IPCG

INTERNATIONAL POLYMER COLLOIDS GROUP

JUNE, 1989

VOLUME 20 NUMBER 1

NEWSLETTER

INDEX

CONTRIBUTIONS

FROM THE EDITOR'S DESK

My apologies for a slight delay in assembling this edition of the Newsletter. The University of Sydney has just changed from a 3-term system to a 2-semester system with the result that my work load has been frantic for the past 3 weeks. The delay however has allowed me to incorporate all the late arriving contributions.

Conferences

Past

Please find attached a short report by my colleague Bob Gilbert on three conferences he recently attended. Also attached are the programmes for the Gordon Conference on Polymer Colloids and the Polymer Latex III Conference. An updated Schedule of Meetings is appended as well. Professor Nomura in his contribution reports on the 5th Polymer Microspheres Symposium, Japan, which I had the good fortune to be invited to attend. The excellence and vigour of polymer colloids in Japan was well known to me before my visit but I still marvelled at the breadth and the technological ingenuity that the papers presented at the meeting displayed. The wonderful hospitality that I experienced is never to be forgotten.

Future Conferences

Please find attached the tentative programme for the 1990 Colloid and Surface Science Symposium to be held at Lehigh University, 18-20 June, 1990. This meeting will honour John Vanderhoff.

FAX Numbers

I have attached a list of FAX (telecopier) numbers. There was insufficient response to the BITNET numbers to justify their listing. The response to the request for computer programmes (just 2 replies) was also such as to not justify the matter being taken further.

Change of Address

Please note that Dr. S. Muroi is now Manager, Polymeric and Construction Materials, Japan Research Centre, Grace Japan K.K., 100 Kaneda, Atsugi, Kanagawa 243, JAPAN. Also Dr. K. Takamura has moved to BASF Canada, P.O. Box 3077, 453 Christina St, S. Sarnia, Ontario, CANADA N7T 7Z1.

Next Newsletter

Contributions to be forwarded to me by AIRMAIL by 30 September 1989.

D. H. Napper
Secretary

CONFERENCE REPORT

Three reports on conferences of interest to the Polymer Colloid Group:

The Second International Colloqium on Copolymerizations and Copolymers in Dispersed Media was held in Lyon, April 3-7 1989. This was very successfully organized by Christian Pichot, Jean Guillot and Alain Guyot of CNRS, and followed the first such conference held several years previously. A large number of idustrial and academic scientists from a wide range of countries attended. As well as plenary lectures and contributed papers, the conference featured lively discussion and a seminal "Round Table". Papers preented at the meeting will be published in Makromolekulare Chemie, Macromol. Supp.

A Microsymposium on Radical Polymerization in Heterogeneous Systems was held in Smolenice, Czechoslovakia, April 10-14 1989. This was organized by Jaroslav Barton of the Polymer Institute of the Slovak Academy of Sciences. The quality of the science was superb, and so was the environment: a castle in wooded hills. Scientists from nine countries attended, and the meeting provided an excellent forum for new contacts between researchers from East and West. Papers presented at the conference, as well as a summary of the final discussion session, will be published in Makromolekulare Chemie.

As part of the fourth Rolduc Polymer Meeting (organized by Pieter Lemstra), Ton German of Eindhoven University of Technology organized an extensive programme of papers on emulsion polymerization. The meeting was held on April 24-27 in Rolduc Monastery in the Netherlands. The meeting provided particularly valuable insights into the intergation of fundamental polymer science and technology. Papers will be published in a special volume by Elsevier.

R. G. Gilbert

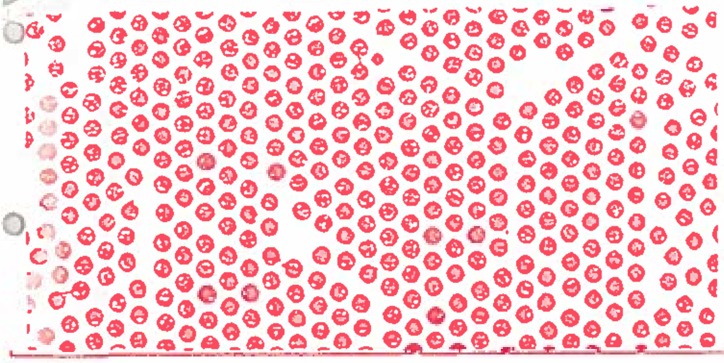
SCHEDULE OF MEETINGS

1989

Meeting/Course	Location	Date(s)	Contact
7th Gordon Conference	Proctor Academy Andover	9-11 July	I. Piirma
Lehigh European Short Course	Davos	21-25 Aug.	M.El-Aasser
ACS National Meeting	Miami Beach	10-15 Sept.	-
3rd Berlin Workshop on Polymer Reaction Engineering	Berlin	27-29 Sept.	-
PAC-CHEM	Hawaii	14-16 Dec.	M.Croucher D.H.Napper

1990

Meeting/Course	Location	Date(s)	Contact
199th ACS National Meeting	Boston	22-27 April	-
8th International Symposium on Surfactants	Gainesville	10-15 June	-
Vanderhoff Symposium (part orf 64th Colloid & Surface Science Symposium)	Lehigh Uni	18-20 June	M.El-Aasser
33rd IUPAC Polymers (Macro 90)	Toronto	8-13 July	T.van de Ven
200th ACS National Meeting	Washington	26-31 Aug.	-
Faraday Discussion 'Colloid Stability'	Bristol	10-12 Sept.	R.H.Ottewill
European Conference on Colloid and Surface Science	Bristol	13-14 Sept.	R.H.Ottewill



IPCG

INTERNATIONAL POLYMER COLLOIDS GROUP
Secretary: D. H. Napper
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University of Sydney
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IPCG Membership FAX (Telecopier) Numbers

*Please note that zeros have been omitted from area codes as required for international faxing. Local faxing may need a 0 (or a 9 in Spain).

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R. E. Uschold	1-302-695-2645
A. Vry	31-30-52-1877
T. G. M. van de Ven	1-514-398-7249
J. A. Waters	*44-753-69-4665

30 June 1989

POLYMER LATEX III - PROVISIONAL PROGRAMME

7 MAR Recd

TUESDAY 27 JUNE 1989

08.30-09.30		**Registration**
09.25		**Opening Remarks** T Pendle (Conference Chairman)
09.30		**Keynote Address** J Vanderhoff (Emulsion Polymers Institute, Lehigh University, USA)
Session 1		
10.15	(1)	**Copolymerization in continuous reactor systems** G W Poehlein, R N Mead, G L Shoaf and D M Lange (Georgia Institute of Technology, USA)
10.45	(2)	**The formation of latex particles in emulsion polymerisation systems** A S Dunn (University of Manchester Institute of Science and Technology, UK)
11.15		**Coffee**
11.35	(3)	**Emulsion polymerisation of butadiene, a kinetic study** P A Weerts, G H J van Doremaele and J L M van der Loos (Technical University Eindhoven, Netherlands)
12.05	(4)	**Synthesis of poly(methyl methacrylate)-graft-poly (oxyethylene) for use as a polymeric surfactant in the emulsion polymerization of methyl methacrylate** G L Jialanella and I Piirma (University of Akron, USA)
12.35		**Lunch**
Session 2		
14.00	(5)	**Evaluation of diphenyl ether disulfonate (dowfax) surfactants in the emulsion copolymerization of polar monomers** V L Dimonie, M S El-Aasser & J W Vanderhoff (Emulsion Polymers Institute, USA) L A Settlemeyer (The Dow Chemical Company, USA)
14.30	(6)	**Characterization of acrylic latexes functionnalized by N-methylol acrylamide** A Guyot, C Bonardi, L Christou, J Guillot and C Pichot (CNRS LMO, France)
15.00	(7)	**Analysis of molecular parameters of the vinyl acetate-u-butylacrylate copolymer latexes** D Lath (Slovak Academy of Sciences, Czechoslovakia)
15.30		**Tea**
15.50	(8)	**Geometrical details of the internal morphology of a polymer colloid particle** O Pekcan, M D Croucher and M A Winnik (Istanbul Technical University, Turkey)
16.20	(9)	**The surface chemical analysis of polymer latex particles using SIMS and XPS** R A P Lynn, R D Short, S S Davis, J Hearn, D Johnson and M C Davies (University of Nottingham, UK)
16.50	(10)	**Latex particle size determination using light scattering and particle chromatography. Evaluation of the methods and their application to on-line measurements** T Kourti, J F MacGregor and A E Hamielec (McMaster Institute for Polymer Production Technology, Canada)
17.20		**Close of Session**
17.30		**Cheese and Wine Reception**

WEDNESDAY 28 JUNE 1989

Session 3		
09.00	(11)	**The effects of ammonium persulphate/sodium metabisulphite redox initiator stoichiometry on molecular weight and colloid stability in a vinylidene chloride-based model latex** D V Keight, J C Padget and C R Towns (ICI Chemicals and Polymers Ltd, UK)
09.30	(12)	**Polymer conformations in the steric layer** D T Wu, C Y Wang and R L Setterquist (E I DuPont de Nemours Company Inc, USA)
10.00	(13)	**Polystyrene latexes obtained with various amphoteric sulfobetaine surfactants: colloidal and rheological properties** C Pichot, C Graillat, B Dumont and A Guyot (CNRS LMO, France)
10.30	(14)	**Correlation between structure of polymer dispersions and their stability and viscosity respectively** D Kranz, M Merkel and G Penners (Bayer AG, Federal Republic of Germany)
11.00		**Coffee**
11.30	(15)	**Electrokinetic properties of polystyrene latices in alcohol-water mixtures** F J de las Nieves, R Hidalgo-Alvarez and F J Rubio-Hernandez (University of Granada, Spain)
12.00	(16)	**The use of singlet oxygen to effect molecular weight reduction in NR latex** A Coomarasamy, W N G Seneviratne and N Wickramasinghe (Rubber Research Institute of Sri Lanka, Sri Lanka) U Hoffman and M Nadarajah (Weber & Schaer, Federal Republic of Germany)
12.30		**Lunch**

Session 4

14.00	(17)	The relevance of phase heterogeneity in epoxidations using formic acid and hydrogen peroxide D S Campbell (The Malaysian Rubber Producers' Research Association, UK)
14.30	(18)	Latex interpenetrating polymer networks based on natural rubber D J Hourston and J Romaine (University of Lancaster, UK)
15.00	(19)	Toughening of poly(methyl methacrylate) using multiple-phase particles prepared by sequential emulsion polymerisation P A Lovell, J McDonald, D E J Saunders and R J Young (Univeristy of Manchester Institute of Science and Technology, UK)
15.30		Tea
16.00	(20)	Polysulphide water dispersions for radon protection T Rees (Thiokol Chemicals, UK)
16.30	(21)	Synthetic polyisoprene latices as models for natural rubber latex D C Blackley, W F H Burgar and O Siswantoro (London School of Polymer Technology, UK)
17.00	(22)	Recent developments in natural rubber latex concentrate production J Morris (
17.30		Close of Session

THURSDAY 29 JUNE 1989

Session 5

09.00	(23)	The peculiarities of vulcanization of films from carboxylic styrene-butadiene latex produced by ionic deposition D P Trofimovich, S A Shteinberg, T D Gulichkina and V L Kuznetsov (Moscow Scientific Research Institute of Rubber and Latex Goods, USSR)
09.30	(24)	Sulphur prevulcanisation of purified natural rubber latex A D T Gorton and Hafsh bte Mohd Ghazaly (The Malaysian Rubber Producucers' Research Association, UK) D C Blackley (London School of Polymer Technology, UK)
10.00	(25)	Factors influencing the strength properties of prevulcanized and post-vulcanized latex films and of bulk rubber vulcanizates M Porter and W S Wong (University Sains Malaysia, Malaysia)
10.30		Coffee
11.00	(26)	The morphology of latex films and its relationship to permeability J Hearn, B Roulstone and M C Wilkinson (Trent Polytechnic, UK)
11.30	(27)	The effect of morphology of butadiene-methylvinylpyridine copolymer latices on their adhesion properties I L Shmurak, I A Litvinov, Yu N Dyshlevskiy and E A Salnikova (The Tyre Research Institute, USSR)
12.00	(28)	Improvement in the rheology of emulsion explosives by use of rubber latex D N Bhattacharyya and S V Chikale (Alchemie Research Centre, India)
12.30		Lunch

