langmuir* 1991, 7, 2970-2980

## Electrophoretic Fingerprinting of a Single Acid Site Polymer Colloid Latex

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The electrophoretic fingerprint of a system of colloidal particles is the contour diagram of the measured mobility as a function of the measured pH and the measured  $p\lambda$  (logarithm of the specific conductance in S/m). In earlier work the electrophoretic fingerprint was shown to be a characteristic property of a system of charged colloidal particles. In the present work, the electrophoretic fingerprint of a carboxylic polystyrene latex is compared with theoretical calculations in order to explore the nature of the surface electrochemical properties and the structure of the double layer. Theoretical calculations include fingerprints (pH- $p\lambda$  contour plots) of the surface potential, the zeta potential, and the electrophoretic mobility. An explanation of the anomalous maximum in the zeta potential is offered and the sensitivity of electrokinetic properties to electrophoretic relaxation, shear plane expansion, and conductance within the shear plane is quantitatively investigated for the model carboxylic acid polystyrene latex.

# Particle Size Distribution II

## Assessment and Characterization

Theodore Provder, EDITOR

*The Glidden Company*

*(Member of ICI Paints)*

Developed from a symposium sponsored  
by the Division of Polymeric Materials:  
Science and Engineering  
at the 199th National Meeting  
of the American Chemical Society,  
Boston, Massachusetts,  
April 22-27, 1990

American Chemical Society, Washington, DC 1991

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### Chapter 21

## Electrophoretic Fingerprinting for Surface Characterization of Colloidal Particles

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The classical characterization of the surface chemistry of colloidal particles is by the zeta potential, a calculated quantity derived from measurements of the electrophoretic mobility. We show that the average mobility is a more fundamental and characteristic property and that the average mobility may be represented as a function of the characteristic state variables pH and  $p\lambda$  (the negative log of the specific conductance) in the form of an electrophoretic fingerprint (EF). The EF is therefore a contour diagram of mobility in pH- $p\lambda$  space. A variety of EFs are discussed in order to illustrate the use of the EF as a sensitive probe of the surface electrochemical state and a measure of colloid stability. The fingerprinting approach is extended to hydrodynamic fingerprinting (HF), a representation of the hydrodynamic particle size as a function of pH and  $p\lambda$ .

pp. 326-336



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**Recent Publications and Presentations:**

K.A. Landman and W.B. Russel, "Filtration at large pressures for strongly flocculated suspensions" *Phys. Fluids A* 5 550-60 (1993).

M. C. Grant and W.B. Russel, "Volume-fraction dependence of elastic moduli and transition temperatures for colloidal silica gels" *Phys. Rev. E* 47 xx-xx (1993).

R.P. Lionberger and W.B. Russel, "Dynamics of concentrated dispersions: Tests of many-body closures" *64th Annual Meeting of the Society of Rheology*, Santa Barbara, California, February 1993.

R.P. Lionberger and W.B. Russel, "Nonequilibrium statistical mechanics: Tests of new closures" *SDLS II*, Fehmarn, Germany, March 1993.

## Adsorption of diblock copolymer on silica in a non-selective solvent

**Ramesh Hariharan and William B. Russel**

Our's is an experimental study to understand the physics of copolymer adsorption using low polydispersity diblock copolymer of dimethyl amino ethyl methacrylate (DMAEM) and butyl methyl acrylate, adsorbed on fairly monodisperse silica in isopropanol. The solvent is non-selective in the sense that it dissolves both blocks effectively, although the DMAEM block shows specific affinity for the surface. The variation of the hydrodynamic thickness and the adsorbed amount with variations in block sizes at the plateau of the adsorption isotherm was studied for the same system by Wu et al. for a wide range of block asymmetries. Our research extends their study by studying the adsorption over a range of block copolymer bulk concentrations, thus covering various regions of the adsorption isotherm. Primarily variations in hydrodynamic size, the adsorbed amounts and the pair interactions in the system will be examined. Dynamic light scattering can be used to measure the hydrodynamic layer thickness whereas static light scattering can be used to probe the interactions. Depletion method (using infrared spectroscopy to measure polymer concentrations) or thermal gravimetry is used to get the adsorbed amounts on the silica surface. Light scattering has not been used earlier to probe interactions for adsorbed diblock copolymers, although extensive work using the surface force apparatus has been done to study interparticle interaction potential. The study of interactions in the various regions of the sorption isotherm helps better understand the adsorption process (especially the existence of a plateau). Also results from light scattering can be compared against interactions studied on an analogous system using the surface force apparatus.