Session 6

14.00	(29)	The use of nonaqueous latexes as liquid developers in electronic printing M D Croucher (Xerox Research Centre of Canada, Canada)
14.30	(30)	The assessment of SBR latices in concrete repair compositions R M Edmeades and P C Hewlett (British Board of Agrement, UK)
15.00	(31)	The thermo-oxidative stabilisation of natural and synthetic latices and latex products R Baur (Ciba Geigy AG, Switzerland)
15.30		Close of Conference followed by tea

MP13

GORDON RESEARCH CONFERENCES

Polymer Colloids
Title of Conference

Proctor Academy
Host School (Site)

Irja Piirma Chairman Mohamed El Aasser Vice Chairman

July 10, 1989
Date

Monday 9:00 a.m.	D. Bassett Discussion Leader
1. R. H. Ottewill	Particle Morphology
2. M. A. Winnik	New Results on Latex and NAD Morphology
3. D. C. Sundberg	Morphology Development in Polymer Microparticles
Monday 7:30 p.m.	J. S. Dodge Discussion Leader
4. J. A. Waters	Preferred Structures for Composite Latex Particles
5. O. Pekcan	Particle Morphology and Film Formation

July 11, 1989
Date

Tuesday 9:00 a.m.	R. H. Ottewill Discussion Leader
1. B. Vincent	Adsorption of Latex Particles on Larger Particles and Particle Bridging Flocculation
2. T.G.M. van de Ven	Deposition of Latex Particles on Surfaces
3. S. Granick	Molecular Tribometry of Ultrathin Liquid Films
Tuesday 7:30 p.m.	M. Winnik Discussion Leader
4. R. L. Rowell	Characterization of Polymer Colloids
5. J. W. Goodwin	Relaxation Spectra and Interparticle Forces in the Rheology of Polymer Colloids
6. M. Laun	Rheology and Shear Induced Particle Structures of Polymer Dispersions

July 12, 1989
Date

Wednesday 9:00 a.m.	G. Poehlein Discussion Leader
1. J. W. Vanderhoff	Behavior of Emulsifiers in Emulsion Polymerization
2. D. Blackley	Novel Azo Initiators for Emulsion Polymerization Reactions
3. R. Fleckstelner	Emulsion Polymerization with Mixed Emulsifiers
Wednesday 7:30 p.m.	M. Croucher Discussion Leader
4. C. Pichot	Preparation, Characterization and Some Properties of Amphoteric, Sulfobetaine-Stabilized Latices
5. J. M. Asua	A New Approach for the Estimation of Kinetic Parameters in Emulsion Polymerization Systems

July 13, 1989
Date

Thursday 9:00 a.m.	R. Fitch Discussion Leader
1. M. S. El-Aasser	Mechanism and Kinetics of Dispersion Polymerization of Styrene in Ethanol
2. F. Candau	Percolation and Polymer Particle Formation in Micellar Systems
3. R. G. Gilbert	Diffusion Controlled Processes in Polymerization
Thursday 7:30 p.m.	F. Candau Discussion Leader
4. A. J. Paine	Mechanism of Dispersion Polymerization of Styrene in Polar Solvents
5. R. Pelton	Nonaqueous Sterically Stabilized PMMA
6. G. J. van Oss	Solubility of Polar Polymers

July 14, 1989
Date

Friday 9:00 a.m. M. El-Aasser
Discussion Leader

1. W. B. Russel	The Phase Behavior of Latices Containing Associative Thickeners
2. Th. F. Tadros	Investigation of the Interaction Forces Between Particles in Concentrated Polymer Colloids Using Viscoelastic Measurements
3. J. S. Dodge	Effect of Polymerization Surfactant and Added Surfactants on the Rheology of Acrylic Latices

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TENTATIVE OUTLINE FOR THE 1990 64th COLLOID and SURFACE SCIENCE SYMPOSIUM

LEHIGH UNIVERSITY
BETHLEHEM, PENNSYLVANIA
U.S.A.

JUNE 18,19,20, 1990

1. ADHESION OF PROTEINS AND CELLS TO PARTICLES/SURFACES

Janice Phillips
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Lehigh University
111 Research Drive
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215-758-4258

Daniel A. Hammer
Assitant Professor
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Cornell University
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Ithaca, NY 14583-5201

2. ORGANIC THIN FILMS

Steve Regen
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Seeley Mudd Building
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Bethlehem, PA 18015
215-758-4248

Ralph G. Nuzzo
AT&T Bell Laboratories
Murray Hill, N.J. 07974
201-582-5486

3. COLLOIDAL AND SURFACE CHEMISTRY OF COALS

John Larsen
Department of Chemistry
Seeley Mudd Building
Lehigh University
Bethlehem, PA 18015
215-758-3489

Dennis Finseth
Pittsburgh Energy
Technology Center
P.O. Box 10940
Pittsburgh, PA 15236
412-892-4660

4. RHEOLOGY OF CONCENTRATED DISPERSIONS AND ASSOCIATIVE THICKENERS

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William B. Russel
Chemical Engineering
Department
Princeton University
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5. MONOLAYERS AND THIN POLYMERIC FILMS IN ELECTRONICS

Ralph Jaccodine
Sherman Fairchild Laboratory
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Ike Durn
Sinclair Laboratory
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Bethlehem, PA 18015
215-758-3570

C.P. Wong
AT&T Bell Labs
Engineering Research Center
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Princeton, N.J. 08540

6. CATALYSIS/SURFACE SCIENCES

CATALYSIS BY OXIDIC, SULFIDIC, AND COLLOIDAL SYSTEMS

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R.R. Chianelli
Corporate Research Labs
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Engineering Company
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201-730-2563

MOLECULAR DESIGN OF METAL OXIDE CATALYSTS

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215-758-4274

Lawrence L. Murrell
Engelhard Corporation
Speciality Chemical Division
Menlo Park, CN-28
Edison, N.J. 08818
201-321-5274

7. NEW SURFACE ANALYSIS TECHNIQUES/ADVANCES IN ELECTRON SPECTROSCOPY

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Lennie Klebanoff
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8. POLYMER COLLOIDS

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Gary Poehlein
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9. SUBSTRATE/INTERFACE/POLYMER:CHEMISTRY AND STRUCTURE

Richard Granata
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Ray A. Dickie
Scientific Research
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10. GENERAL PAPERS

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215-758-3596

P. Pendleton
Olin Hunt
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Palisades Park, N.J. 07650
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11. NUCLEATION SYMPOSIUM**

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** This is an international symposium which will be held simultaneously with the 64th Colloid and Surface Science Symposium at Lehigh University.

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

Monomer Addition Policies for Copolymer Composition Control in Semicontinuous Emulsion Copolymerization

(Gurutze Arzamendi and José M. Asua)

The effect of various monomer addition policies on the composition of a copolymer synthesized by semicontinuous emulsion copolymerization of vinyl acetate and methyl acrylate was studied by both mathematical simulation and experimentally. Four policies were considered. In the first, both monomers were added under starved conditions. In the second, the reactor was initially charged with all of the less reactive monomer plus the amount of the more reactive monomer needed to initially form a copolymer with the desired composition. Subsequent addition of the remaining monomer was made at a flow rate that ensured the formation of a copolymer of constant composition. In the third, the inital charge was the same as in the previous case with subsequent addition of the remaining monomer at a constant feed rate. In the fourth, the time dependent addition rate for the second case was decomposed into the three periods of constant feed rate. The last three strategies are called semi-starved processes.

In order to calculate the feed rate profile corresponding to the second strategy, the knowledge of the time evolution of both average number of radicals per particle, $\bar{n}$, and total number of polymer particles was needed. The number of polymer particles was partially controlled using a seeded system. The value of $\bar{n}$ was estimated by assuming that the time evolution of $\bar{n}$ was insensitive to the addition rate. Therefore, an experiment using the a constant feed rate was carried out and $\bar{n}$ was calculated from the experimental polymerization rates. It was found that, for a given process time, the quality of the copolymer (in terms of constancy of composition) obtained through the second strategy is better than that obtained by decomposing the feed rate profile into three periods of constant feed rate and even better than the one obtained using a constant feed rate. The copolymer quality using the latter process was similar to the one obtained through the starved process (first strategy). In order to produce copolymers of similar qualities, the process time for the starved process has to be four times greater than that of the second strategy.

The mathematical simulation is described in detail in a paper accepted for publication in J. Appl. Polym. Sci. The experimental results were presented at the II International Symposium on "Copolymerization and Copolymers in Dispersed Media", Lyon 1989.

Parameter Estimation in Emulsion Copolymerization

(Jose C. de la Cal, M.E. Adams[1] and José M. Asua)

A method for parameter estimation in emulsion copolymerization has been developed. The method is based on an algorithm for parameter estimation in stiff differential equations and uses the evolution of the monomer conversions in chemically initiated seeded emulsion copolymerization systems. In order to check the usefulness of the present approach, a classic methodology was used. Chemically initiated seeded emulsion copolymerizations of two monomers of widely different reactivity ratios, vinyl acetate and methyl acrylate, were simulated using a model useful for predictive work. Arbitrary but reasonable values of the rate coefficients were used. Then, the present approach was applied to the generated data in an attempt to estimate these rate coefficients. The fit of the data and a comparison of the values of the rate coefficients used in the data generation and the estimated ones gave a measure of the usefulness of this approach.

1. Emulsion Polymers Institute, Lehigh University, Bethlehem, PA 18015, USA.

The mathematical model chosen included material balances for both monomers, population balances for particles containing i radicals and the free radical balance in the aqueous phase. The complicated processes involved in emulsion copolymerization were represented in these balances by fundamental kinetic parameters such as the entry and exit rate coefficients. The model included the following parameters:

$$kp_{AA}, kp_{BB}, kp_{AB}, kp_{BB}, \overline{k_d}, k_a, k_I \text{ and } \overline{k_t}$$

were kp_{ij} is the propagation rate constant, $\overline{k_d}$ the average desorption value coefficient, k_a the entry rate coefficient, k_I the rate constant for initiator decomposition and $\overline{k_t}$ the average termination rate coefficient.

All these parameters, but $\overline{k_t}$ which is correlated with k_a, can be accurately estimated by using the present methodology and no parameter value from literature is needed.

This work was presented at the II International Symposium on "Copolymerization and Copolymers in Dispersed Media", Lyon 1989. In addition, details about the application of this method to emulsion homopolymerization systems are given in a paper accepted for publication in J. Appl. Polym. Sci. (J.M. Asua, M.E. Adams and E.D. Sudol).

SULPHUR PREVULCANISATION OF PURIFIED NATURAL RUBBER LATEX

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

The subject of the sulphur prevulcanisation of natural rubber (NR) latex was introduced in our previous contribution to the Polymer Colloid Group Newsletter. It was pointed out there that it has sometimes been supposed in the past that the presence of various non-rubber substances in NR latex is essential for the occurrence of the sulphur-prevulcanisation reaction, and that it is the presence of some of these substances which explains why a seemingly most unlikely reaction in fact occurs in a facile manner. In particular, the presence of various proteinaceous substances has been regarded as essential. One hypothesis which has been proposed is that some of the non-rubber substances facilitate transfer of the vulcanising ingredients from the water-insoluble particles initially added to the latex to the interior of the rubber particles. It was also pointed out in our previous contribution that at least three pieces of experimental evidence now demonstrate that the presence of the non-rubber substances is not essential for sulphur prevulcanisation to occur. One of these pieces of evidence is that it is possible to prevulcanise highly-purified NR latex from which much of the non-rubber material has been removed, although the rate of prevulcanisation is somewhat reduced. This present contribution gives further information concerning this aspect of our investigations. A fuller paper on the subject will be presented to the Plastics and Rubber Institute Polymer Latex III Conference to be held in London in June this year. In this work, we have also investigated the effect of purifying the vulcanising ingredients; normal practice is, of course, to use industrial grades of these ingredients.

NR latex was purified by enzymatic deproteinisation followed by multiple centrifuging. It was necessary to stabilise the latex colloidally by adding a non-ionogenic surfactant prior to these treatments. HA latex of Malaysian origin containing an enzyme (0.5% Nova SP88 on the whole latex) and an ethoxylate stabiliser (1.5% Texofor FN30) was diluted to approximately 10% TSC with distilled water. The enzyme was added as a suspension in distilled water. The diluted latex was incubated at 35°C for not less than 24 hours, allowed to cool, and then centrifuged three times using a Westfalia centrifuge. The cream obtained from the first and second centrifugings was diluted to approximately 10% TSC before being re-centrifuged. The final latex had TSC of 57.24% and DRC of 55.90%. The alkalinity (expressed as $\%NH_3$ on the aqueous phase) was 0.009%, compared to 1.62% for the untreated HA latex. The pH was 7.4 compared to 10.4 for the untreated HA latex. The extent to which the NR latex had been purified by this treatment was assessed by determining the nitrogen and ash contents of dried film from the latex. Values of 0.02% and 0.01% respectively were obtained, compared with 0.34% and 0.48% respectively for films from the untreated HA latex. These results indicate that considerable proportions of the non-rubber substances had been removed by the above process. The difference of 1.34% between the %TSC and %DRC of the purified latex was higher than expected, but was considerably less than the corresponding figure for the untreated HA latex (2.12%). It is presumed that the residual Texofor FN30 contributed significantly to the non-rubber solids content of the purified latex.

Two grades of sulphur were used: (a) an industrial grade ("flowers of sulphur") supplied by Hughes and Hughes), and (b) "pure" sulphur (>99.999%) supplied by Fluka Chemicals. The vulcanisation accelerator was zinc diethyldithiocarbamate (ZDEDC). Again two grades were used: (a) an industrial grade supplied by Vulnax, and (b) a purified grade obtained by recrystallising the industrial grade from chloroform. The recrystallisation procedure was as follows: ZDEDC (100 g) was heated in chloroform (465 cm^3) to boiling (61°C). The hot saturated mixture was rapidly filtered through a 15-µm nylon cloth, and allowed to stand at room temperature. The crystals of ZDEDC which separated were then recrystallised by the same procedure. The final crystals were large and clear, and gave a white powder when ground. The purity was 92.0% as judged by sulphur content, and 96.0% as judged by zinc content.

The overall conclusions which have been drawn from prevulcanisation experiments using purified and unpurified ingredients can be summarised as follows: Purified NR latex is capable of being prevulcanised by heating with sulphur and zinc diethyldithiocarbamate. This indicates that the presence of the non-rubber substances in NR latex is probably not essential for the occurrence of sulphur prevulcanisation, and confirms what has become evident from other work that the primary requirement for the sulphur prevulcanisation of polyisoprene to occur is that the polymer should be in the form of a stable colloidal dispersion in water. However, the rate of insertion of crosslinks into the rubber is reduced considerably by purifying both the latex and the vulcanising ingredients. In particular, purifying the latex results in a significantly increased induction period for crosslink insertion. It is not possible to speculate at present on the implications of these results for the mechanism of the sulphur prevulcanisation of NR latex, because at present so little is known concerning the details of that mechanism. All that can be said at present is that the reaction is facilitated by the presence of non-rubber substances, and it may well be that, although the primary requirement for sulphur prevulcanisation is that the polymer should be in the form of a stable colloidal dispersion in water, the reaction is particularly facilitated by the presence of colloid stabilisers.

Experiments have also been carried out using purified NR latex in which the effects of various additives upon prevulcanisation behaviour were investigated. Some of the added substances were typical of substances which were thought to have been removed by the latex purification procedure. The objective of this part of the investigation was to ascertain the extent to which the rate of sulphur prevulcanisation of purified NR latex could be restored to that of untreated HA latex by making suitable additions. Rather surprisingly, it was found that the addition of ammonia had no effect upon the induction period for crosslink insertion observed when using purified NR latex. As regards the other additives which have been investigated, several have been found to accelerate the sulphur prevulcanisation of purified NR latex to various extents, but the rate is not restored to that observed when untreated HA latex is used. The addition of the serum from HA latex was found to be particularly effective. These results confirm that the serum of HA latex contains at least one substance which is able to facilitate sulphur prevulcanisation.

By comparing the network-combined sulphur with the concentration of chemical crosslinks in the vulcanisate, as determined by equilibrium swelling measurements, it was possible to calculate the average number of sulphur atoms per crosslink in the vulcanisate - the so-called "E-value". The E-values for all the vulcanisates obtained in this work were high, ranging from *ca.* 8 to *ca.* 70, thus indicating that latex sulphur prevulcanisation is very inefficient. This was expected, although the wide range of E-values was not. Furthermore, the higher E-values were obtained at the shorter prevulcanisation times and using reaction systems containing purified reactants. The E-values for the vulcanisates obtained from purified NR latex were considerably higher than those obtained from untreated HA latex. Thus not only does purification of the latex cause sulphur to combine with the rubber more slowly; it also results in the sulphur being utilised less efficiently in crosslink formation.

It was also observed that very high E-values appeared to correlate with low values of crosslink concentration. When E is plotted against crosslink concentration for the various vulcanisates obtained in this work (Figure 1), it is indeed found that all the points form a single broad correlation. The relationship between E and crosslink concentration is approximately hyperbolic, such that E falls rapidly as crosslink concentration initially increases, and then asymptotically approaches a constant value as the crosslink concentration increases further. This interesting observation suggests that the removal of non-rubber substances during the purification of NR latex does not fundamentally alter the chemistry of the sulphur-prevulcanisation reaction, although it does affect both the rate of sulphur combination and the rate at which combined sulphur is utilised to form crosslinks. The very high E-values observed for vulcanisates having low crosslink concentrations indicates that the removal of non-rubber substances has a profound effect upon the rate of those processes which lead to the rearrangement of combined sulphur to form sulphur crosslinks.

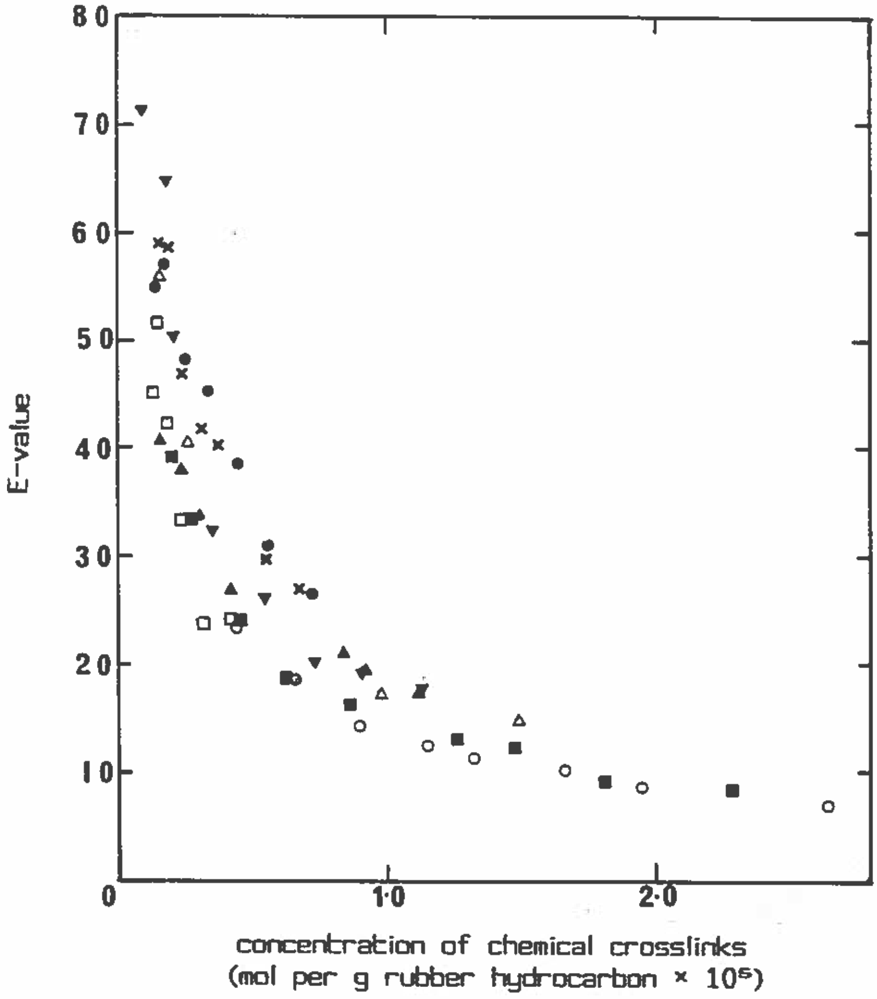

Figure 1

POLYMER COLLOID GROUP NEWSLETTER

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

Françoise CANDAU

RHEOLOGICAL STUDY OF POLY(ACRYLAMIDE-CO-SODIUM ACRYLATES) LATEXES
(in collaboration with D. Collin and F. Kern).

We have studied the rheological behavior of poly(acrylamide-co-sodium acrylates) latexes prepared in inverse microemulsions. The nonionic emulsifier blend consists of sorbitan sesquioleate and a polyoxyethylene sorbitol hexaoleate (HLB ≃ 9) and the continuous phase is isopar M. These inverse microlatexes differ from the more conventional aqueous or non aqueous colloidal dispersions by several aspects :

i) The particle size is lower than 100 nm.

ii) The particles are swollen by large amounts of water (e.g. 50% water, 50% polymer).

iii) With this particular process, large volume fractions of the disperse phase can be reached (up to 60%).

Figure 1 shows an example of the variation of the relative viscosity with the shear stress for a typical latex. Qualitatively, one has the usual behavior observed for colloidal dispersions, that is a newtonian behavior at low volume fractions and a shear thinning effect for the largest volume fractions investigated.

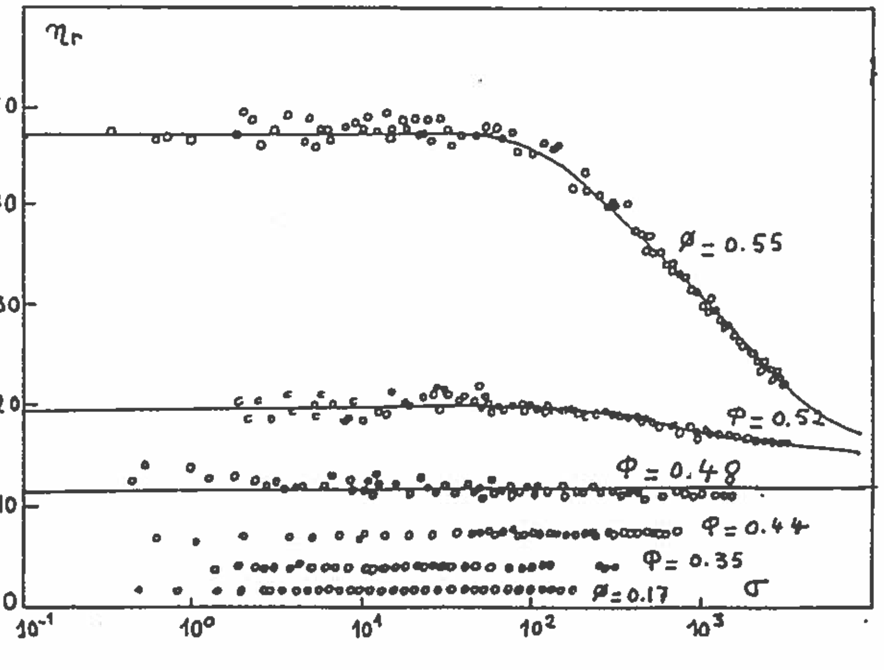

Figure 1. : Variation of the relative viscosity with shear stress for a sample containing 9.10% sodium acrylate (wt/wt) and with a particle size of 62 nm.

However, the shear-thinning effect occurs at volume fractions much higher than those observed for conventional latexes (50-53% as against 25%). This result indicates that in the case of inverse microlatexes, the brownian forces overcome the hydrodynamic forces over a large range of volume fractions. A possible explanation of this effect is the small size of the particles which makes them more mobile. The small thickness of the hairy larger (an oleate chain) which surrounds the particles and ensures their steric stability should also be taken into account. The full lines in Figure 1 represent the best fit of the well-known Williamson equation $[\eta = \eta_\infty + (\eta_0 - \eta_\infty)/(1 + \sigma/\sigma_m)$ where η_0 and η_∞ are the low shear and high shear limiting viscosities and σ_m the shear stress for which $\eta = (\eta_0 + \eta_\infty)/2]$ to the experimental data.