# NONEQUILIBRIUM STATISTICAL MECHANICS: TESTS OF NEW CLOSURES

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Our objective is a quantitative theory for the dynamic properties of concentrated dispersions on the diffusional time scale. A Smoluchoski description of the nonequilibrium microstructure suffices with proper accounting for many-body couplings. Integration of the conservation equation to the pair leaves an integral containing the unknown three-particle distribution function, thus necessitating an additional equation to completely specify the pair distribution function. Nonequilibrium closures, based on the PY and HNC analogues at equilibrium, approximate the many-body forces in terms of a direct correlation force. In this phase of the work we neglect hydrodynamic interactions.

Our computational algorithm based on Fast Fourier Transforms solves the Smoluchoski equation and the integral equation relating the direct correlation to the pair distribution function and the pair potential. We then calculate the low-shear limiting viscosity and long-time self diffusion coefficient as a function of volume fraction for hard sphere and Yukawa potentials. The nonequilibrium closures also yield the three-body terms in the virial expansions, i.e. the  $O(\phi^3)$  term for the viscosity and the  $O(\phi^2)$  term for the self diffusion coefficient. The predictions will be compared with existing results from simulations.

Contribution to International Polymer Colloids Group  
Fall, 1992

Polymer Research Group  
University of New Hampshire

\* Recent papers published

"Conversion Dependent Morphology Predictions for Composite Emulsion Polymers. 1. Synthetic Latices", C.L. Winzor and D.C. Sundberg, *Polymer*, 33, 3797 (1992).

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

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

\* Emulsion Polymerization Kinetics for Two Component Latex Particles

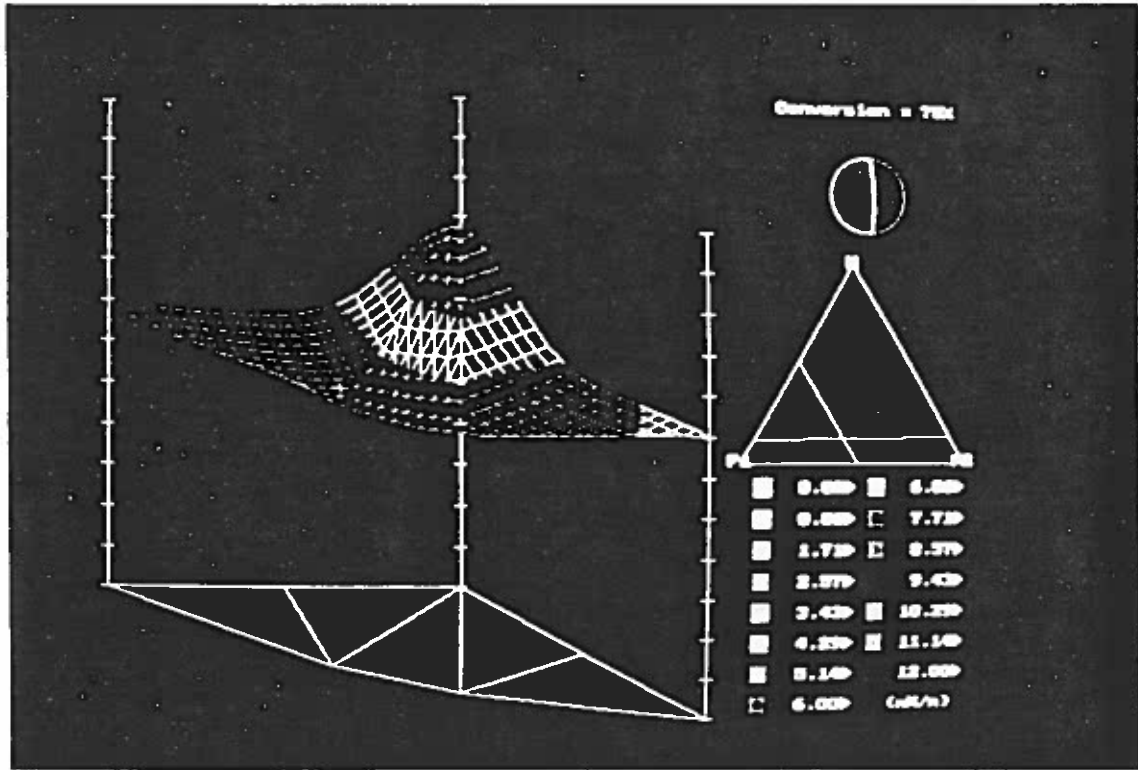
Work has continued on the enhancement of polymerization kinetic models for core-shell, inverted core-shell, hemispherical (or half moon-like), and occluded latex particles. The reaction rates within latex particles are predicted to be significantly different for the various particle morphologies, especially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