We have determined the intrinsic viscosity $[\eta]$ and the close-packing volume fraction φ_m of a series of copolymer latexes containing various contents of sodium acrylate, by using the Krieger-Dougherty equation

$$\eta_r = (1 - \varphi/\varphi_m)^{-[\eta]\varphi m}$$

A value of $\simeq 2.5$ is found for $[\eta]$ in good agreement with was is obtained for hard spheres suspensions. The data shows that φ_m decreases when increasing the percentage of electrically charged sodium acrylate in the comonomer feed. For instance, φ_m is around 59% for a sodium acrylate concentration of 12%. This value is significantly lower than that of 64% predicted for a random packing of hard spheres. On the other hand, other experiments performed on neutral polyacrylamide latexes have given values of φ_m around 64%. The divergence of viscosity which occurs at smaller characteristic volume fractions for poly(acrylamide-co-acrylates)latexes is probably due to the effect of electrical charges in the system, which prevents particles from approaching too closely to each other. Rheological studies on other ionogenic monomers are in progress to check this hypothesis.

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NUCLEATION OF LATEX PARTICLES IN EMULSION POLYMERISATION

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During the last few years, Napper, Gilbert, and co-workers at the University of Sydney have provided abundant evidence that the nucleation of latex particles involves the coalesence of unstable precursor particles (1,2) even in the case of styrene for which the latex particles have long been assumed to be nucleated from emulsifier micelles saturated with solubilised monomer at least under the most commonly used conditions when the concentration of the emulsifier is in excess of its critical micelle concentration (c.m.c.). Evidence has been available for many years that coalescence is involved in the nucleation of the ultimate latex particles in the emulsion polymerisation of more polar, more water-soluble monomers such as vinyl acetate (3,4) on which conventional anionic emulsifiers are less strongly adsorbed. The particle size distribution of the latex is monodisperse when extensive coalescence has occurred. Polystyrene latices produced in absence of emulsifier or below the c.m.c. of the emulsifier are monodisperse: obviously the precursor particles must be formed by oligomeric precipitation (5,6) in these cases - no emulsifier micelles are present at any stage in the reaction.

THE PROBLEM is to explain why, if polystyrene latex particles can be nucleated from micelles above the c.m.c. of the emulsifier, monomer-swollen emulsifier micelles which are thermodynamically stable become unstable when the monomer in them polymerises and coalesce until the ultimate latex particles which are only kinetically stable because of the energy barrier presented by their adsorbed layers of emulsifier which reduces the rate of coalescence practically to zero. The amount of adsorbed emulsifier required to do this is considerably less than that required to form a saturated monolayer at the polymer/water interface because it is normally possible to perform a soap titration on a completely polymerised latex which involves adsorbing as much additional emulsifier as is required to saturate the adsorbed monolayer. This is not possible when abnormally high emulsifier concentrations are used when micelles may remain at the end of the polymerisation (7).

THE SOLUTION seems to be either that micelles are not involved in the nucleation of polystyrene latex particles at all which is the view advocated by Richards, Congalidis, and Gilbert (8,9) or that latex particles are predominantly nucleated from monomer-swollen emulsifier micelles above the c.m.c. of the emulsifier but that the initial rate of increase of surface area of the polymer exceeds the initial rate of adsorption of additional emulsifier so that the growing latex particle passes through an unstable stage during which limited coalescence occurs before the rate of emulsifier adsorption increases sufficiently to prevent further coalesence.

Unfortunately it is difficult to conceive any experiment which could differentiate these possibilities.

The argument that the micelles present much the largest surface area at the beginning of an emulsion polymerisation and are, therefore, the most likely entities to capture radicals generated in the aqueous phase still appears convincing. Fitch and Shih's calculation (10) which showed that there was no significant repulsive energy barrier to prevent a charged radical entering a similarly charged micelle even if it had not added any monomer residues from monomer in true aqueous solution has not been refuted. Moreover no obvious difference has ever been noted between initiators generating radical ions (e.g. persulphate) and those generating uncharged radicals (e.g. Fe^{2+}/H_2O_2) when emulsifier is present although there is a big contrast in the effects of these initiators in absence of emulsifier because the uncharged hydroxyl end-groups do not stabilise the latex particles permitting unlimited coalescence to occur (11).

Tertiary Butyl Styrene is a development monomer which the Dow Chemical Co. has manufactured in limited quantities. Unfortunately the polymer has yet to find applications in which its superior properties would be advantageous. Poly(p-tert-butyl styrene) has a much higher glass transition temperature (134°) compared with poly(styrene) (81 °C) (12). But preliminary results (13) indicate that study of the emulsion polymerisation of this monomer could provide results of great sinificance in relation to the question of the participation of micellar nucleation of latex particles in the emulsion polymerisation of non-polar monomers.

No latex is formed when emulsifier-free emulsion polymerisation of p-tert-butyl styrene is attempted at 50 °C using potassium persulphate as initiator (13): but a latex does form immediately emulsifier is injected in sufficient quantity to give a concentration in excess of the c.m.c. This experiment appears to show that micellar nucleation is the only possible nucleation process in this case. p-tert-butyl styrene has only about one-tenth (12) of the water solubility of styrene. It is possible that soluble oligomer may be formed in the aqueous phase in absence of emulsifier consisting of two or three monomer residues with a sulphate group on each end: if so, a decrease in surface tension should be detectable but this possibility has yet to be tested.

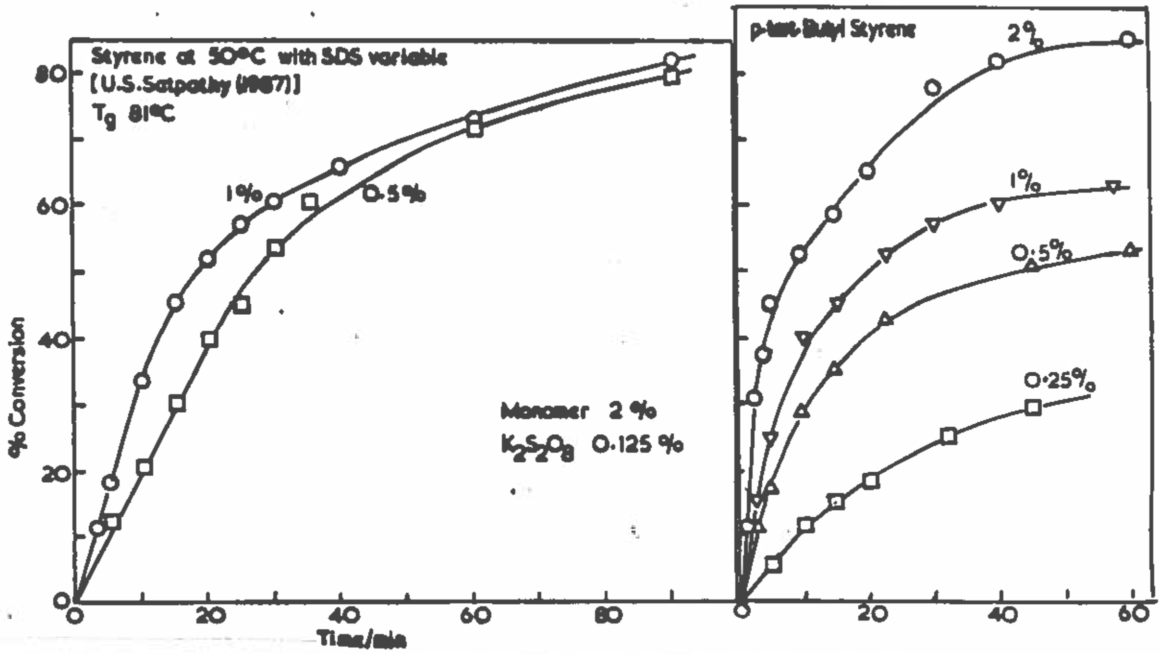

Fig. 1 Contrast between the course of emulsion polymerisation of styrene and p-tert-butyl styrene under similar conditions. 50 °C, $K_2S_2O_8$ 0.125%. Concentration of sodium dodecyl sulphate emulsifier varied. Monomer:water ratio 1:50.

The course of the emulsion polymerisation reaction with styrene is familiar. The effect of varying the emulsifier concentration on the Interval II rate is consistent with a 0.6 order dependence. However, results with p-tert-butyl styrene are entirely different. Electron micrographs indicate that the polymer particles formed are much smaller than with styrene. Although swelling the polymer with monomer will greatly reduce the glass transition temperature, it seems possible that poly(p-tert-butyl styrene) may still be below its glass transition temperature at 50 °C so that precursor particles cannot coalesce although they may coagulate. Without the reduction of the total latex particle surface area through coalescence insufficient emulsifier is avaiable at the lower concentrations used to keep the latex stable. Much of the coagulum formed is inaccessible to radicals generated in the aqueous phase so the reaction stops prematurely before all the monomer is exhausted. If this explanation is correct conversion-time curves similar to those obtained with styrene should be found at higher temperatures and, conversely, styrene should gives curves similar to those found with p-tert-butyl styrene at sufficiently low temperatures (when a redox initiation system would have to be used). The propagation rate constants of styrene and p-tert-butyl styrene might be expected to be similar but the initial rate of polymerisation of p-tert-butyl styrene which may indicate that about twice the number of separate latex particles is present in the polymerisation of p-tert-butyl styrene as in the polymerisation of styrene up to about 25% reaction.

Experimental verification of these deduction should provide valuable insights into the importance of precursor particle coalescence in determining the ultimate number of particles formed and the course of the reaction in emulsion polymerisations.

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DIFFUSION OF LATEX PARTICLES IN POLYACRYLAMIDE GELS

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The dynamics of latex particles dispersed in cross-linked polyacrylamide gels were studied by dynamic light scattering (DLS).

The important characteristic of these (aqueous) polymer gels is that the scattering particles are not free to diffuse throughout the sample but are able only to execute limited random excursions about fixed average positions. This particular phenomenon leads to intensity correlation functions that show a distinct qualitative behaviour when compared to correlation functions obtained from freely-diffusing systems.
For a freely-diffusing system the time-averaged correlation function of the scattered intensity, the quantity obtained from a single DLS experiment, is equal to its ensemble average. In systems where the diffusion of the particles is constrained the time-averaged correlation function constitutes an ensemble average over a particular sub-ensemble of configurations. This implies that a single DLS experiment does not yield the appropriate full ensemble-averaged correlation function.

We show that the polyacrylamide gels exhibit this so-called non-ergodic behaviour. By virtue of this non-ergodicity the analysis of correlation functions requires a special procedure.

We studied aqueous polyacrylamide gels made by co-polymerizing acrylamide (AA), and bisacrylamide (BAA). The total monomer concentration ([AA] + [BAA]) is 2.5 wt.% whereas the crosslink content [BAA]/[AA]+[BAA] was varied from 0 wt.% to 4 wt.%. As tracers we used polystyrene spheres (radius = 41 nm) at a concentration of 2×10^{-4} wt.%. The ensemble averaged scattered intensity of these systems is 40 times larger than that of the pure gel at all scattering angles. Using a recently developed theory[1] for analyzing experimental correlation funtions obtained from non-ergodic systems we find that the short time diffusion coefficient of the particles is nearly independent of scattering angle and does not vary very much by increasing the crosslink content from 0 to 4 wt.%. The long time mean square displacement of the particles is found to be 32 nm, 16 nm and 6 nm for [BAA]/[AA]+[BAA]= 1.5, 1.8 and 4 wt.% respectively.

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Contribution to the Polymer Colloids Group Newsletter

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The titles of our current research projects are given in the enclosed Contents of our Graduate Research Progress Reports, No. 31, January 1989. Copies of any of these reports can be obtained by contacting Ms. Debra Nyby at the above address. Summaries of progress in several research areas are presented here along with titles of papers recently presented and published.

1. Synthesis and Characterization of Core/Shell Type Ionomeric Latexes
(R. Jourdan & E.S. Daniels)

Core/shell latexes comprised of a monodisperse polystyrene core and a 56/14/30 n-butyl acrylate/styrene/methacrylic acid copolymer shell were prepared by seeded semicontinuous emulsion polymerization. Previous studies with a terpolymer latex with the same composition as the second stage shell polymer demonstrated that this latex exhibited ionomeric behavior at an overall acid content of 30%. Figure 1 shows the glass transition temperature (T_g) of this terpolymer latex as a function of the degree of neutralization with sodium hydroxide, as determined by dynamic scanning calorimetry (DSC). The measured T_g of this latex increased with increasing pH, beyond that which could be predicted using a Flory-Fox equation, taking into account the presence of sodium methacrylate. A critical concentration for methacrylic acid in the particle was necessary for this phenomenon to occur. This is related to the ability of the sodium ion to diffuse within the latex particle. In the case of the latex containing 30% methacrylic acid, the electrostatic interactions between dissociated acid groups expanded the polymer backbone allowing for a fast diffusion of sodium counterions into the particle and led to homogeneously neutralized particles. The enhancement in T_g resulted from the association of ionic pairs into clusters which results in the formation of physical crosslinks. These clusters restricted the motion of the polymer backbone chains containing the carboxyl groups which led to an increase in T_g. It was thought that a study of an ionomeric core/shell latex system based on the phenomenon described above would exhibit very interesting physical properties when processed into films. The current investigation therefore examined the influence of parameters such as second stage (shell polymer) to seed polymer (core) ratio, the distribution of carboxyl groups in the shell layer, the behavior of the methacrylic acid during the seeded polymerization and the type of counterion used during the neutralization of the core/shell latex on the composite particle size and morphology, on the alkali swelling behavior of these latexes and on their mechanical properties.

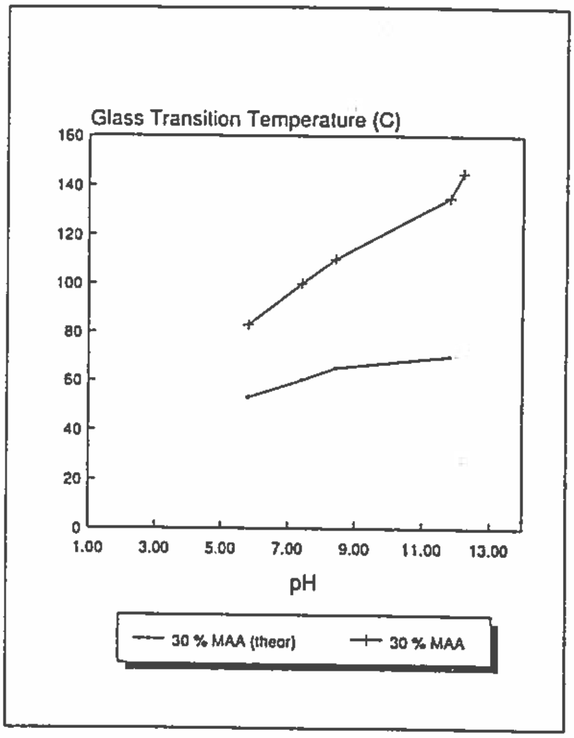

Figure 1. Variation of T_g *of Carboxylated Latexes as a Function of pH.*

2. <u>Spontaneous Emulsification in a Dilute Gel Phase</u>
(R.J. Goetz)

The dilute gel phase of cetyl alcohol (CA), sodium lauryl sulfate (SLS) and water is used in the formation and stabilization of miniemulsions. These emulsions are used in emulsion polymerization reactions and in the preparation of artificial latexes. The remarkable characteristic of this system is the spontaneous formation of a miniemulsion upon addition of an oil phase. Although organized surfactant phases have been associated with spontaneous emulsification, this research represents the first investigation of spontaneous emulsification within a gel phase. The structure of the gel is similar to the lamellar liquid crystalline phase and consists of bilayers of the alcohol and the surfactant separated by water. However, the hydrocarbon chains of the gel are in the solid state. Thus, spontaneous emulsification in a gel presents a unique problem since equilibrium swelling and solubilization will not occur. The objective of this research is to understand the structural changes that occur with the frozen bilayer structure of the gel that result in the spontaneous formation of submicron emulsion droplets.

Figure 1 shows the ternary phase diagram of the CA/SLS/water system in the dilute corner. The compositions were prepared by heating the components to 70°C before cooling to room temperature. The blackened region represents the compositions used in the formation and stabilization of miniemulsions, which exists at the extreme dilute corner of the gel phase region. The gel phase region exists at compositions in which the molar ratio of CA/SLS is greater than one. At compositions with a molar ratio less than one, the system is comprised of SLS micelles and sedimented CA crystals. At intermediate molar ratios, the system consists of a mixture of the gel and precipitated CA crystals; this is defined as the coagel phase.

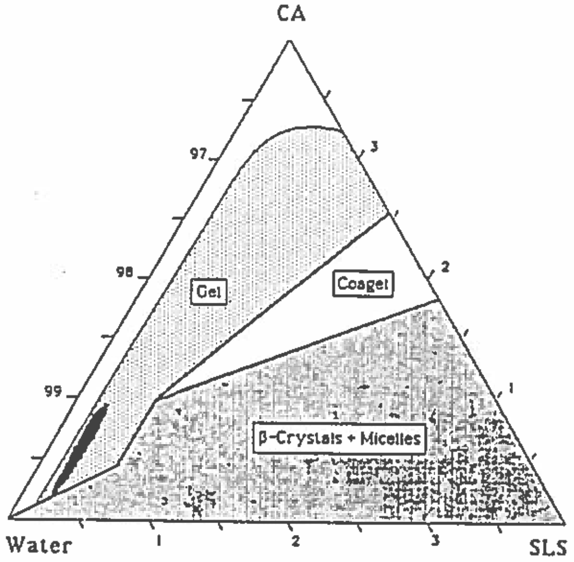

Figure 1. Phase Diagram of CA/SLS/Water in the Dilute Corner.

The structural characterization of the dilute gel phase, before and after the addition of an oil phase (toluene), was interpreted through the self diffusion coefficients measured from the Fourier transformed pulsed gradient spin-echo NMR technique. Two different diffusion coefficients for water were measured with three orders of magnitude difference between them. The fast diffusion coefficient represented the water diffusing outside the gel phase and was lower than pure water since it was obstructed by the gel phase. The slow diffusion coefficient of water represented water entrapped within the gel.

Figure 2 shows a plot of the fraction of slow diffusing water and reduced diffusion coefficient of the fast diffusing water D/Do (where Do is the diffusion coefficient of pure water) as a function of oil added to the system. As the oil concentration is increased, the fraction of slow diffusing water monotonically decreased, indicating the disappearance of the gel phase. The fast diffusion coefficient monotonically increased as the effect of obstruction by the gel phase decreased. At an oil volume fraction of 5%, the gel phase had completely disappeared, as shown by the absence of slow diffusing water (Figure 2). These results do not indicate that a swollen liquid crystalline phase formed as a stable precursor to miniemulsion formation. A lamellar phase would further obstruct the diffusion of the free water (water not bound in the gel) until the emulsion droplets formed. Moreover, emulsion droplets did not form uniformly but were initially detected at an oil concentration of 0.5% (by volume).

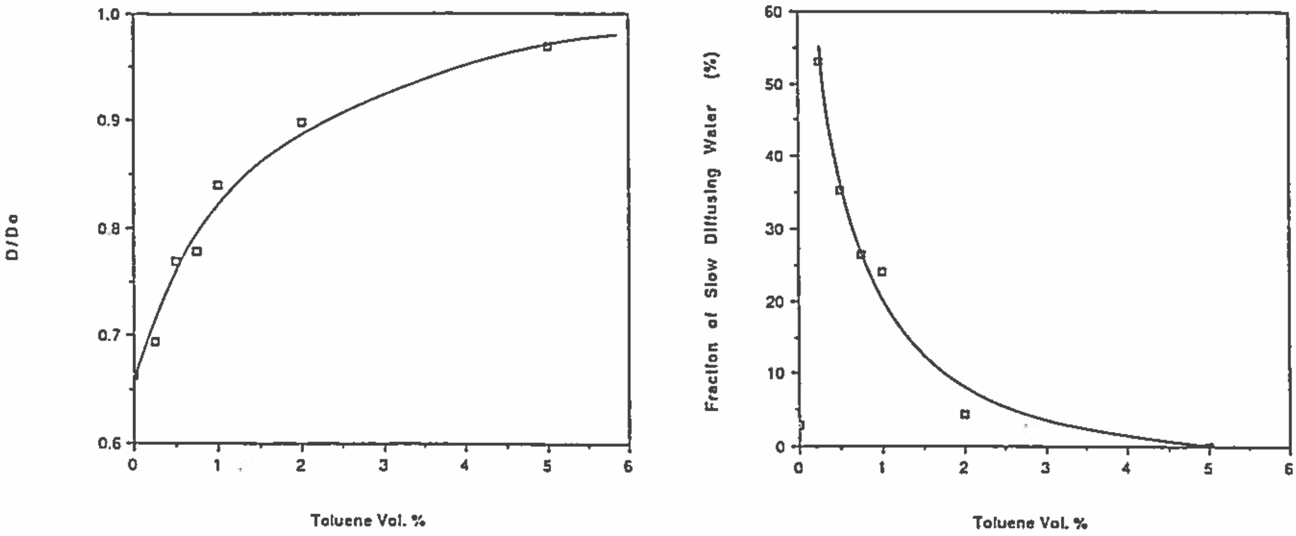

Figure 2. D/Do (left) and Fraction of Slow Diffusing Water (right) as a Function of Oil (toluene) Added.

Upon the breakdown of the gel structure by an oil phase, the stability of the bilayer structure depends on the balance of different forces. In the gel phase the bilayer structure originated from the crystalline form of CA. However, once dissolved, the balance between van der Waals, electrostatic and hydrophobic forces determine the equilibrium structure. Currently, a model is being developed to predict the initial droplet size based on the resultant of these new forces.

3. Polymerization of Styrene O/W Microemulsions

(J.S. Guo)

Microemulsions are optically transparent, thermodynamically stable and isotropic dispersions consisting of microdomains of oil or water stabilized by an interfacial film of surface active molecules. Polymerizations of oil-in-water microemulsions formed by styrene, water, sodium dodecyl sulfate and 1-pentanol (cosurfactant) were carried out. The effects of the amount of styrene, 1-pentanol and sodium dodecyl sulfate (SDS) on the polymerization kinetics and final latex particle size were investigated by dilatometry and transmission electron microscopy. In all cases, the final polymer latexes were stable, bluish and less translucent than the original microemulsions and the polymerization kinetic features were similar with no constant rate interval and no gel effect. Both the polymerization rate and the particle size increased with an increasing amount of monomer. Increasing the amount of 1-pentanol in the microemulsion gave a lower polymerization rate and similar particle size. The higher polymerization rate in both cases was attributed to the higher monomer concentration inside the particle due to the partitioning of 1-pentanol. It was also demonstrated that the polymerization rate is almost the same for different surfactant concentrations and the particle size increases with an increasing amount of surfactant.

In order to clarify the polymerization mechanism it is necessary to understand more about the structure of styrene oil-in-water microemulsions (most research has been devoted to water-in-oil microemulsion systems) and correlate this with the polymerization behavior. Thus, the structure of oil-in-water microemulsions was modeled in terms of three phases: oil (core) phase, membrane phase and aqueous (continuous) phase. The compositions of the oil and continuous phases were determined using a diffusion method and a partitioning measurement of the two-phase three-component (styrene, 1-pentanol and water) systems. The membrane phase was composed mainly of 1-pentanol and SDS. The solubilization of styrene in the hydrophobic region created by the SDS in the membrane phase was considered and studied using a C^{13} NMR chemical shielding experiment. A thermodynamic model based on Flory-Huggins lattice theory is being developed to predict the composition of each phase of a styrene microemulsion in the different phase regions.

A number of research programs recently initiated in the Institute are briefly described in the following:

1. Interfacial Mass Transport of Monomers into Latex Particles

(J.I. Kim)

Generally, the adsorbed surfactant on a polymerizing latex particle is not considered to impede the transport of monomer into the the particle and thus not affect the polymerization rate. However, when this adsorbed material consists of mixtures of ionic, nonionic and polymeric emulsifiers which can form a densely populated interfacial region or "condensed" emulsifier film, then the interfacial mass transfer may be a kinetic factor. Mass transfer resistances for such a system are being studied using both monomer liquid and vapor phase addition methods.

2. Polymerization of Reactive Surfactants

(M.B. Urquiola)

The loci and extent of polymerization and copolymerization of reactive surfactants are being investigated in the emulsion polymerization of styrene. Increased particle stability is anticipated provided that the surfactant does become chemically bound to the surface of the latex particles. The aqueous phase, particle/water interface and polymer phase will be analyzed for the presence of the surfactant including its degree of polymerization and copolymerization.

3. Particle Morphology in Seeded Composite Latexes

(Y.C. Chen)

Polymer/aqueous phase interfacial tensions and particle surface polarities are being examined in terms of the extent of their roles in determining the development of particle morphology in emulsion copolymerization systems. Experimental results are being compared to the predictions of a thermodynamic model.