Contribution to International Polymer Colloids Group (Continued)

\* Software Development for Conversion Dependent Latex Morphology Predictions

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

D.C. Sundberg



Contribution to the 1993 Spring  
IPCG Newsletter

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Recent Publications:

"Conversion Dependent Morphology Predictions for Composite Emulsion Polymers: 2. Artificial Lattices," *Polymer*, **33**, 4269 (1992), C.L. Winzor and D.C. Sundberg.

"Morphology Development for Three-Component Emulsion Polymers: Theory and Experiment," *J. Appld. Poly. Sci.*, **47**, 1277 (1993), E.J. Sundberg and D.C. Sundberg.

Current Research:

1). Surface Science Instrumentation

An interfacial tension meter (ITM) has been developed which allows for surface and interfacial tension measurements based on the pendant drop method. The drop formed by using a positive displacement syringe inserted into a cuvette held within an environmental chamber capable of maintaining temperatures from subambient to 150°C. The drop is backlighted with an homogeneous, narrow wavelength, parallel light beam. The drop image is projected onto a monitor screen by means of a high resolution camera and the signal is digitalized and stored in a PC. The interfacial profile of the drop is obtained by using robust shape comparison and the shape factor is computed. With proper calibration and precise density differences between the drop and its surrounding medium, the interfacial or surface tension is calculated. The experimental reproducibility of the instrument is better than its theoretical precision (cummulative errors), the latter being 1%. A modification of the environmental chamber and the use of different software allows for the measurement of contact angles between liquid and solid. The accuracy of contact angle measurement is better than 0.5°. This instrument is currently being used to study latex surface tensions, polymer/water interfacial tensions, and polymer/polymer interfacial tensions.

2). Polymer (plus monomer)/Water (plus surfactant) Interfacial Tensions

The Prigogine - Marechal theory (*J. Colloid. Sci.*, **7**, 122 (1952)) has been modified to take into account the fact that the interaction parameter between polymer and solvent (monomer) is not constant with concentration, but more likely to possess a reasonably strong dependence. Noting that in many instances there is likely to be a

significant interfacial excess of solvent (monomer), a new model has been written which yields significant improvements in the predictions of interfacial tensions of polymer solutions. The model has been extensively compared with experimental data obtained on the ITM (see above) for pairs of polymers and solvents (monomers) of greatly varying polarity and their interfacial tensions against aqueous surfactant solutions. Good agreement has been found over the complete range of polymer - solvent (monomer) concentration.

### 3). Effect of Initiator End Groups on Latex Particle Interfacial Tension

By use of the ITM (see above) we have been able to determine the relative effectiveness of  $\text{SO}_4^-$  end groups and sodium dodecyl sulfate (SDS) on the interfacial tension between polystyrene and water. By measuring the adsorption of SDS on latex particles of different charge densities, the SDS was found to occupy an area equivalent to 3.5 times the area of an  $\text{SO}_4^-$  end groups at the surface of a latex particle. The chemical structure and spatial arrangement of an  $\text{SO}_4^-$  coming from an SDS molecule or from a polymer end group are similar enough to consider that their effect on lowering the interfacial tension is equivalent. It is thus possible to obtain the effect of the polymer end group on the interfacial tension by calculating the number of  $\text{SO}_4^-$  groups at the interface, whatever their origin.

### 4). Importance of Polymer End Groups in Determining Latex Particle Morphology

As described in (3) above,  $\text{SO}_4^-$  end groups coming from the initiator can significantly impact the interfacial tension between a polymer and the aqueous phase. Using potassium persulfate (KS) or azobisisobutyronitrile (AIBN) as alternative initiators would thus be expected to alter the interfacial tensions at the latex surface. A series of seed latices was made from polystyrene, poly(n-butyl acrylate) and PMMA using KS and AIBN separately. Second stage polymerizations of the above monomers were carried out using KS or AIBN to create a matrix of composite latex particles. The morphologies were measured by TEM and correlated well with the effect of the initiator type. Structures ranged from core-shell to inverted core-shell, including hemispheres. It is clear that the effect of the initiator end group on interfacial tension needs to be considered along with that of the surfactant in anticipating the ultimate morphology of the latex particle.

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