(Some of this work was recently presented at the *Deuxieme Colloque International sur les Copolymerisations et les Copolymeres en Milieu Disperse*)

4. Preparation of High-Molecular-Weight Copolymers as Fuel Additives
(I. Segall)

The use of polymers to control the antimisting behavior of jet fuels received much media coverage when the FAA deliberately crashed a jet airplane to test such a material. Despite the poor execution of the test which resulted in much damage by the ensuing fire, interest has continued in further development of these materials. Emulsion polymerization is being used to prepare copolymers for evaluation in conjunction with Aberdeen Proving Grounds.

Papers Presented

Four papers were presented at the *Deuxieme Colloque International sur les Copolymerisations et les Copolymeres en Milieu Disperse* in Lyon, April 3-7, 1989. The titles are:

"Miniemulsion Coplymerization of Styrene-Methyl Methacrylate: Effect of Transport Phenomona", M.S. El-Aasser, J.M. Asua, V.S. Rodriguez and C.A. Silebi.

"Interfacial Phenomena Controlling Particle Morphology in Composite Latexes", V.L. Dimonie, Y.C. Chen, M.S. El-Aasser and J.W. Vanderhoff.

"Effect of Alkyl Substitution of DOWFAX™ Surfactants in Styrene-Butadiene Emulsion Copolymerization", V.L. Dimonie, M.S. El-Aasser, J.W. Vanderhoff and L.A. Settlemayer.

"Vinyl Acetate/Butyl Acrylate Emulsion Copolymerization using Poly(Vinyl Alcohol) Emulsifier", J.W. Vanderhoff, N.J. Earhart, V.L. Dimonie and M.S. El-Aasser.

Recent Publications

"The Role of the Cosurfactant in the Miniemulsion Copolymerization of Vinyl Acetate and n-Butyl Acrylate", J. Delgado, M.S. El-Aasser, C.A. Silebi and J.W. Vanderhoff, Macromol. Chem., Macromol Symp., 20/21, 545 (1988).

"Theory of Colloids", J.W. Vanderhoff and M.S. El-Aasser in "Pharmaceutical Dosage Forms: Disperse Systems", Marcel Dekker, 1, Chapter IV, 55pp (1988).

"Miniemulsion Copolymerization of Vinyl Acetate and Butyl Acrylate. III. Experimental Evidence for the Role of the Cosurfactant", J. Delgado, M.S. El-Aasser, C.A. Silebi and J.W. Vanderhoff, J. Polym. Sci., Polym. Chem., 27, 193 (1989).

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

"Miniemulsion Copolymerization of Vinyl Acetate and Butyl Acrylate in a Tubular Reactor", M.S. Report by Scott A. Adamec.

"Interparticle Monomer Transport in Miniemulsion Copolymerization", Ph.D. Dissertation by Valmore S. Rodriguez.

"Separation of Submicron Particles by Flow Fractionation: Capillary Hydrodynamic Fractionation (CHDF)", Ph.D. Dissertation by Jose G. Dos Ramos.

"Modeling and Control of Semicontinuous Emulsion Copolymerization", Ph.D. Dissertation by Yiannis N. Dimitratos.

Copies of the Abstracts are available upon request.

The Emulsion Polymers Institute's 20th Annual Short Course "Advances in Emulsion Polymerization and Latex Technology" will be held at Lehigh on June 5-9, 1989. The European Short Course will be given August 21-25, 1989.

The 64th National Colloid and Surface Science Symposium will be held at Lehigh University on June 18-20, 1990. For further information contact Mohamed El-Aasser.

EMULSION POLYMERS INSTITUTE
Lehigh University

Graduate Research Progress Reports
No. 31 January 1989

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PREPARATION OF POLYMER COLLOIDS

CHARACTERIZATION OF POLYMER COLLOIDS

POLYMERIZATION KINETICS, REACTOR DESIGN AND CONTROL

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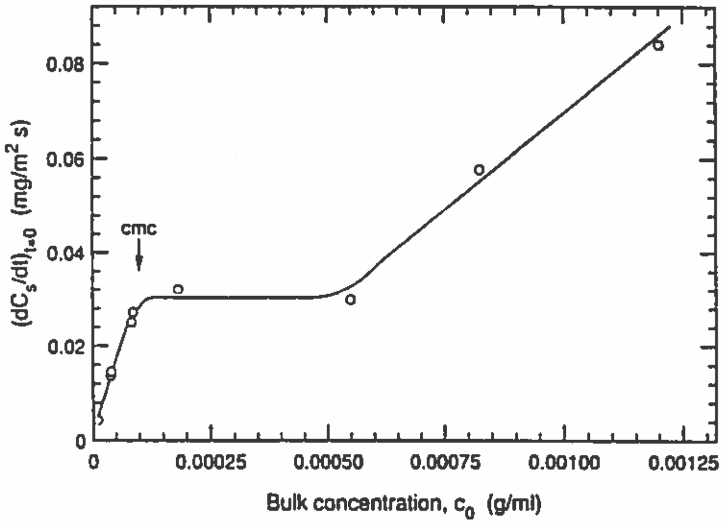
Contribution to Polymer Colloids Newsletter
Current Research Projects - Alice P. Gast
April 1989

Kinetic Studies of Poly(ethylene-oxide)-polystyrene Diblock Copolymer Adsorption

with Mark R. Munch

Goal: To understand the mechanisms involved in diblock copolymer adsorption as a function of copolymer concentration above and below the critical micelle concentration.

Summary: A non-invasive, optical technique for studying the kinetics of block copolymer adsorption at the dielectric solid-liquid interface has been developed. Laser light is directed through a sapphire reflection prism designed to give many total internal reflections. The light experiencing reflection undergoes a phase change monitored by a Mach-Zehnder type interferometer that is thermally and vibrationally isolated. We can calculate the amount of adsorbed copolymers from this phase change. Computerized data acquisition allows tenth second sampling. The experiments are performed under gentle flow conditions to limit diffusion at the rate-controlling process for adsorption. The time evolution of the surface concentration of poly(ethylene-oxide)-polystyrene copolymer of molecular weight 184,000 in cyclopentane at 23°C was monitored. The bulk copolymer concentration drastically affects the adsorption kinetics. In particular, micellization of block copolymers affects the rate of adsorption as shown in Figure 1 where the initial rates of adsorption are plotted as a function of the overall copolymer concentration. The results indicate adsorption of micelles above the critical micelle concentration and adsorption of single chains below the critical micelle concentration. Also the adsorption of block copolymers is irreversible with respect to the addition of pure solvent.



Initial rate of adsorption as a function of bulk copolymer concentration, c_0. The critical micelle concentration is marked at 1×10^{-4} (g/ml).

Mobility of Proteins Adsorbed at the Solid-Liquid Interface

with Robert D. Tilton

Goal: To characterize the lateral mobility of adsorbed proteins and determine the mechanism of their motion.

Summary: The mobility of adsorbed proteins may play a fundamental role in the formation of ordered arrangements of proteins on solid surfaces. We measure the surface diffusion coefficient and the fraction of mobile proteins by a combination of total internal reflection fluorescence and fluorescence recovery after pattern photobleaching. A key feature of the technique is the use of intersecting coherent laser beams to create an interference fringe pattern for pattern photobleaching and for monitoring the fluorescence of adsorbed fluorescently labelled proteins. By changing the angle of intersection, we change the characteristic length for transport in order to distinguish between diffusion and linear flow. We are currently studying the mobility of eosin isothiocyanate-labelled bovine serum albumin (BSA) adsorbed to a spin coated poly(methyl methacrylate) film.

Microstructure Identification During Crystallization of Charged Colloidal Suspensions

with Yiannis Monovoukas

Goal: To investigate the effect of volume fraction and cell thickness on the microstructure, orientation, and twinning in coloidal suspensions.

Summary: Control of the microstructure of colloidal crystals leading to defect-free structures motivates investigation of the important early stages of crystallization. We use a polarized light microscope in its orthoscopic and conoscopic arrangements to study the effect of particle volume fraction and cell thickness on the microstructure of crystallizing suspensions of negatively charged polystyrene microspheres. We show that the crystallites grow by parallel stacking of the (111) layers to non-perfect face-center cubic (FCC) structures exhibiting a symmetry axis (optic axis) normal to the (111) planes. Evidence for this anisotropy is provided by the existence of rotation-dependent extinction positions when the crystallites are observed under crossed polars. At high volume fractions, $\phi \approx 9\%$, the structures change little with time as the crystallites are essentially "frozen" in space by their neighbors. At lower concentrations, $\phi \approx 5\%$, the crystallites are larger with smoother boundaries and develop to normal FCC structures with the (111) planes parallel to the cell walls, evidenced by the FCC Kossel lines from laser light diffraction experiments. Crystallites in flat 50 μm glass cells remain anisotropic and at $\phi \leq 3\%$ they orient with their optic axis normal to the cell walls. We demonstrate that striated crystallites with lamellae of alternating colors of varying broadness are FCC twins with (111) twin plane. The number density of twinned crystals and the frequency of striations decrease at lower rates of crystal growth. We are currently extending and quantifying these results.

The Dichroism and Birefringence of a Hard Sphere Suspension in Combined Electric and Shear Fields

with Paul M. Adriani

Goal: To model the anisotropic particle pair distribution created by combined electric and shear fields, and determine the optical properties of this anisotropic suspension.

Summary: We model the pair distribution as a linear superposition of the anisotropic structures induced by the electric field and the shear field. We then calculate the birefringence by renormalizing a nonconvergent integral arising in the Onuki and Doi theory for birefringence. The principal axes of the birefringence and dichroism tensors vary with the Mason number, which measures the relative strength of shear forces to electric dipole interaction forces. The angle of the axes varies from 45° in the shear dominated limit, to 0° in the electric field dominated limit. The magnitudes of birefringence and dichroism are sensitive to the size of the particles compared to the wavelength of light employed; this is important for experimental tests of theoretical predictions. We compare these theoretical results to experiments of suspensions under shear by Wagner, Fuller, and Russel, and we will be comparing these results to experiments of suspensions in an applied electric field by Smith and Fuller. For the particle distribution under shear we employ a simple theory neglecting hydrodynamic interactions which yields fair agreement with experiment for the dichroism but poor agreement for the birefringence. For the effect of the electric field on the particle structure we employ the mean field theory of Adriani and Gast, and the aligned dipole pair distribution of Hayter and Pynn. The predictions of optical properties provide both a test of theories of microstructure and insight into the effects of shear and electric fields on microstructure.

An interesting dynamic phenomenon in the flocculation of polymer colloids by polymers

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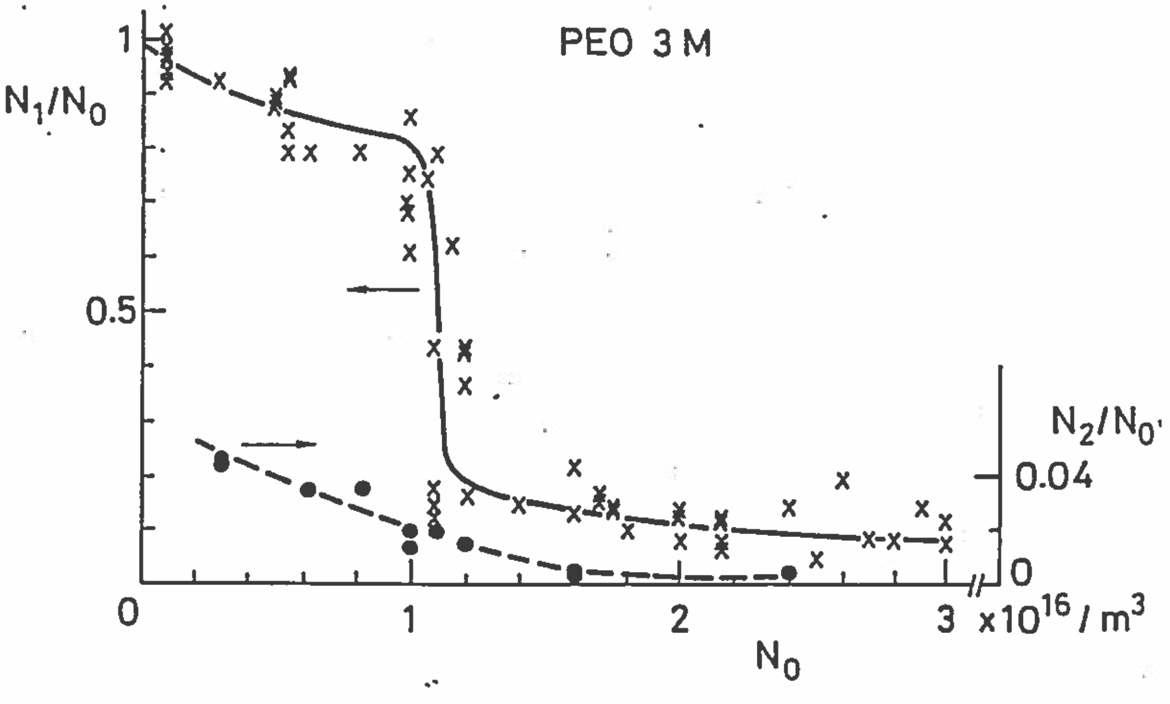
Based on work done by E.G.M. Pelssen, M.A. Cohen Stuart and G.J. Fleer (subm.to J.C.S.Faraday Trans (I)).

At a previous ocassion we reported on an apparatus for single particle counting, developed in our Department. (E. Pelssers, J. Lyklema, Polymer Colloid Newsletter 17 (1987) # 1, 14-19).

Using this apparatus, a study was made of the kinetics of the flocculation of polystyrene latices by poly (oxyethylene).

Flocculation takes place by bridging. As in the apparatus singlets, doublets,...up to hexaplets or even heptaplets can be recognized and counted, it was possible to monitor the changes in particle composition in detail and it was found that Smoluchowski-type kinetics did not apply.

As a typical example we present in the figure the decay of the fractions of singlets and doublets as function of the initial concentration of singlets. The poly (oxyethylene) dose was 0.34 mg m^{-2}. Pictures like this one are rather insensitive of the time of observation after mixing latex and polymer. The most prominent feature is that at $N_0 = 1.1 \times 10^{16}\ m^{-3}$ the ratio N_1/N_0 suddenly drops to a low value, after which it remains more or less constant. This reduction in the monomer concentration is not reflected in a corresponding growth of N_2/N_0; in fact it means that singlets disappear under the formation of higher aggregates.



This typically non-Smoluchowski behaviour is attributed to the dynamics of polymer adsorption on the particle surface. The basic idea is that a certain time τ (of the order of seconds) is required for polymers to attach and attain a (relatively flat) equilibrium conformation. For $t>\tau$, the polymers are inactive as bridgers, for $t<\tau$ they are active, because their adsorbed conformation is much more extended.

The characteristic dependence of N_1/N_0 on N_0 as in the figure is due to the fact that, with increasing N_0, suddenly a situation is reached where particle collisions are so frequent that the polymers form bridges before they have the time to unfold and adsorb in a flat conformation. Obviously, this observation lends itself very well for studies of the dynamics of polymer adsorption.

Extended Abstract of a paper to be presented at IUPAC International Symposium on Molecular Design of Functional Polymers, June 26-28, 1989, Seoul, Korea.

The Control of Structure in Emulsion Polymerization - Do Ik Lee

THE CONTROL OF STRUCTURE IN EMULSION POLYMERIZATION

EXTENDED ABSTRACT

Free-radical addition polymerization can be carried out using four different processes: mass or bulk, solution, suspension, and emulsion polymerization. Of these four processes, emulsion polymerization is unique because it is a heterogeneous process, in which the four reactions of polymerization: initiation, propagation, termination, and transfer, can take place in the continuous aqueous phase, on the surface of growing particles, and within the growing particles. This unique feature of emulsion polymerization offers many possibilities for designing different polymers and latexes: e.g., uniform size latex particles, high molecular-weight polymers, copolymers of difficult-to-copolymerize monomers, functionalized (surface-modified) latexes, grafted latexes, and structured latexes having core-shell, microdomain morphologies, interpenetrating polymer networks, etc. This paper will describe several aspects of the control of structure in emulsion polymerization.

Mechanism of Emulsion Polymerization and Mode of Monomer Additions - Latex particles are initially formed by three different mechanisms: micellar nucleation (1, 2), homogeneous nucleation (3), and polymerization in sub-micron sized monomer droplets (4). After the formation of particles, they will continuously grow as segregated polymerization reactors. Emulsion polymerization can be carried out by three different processes depending on the mode of monomer additions: batch, semi-continuous, and continuous processes. These different processes again offer many additional possibilities for control of the structure of latex polymers and multi-phase particles. The semi-continuous process is particularly versatile for designing structured latexes.

Preparation of Uniform Particles - Emulsion polymerization is capable of producing uniform particles having diameters ranging from 100 nm to 1000 nm. Usually, sequential emulsion polymerizations are used to prepare uniform particles larger than 500 nm. Uniform particle-size latexes are used for calibration of analytical measurements, and for a variety of medical diagnostic tests.

Preparation of High Molecular-Weight Polymers - Because the rate of emulsion polymerization depends only on the number of particles and the monomer concentration and is independent of the radical concentration during the steady-state growth period, molecular weights can be increased by increasing number of latex particles without slowing down the polymerization rate, unlike the other polymerization processes:

$R_p \ \alpha \ N$ (number of particles)

$DP \ \alpha \ N/\rho$ (rate of radical generation)

Emulsion Copolymerization - Emulsion copolymerization depends not only on the comonomer reactivity ratios, but also on the water solubilities and partition coefficients between the aqueous phase and polymer particles, which would determine the actual monomer concentrations at the polymerization loci. By controlling the monomer feeds based on the above knowledge, emulsion polymerization can lead to copolymers of desired compositions. In addition, emulsion polymerization can produce copolymers of difficult-to-copolymerize monomers by keeping the feeds of monomers of any given ratios close to the rate of monomer consumption.

Functionalized Latexes - It is relatively easy to functionalize latexes with polar or water-soluble monomers containing carboxylic, sulfonic, hydroxyl, epoxide, aldehyde, amide, amine, and quaternary ammonium groups. These polymerize in the aqueous phase, and the growing chains adsorb onto the growing particle surfaces, and then continue to polymerize either on the surface of particles or within the particles, resulting in functionalized latexes.

Grafted Latexes - Various polymers can be grafted onto latex particle surface layers containing double-bonds. SAN (styrene-acrylonitrile copolymer)-grafted polybutadiene latexes are well-known examples of grafted latexes, which are widely used as impact-modifiers for ABS (acrylonitrile-butadiene-styrene) plastics. Similarly, PMMA (polymethyl methacrylate)-grafted rubber latexes are widely used for PVC (polyvinyl chloride) plastics.

Structured Latexes (5, 6) - Emulsion polymerization is well suited for the production of multi-phase polymers. For this reason, a great deal of research on multi-phase polymer latex systems has been carried out in both academic and industrial laboratories. Many different structured latex products have been patented for a variety of industrial applications. Also, many papers have been published on the morphology of structured latex particles, processes to control latex particle morphology, morphology-property relationships, etc. Currently, a deeper understanding of the morphology of structured latex particles is being gained by both theoretical and ever-improving experimental methodology.

In summary, emulsion polymerization is widely used to produce latexes (polymer colloids: aqueous dispersions of colloidal polymer particles) for a variety of applications. These include rubber products, paints, coatings, adhesives, high-impact modifiers for various plastics, calibration standards, diagnostic tests, etc. Polymer colloids are also used as model colloids in research areas involved with colloid and surface science. Certainly, wide use of emulsion polymerization can be attributed to versatility and flexibility in controlling the structure of latexes, as shown in the present paper, along with the ease of latex manufacturing processes (low viscosity at high solids, easy heat removal, etc.).

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5. Daniel, J., Makromol. Chem., Suppl. 10/11, 359 (1985).
6. Eliseever, V., Prog. Org. Coatings, 13, 195 (1985).

CONTRIBUTION TO THE INTERNATIONAL POLYMER COLLOIDS GROUP NEWSLETTER

Frank L. Saunders, Do Ik Lee
The Dow Chemical Company
Midland, Michigan 48674

Abstract and Introduction of a paper presented at International Symposium on Pigment Coating Structure and Rheology, February 8-9, 1989, Helsinki, Finland.

High Solids Latex Coating Rheology and Performance - Ron Van Gilder

ABSTRACT

The pursuit of higher coating color solids content is limited by the solids content of the latex binders. Most of the current styrene(S)-butadiene (B) latex binders used in blade coating are in the range of 48-52% solids. The solids-viscosity relationship of such latexes is largely dependent on the average particle size and on particle size distribution.

Modification of the latex particle size distribution from a monodisperse to a particular bimodal distribution can affect advantageously both (a) the latex viscosity-solids relationship and (b) the paper coating color rheology for blade coater runnability. With such a modification a high-solids latex can be designed for high solids paper coatings. The use of a high-solids latex can contribute to an improvement in coating properties, because it can increase the color solids approximately 2% beyond the solids contents level achievable with conventional latexes. Coating surface structures at the higher solids level are smooth and uniform in microporosity.

INTRODUCTION

Coating colors need to be higher in solids content in order to improve properties of the coated paper, increase production rates, and reduce energy costs. This limitation is significant not only in the pigmented latex coating colors but also in the case where natural binders such as starch are included in the clay/latex coating color. Because of the high viscosity, for handling purposes the maximum solids for the clay slurry is 70%, while that of the starch solutions is in the range of 25-30%. This leaves synthetic latex as the remaining color component that could increase solids content. For these reasons, we decided to determine the effect of using a latex that had a higher solids content with good handling viscosity and that also resulted in good blade coater runnability at high coating color solids.

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Polymer Colloids at the University of Sydney

Reporter: D. H. Napper

The Mechanism of Entry of Free Radicals into Latex Particles

The mechanism whereby free radicals generated in the aqueous phase are able to enter latex particles has long been a source of speculation. It seems reasonable to postulate, as did Priest in 1952, that e.g., sulfate anion free radicals $SO_4^{\cdot -}$ were unlikely *per se* to enter latex particles; rather, it would be expected that such charged, hydrophilic species would undergo entry only after the addition of one or more monomer molecules. This addition of monomer molecules would be expected to render the free radical species surface active or, if sufficient monomers were added, even to render the free radical species insoluble. Entry would then result either from the adsorption of the surface active species onto the particle surfaces and/or the heterocoagulation of the precipitated species with the latex particles.

Not surprisingly, the actual rate determining step in entry has also been the subject of considerable speculation. At least three models have been proposed with somewhat different rate determining steps: one model is collisional (Gordon), a second is diffusive (Fitch *et al.*; Hansen and Ugelstad) and a third is colloidal (Penboss *et al.*) in character. The difficulty has always been to reconcile the predictions of theory with the experimental results. The measured second order rate coefficient for entry k_e (defined by $\rho = k_e [M\cdot]_{aq}$, where ρ = pseudo-first order entry rate coefficient and $[M\cdot]_{aq}$ = aqueous phase concentration of free radicals) is found for styrene to be of order 10^5–10^6 $dm^3\ mol^{-1}\ s^{-1}$. All three theoretical models predict values of k_e orders of magnitude larger than this. Further, it was found that the measured first order entry rate coefficient is independent of (i) the ionic strength for a charged essentially primary free radical; (ii) the presence or absence of charge on the primary free radical; (iii) the degree of surface coverage of the latex particles by surfactant with a charged primary free radical and (iv) the concentration of monomer in the latex particles. Although collisional theory could be virtually eliminated by these experimental findings, it was not possible to differentiate experimentally between the diffusive and colloidal theories, although neither theory seemed fit with all the experimental data. Both theories postulate that the rate determining step in entry is associated with the diffusion of some free radical species(be it a dissolved oligomeric surfactant or an insoluble colloidal entity) into the latex particle. The relatively small experimental value of k_e require, however, a significant barrier to diffusion, the physical origin of which far from obvious.

Ian Maxwell and Brad Morrison in the Sydney Group have shown that the difficulties associated with entry can be resolved, at least in the case of styrene, if it is postulated that the rate determining step for entry is the propagation of the free radicals in the aqueous phase. The aqueous phase processes can be modelled by an extension of HUFT theory. When applied to experimental data, the resulting theory yields *inter alia* the number of monomer molecules that must be added to the primary sulfate anion free radicals to render them capable of entry. For styrene, only one or two monomer units are required according to this theory to impart surface activity. Monomers like butyl acrylate and butyl methacrylate, which display comparable saturation solubilities in water, give similar values for the number of monomer units that must be added to the primary sulfate free radical to impart surface activity. The results obtained in this way can be rationalized by thermodynamic consideration of the free energies of adsorption (or dimerization) of the oligomeric chains. This model for entry also provides an interesting explanation for many of the curious phenomena observed in butadiene emulsion polymerization. It further predicts accurately the activation energy (ca. 24 kJ mol^{-1}) observed experimentally for entry in styrene systems.

Ofcourse, if the rate determining step is propagation in the aqueous phase then it would be expected that the entry rate coefficient would be independent of the electrical nature of the primary free radicals, of the ionic strength of the continuous phase, of the surfactant surface coverage and of the degree of monomer swelling of the particles as was indeed experimentally. The entry rate coefficient is, however, a sensitive function of the latex particle concentration and thus, for a fixed volume fraction of latex particles, a function of the particle size.

Contribution to Polymer Colloids Group Newsletter

by
Mamoru Nomura
Department of Materials Science and Engineering
Fukui University, Fukui, Japan

Our Industrial Chemistry Department has recently been reorganized and changed its name as above to cover wider educational and research area than before.

We held a biennial three days symposium, "The 5th Polymer Microspheres Symposium, Japan" in Yokohama this time in November 11-17, 1988. This meeting was very successful, gathering more than 300 participants. Professor D.H. Napper was invited as a plenary lecturer. The titles of the papers presented are listed below for reference. Preprints are available, although written in english. Please write me for more information on the preprint.

We have published two papers "Investigation on the Locus of Particle Formation Containing Partially Water-Soluble Monomers., M. Nomura et al. J. Polymer Sci., Part C <u>26</u> 385 (1988)" and "Kinetics and Mechanism of Emulsion Copolymerization. IV. Kinetic Modeling of Emulsion Copolymerization of Styrene and Methyl Methacrylate., M. Nomura et al., J Appl. Polymer Sci., <u>37</u> 1029 (1989)

We are planning to organize "International Symposium on Polymeric Microspheres" in Fukui University on the last week of October in 1991 under the auspices of the Ministry of Education, Japan and in association with Lehigh University(EPI), McMaster University(MIPPT) and CNRS(LMO). First circular will be sent to all the members of the IPCG by the end of this year at the latest.

<u>Titles of the papers presented at 5th Polymer Microspheres Symposium, Japan</u>

102 Preparation of monodisperse polystyrene particles by dispersion polymerization; K Yamamoto, Y. Ikeda, F. Takeuchi, M. Hasegawa and S. Kawase (Soken Chemical & Engineering Co.,Ltd)

103 Preparation of Micron-size Monodisperse Polymer Microspheres having Chloromethyl group M. Okubo, K. Ikegami, and Y.Yamamoto (Dept. of Industrial Chemistry, Kobe University, Rokko, Nada, Kobe 657)

104 Synthesis of polymeric microspheres with active functional groups by means of radiation-induced polymerization in the presence of organic solvents and their reactivities; M. Yoshida, M. M. Asano, and M. Kumakura (Dept. of Development, Takasaki Radiation Chemistry Research Establishment, Japan Atomic Energy Research Institute, Takasaki, Gunma)

105 Synthesis of latex containing thiol groups on the surface; S. Watanabe, K.Yamaguchi, and S. Nakahama (Dept. of polym. chem.,Tokyo Institute of technology, Tokyo 152)

106 Preparation of amphoteric hydrogel microsheres and their features; S. Kataoka, H. Kawaguchi, Y. Ohtsuka (Faculty of Sci. & Technol. Keio Univ., Hiyoshi, Yokohama 223)

107 Application of Microspheres for biotechnology and medical field; M.

Hikata (Japan Synthetic Rubber Co., Tokyo Research Lab.)

110 Preparation, Properties, and possible applications of polymer-complexed lipid vesicles; T.Kondo (Faculty of Phrmaceutical Sciences, Science University of Tokyo, Shinjuku-ku, Tokyo 162)

113 Analysis of receptor on rat hepatocyte; A. Yagawa, A. Maeda, S. Tobe, H. Nomoto, T. Akaike (Faculty of Technology, Tokyo University of Agr. and Tech.,2-24-16, Koganei, Tokyo 184) K.Kobayashi, H. Sumitomo (Faculty of Agriculture, Nagoya University, Chikusa, Nagoya 464)

115 Study on Latex Reagents from the Viewpoint of Colloid Chemistry.
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microspheres by radiation polymerization and possible application in
medical field; Y. Naka, I. Kaetsu (Kinki Univ.) Y. Yamamoto, K.
Kobayashi, M. Miki, and K. Hayashi (Osaka Univ.)

117 Synthesis and characterization of Fluorescent and Magnetic Immunolatex particles; N. Yanase, H. Asakura, T. Suzuta (Dept. of Immunology and Serology, Tokyo Medical College, Tokyo) H. Noguchi, Y. Uchida (Dept. of Industrial Chemistry, University of Tokyo, Tokyo)

119 Interaction of microcapsules with guinea pig polymorphonuclear Leukocytes; S. Yasukawa, N. Muramatsu, H. Ohshima, and T. Kondo (Dept. of Pharmaceutical Sci. and Institute of Colloid and Interface Science. Science University of Tokyo, Shinjyuku 162)

120 Application of Polymeric Microspheres to Functional Analyses of Blood Cells and Blood; M. Miyamoto, S. Sasakawa (Dept. of Research, Central Blood Center, Japanese Red Cross, Shibuya-ku, Toyko 150) T. Ozawa, Y. Mikami, H. Kawaguchi and Y. Ohtsuka (Faculty of Sci. & Technol. Keio Univ., Kohoku-ku, Yokohama 223)

121 Preparation of fluorogenic substrate-bound polymer microspheres and their application to the measurement of lysosomal enzyme activity in phagocyte; S. Hosaka, T. Uchida (Basic Research Lab., Toray Industries, Inc.) K.Suzuki (National Institute of Health, Japan)

122 Preparation and Evaluation of poly- -hydroxybutyric acid (PHB) microspheres containing an anticancer agent; M. Kubota et al.(Dept. of Pharmacy, Kumamoto University Hospital, 1-1-1 Honjo, Kumamoto 860), and K. Junji (Faculty of Pharmaceutical Sci., Josai University, 1-1 Keyakidai, Sakado, Saitama 350-02)

123 O/O type solvent evapolation method for preparation of poly(lactic acid) microspheres containing hydrophilic drug; R. Wada S.-H. Hyon and Y. Ikada (Research Center for Medical Polymers and Biomaterials, Kyoto Univ., 53 Kawahara-cho, Syogoin Sakyo-ku Kyoto, 606)

124 Preparation of DNA chains-carrying latex particles and their applications for protein purification; H. Kawaguch et al. (Faculty of Sci., and Technol., Keio Univ., Hiyoshi, Yokohama 223), and H. Handa (Faculty of Medicine, Tokyo Univ., Hongo, Tokyo 113)

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201 Emulsion polymerization of styrene initiated by AIBN; K. Fujita and M. Nomura (Dept. of Industrial Chemistry, Fukui Univ., Bunkyo, Fukui, 910)

202 A Study on diffusional behavior of mercaptan chain-transfer agents in emulsion polymerization of styrene; H. Suzuki and M. Nomura (Dept. of Industrial Chemistry, Fukui Univ., Bunkyo, Fukui, 910)

203 A study on emulsion polymerization using photoinitiation and scattering method; H. Hashiya and T. Matsuo (Faculty of Engineering, Fukui Univ., Bunkyo, Fukui, 910)

204 Influence of the characterization of the particle surface on the

protein adsorption onto the latex particles; T. Arai and H. Kitamura (College of Industrial Technology, Nihon Univ., Narashino)

205 Flocculation behavior of various polymer latices by albumine; (T. Suzawa et al., (Hiroshima Univ., Saijo-cho, Higashihiroshima, 724)

206 Preferential adsorption behavior of BSA oligomer onto polymer microspheres having various surface hydrophilicities; M. Okubo et al., (Dept. of Industrial Chemistry, Kobe Univ., Rokko, Nada, Kobe 657)

207 Properties and applications of inorganic fine particles; S. Hayakawa (Faculty of Engineering, Chiba Univ., Yayoi-cho 1-33, Chiba city, Chiba)

P01 Copolymerization in W/O microemulsions; K. Kon-no and K. Kumazawa (Fac. of Eng., Sci. Univ. of Tokyo, Kagurazaka, Shinjuku-ku, Tokyo 162)

P02 Radiation-induced cross-linking of poly(Methyl Acrylate) emulsion particles; T. Yamamoto and Y. Doi (Osaka Lab., Showa Highpolymer Co. Ltd., Tatuno, Hyogo), M. Nishi and M. Hatada (JAERI Osaka, Osaka)

P03 ESCA analysis of composite polymer microspheres produced by emulsifier-free emulsion polymerization; M. Okubo et al. (Dept. of Industrial Chemistry, Kobe Univ., Rokko, Nada, Kobe 657)

P04 Competitive and displacement adsorption of proteins onto latex particles; H. Kawaguchi et al. (Fac. of Eng. & Tech., Keio Univ., Hiyoshi, Kohoku-ku, Yokohama 223)

P05 Phagocytosis of fluorescent latex particles with different sizes by the rat alveolar macrophages: Comparison between in vitro and in vivo experiments; K. Moriguchi & T. Arai (College of Ind. Technol. Nihon Univ.) S. Takahashi (National Inst. of Radiol. Sci., Chiba)

P06 Application of latex particles as polymer drug; H. Kawaguchi et al. (Fac. of Sci. & Tech., Keio Univ., Hiyoshi, Yokohama 223) T. Takeuchi et al. (School of Medicine, Keio Univ., Sinanomachi, Shinjuku 160)

P07 Micro-lens based on Moire patterns of dot lines; S. Hayashi et al. (Fac. of Textile Sci. & Technol. Shinshu Univ., Ueda, Nagano, 386), M. Murayama (Daido-Maruta Finishing Co. Ltd., Minamiochiai, Kisshoin, Minami-ku, Kyoto 601)

Invited lecture: The Formation and Growth of Latex Particles; D.H. Napper (Dept. of Physical Chemistry, The University of Sydney, NSW 2006 Australia)

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215 Repeated use of emulsifier-free anionic polymer emulsion in chemical deposition coatings onto anodized aluminum plate; M. Okubo et al. (Fac. of Engi., Kobe Univ. Rokko, Nada-ku, Kobe 657)

216 Lowering of the internal stress of the epoxy resin by the modification with acrylic polymer; Y. Nakamura et al.,(Central Research Lab., Nitto Denko Co., Shimohozumi, Ibaraki, Osaka 567), K. Okubo et al. (Dept. of Industrial Chemistry, Kobe Univ., Nada-ku Kobe, 657)

217 Study of microgel as pigment dispersant; K. Ishii and S. Ishikura (Nippon Paint Co., Ltd, Neyagawa, Osaka)

218 On the stability of combined polymer dispersions with complementary reactive groups; M. Yabuta et al. (Technical R & D Department, Kansai Paint Co., Ltd., Kanagawa)

219 Flocculation of colloidal particles with particles of opposite charge; K. Higasitani (Fac. of Eng. Kyushu Inst. of Tech. Kitakyushu 804)

220 Synthesis of ultra fine platinum particles protected by Polymeric Microspheres and their catalytic action; N. Toshima et al.(Univ. of Tokyo, Fac. of Eng., Hongo, Tokyo)

221 Immobilization of glucose isomerase by microencapsulation; S. Omi et al. (Tokyo Univ. of Agriculture & Technology, Koganei, Tokyo)

222 Permeability of drugs through EVA copolymer microcapsules; T. Kondo et

al. (Science Univ. of Tokyo, Shinjuku, 162)

301 Crystal-like structure of anisotropic polymer colloids; T. Okubo (Dept. of Polymer Chem., Kyoto Univ. kyoto 606)

302 Crystal-like structure of anisotropic polymer colloids at the interface; T. Okubo (Dept. of Polymer Chem., Kyoto Univ. kyoto 606)

303 Optical examination of structured polystyrene latices modified by hydrophilic comonomers; S. Singae (Japan Synthetic Rubber Co., Ltd) & R.H. Ottewill (School of Chemistry, Univ. of Bristol, U.K.)

304 Effect of aqueous polymer on ordering in monodispersed latex systems; K. Furusawa et al. (The univ. of Tsukuba, Tsukuba, Ibaraki, 305)

305 Surface characteristic of concentrated latex dispersion; K. Furusawa (The univ. of Tsukuba, Tsukuba, Ibaraki, 305), Y. Hozumi (Nippon Shokubai Co., Ltd, Kawasaki, Kanagawa, 210)

306 Computer simulation of coagulation colloid; M. Doi et al. (Dept. of Physics, Tokyo Metropolitan Univ., Fukazawa, Setagaya, Tokyo 158)

307 The features of emulsion polymerization in the presence of PVA; K. yuki et al., (Kuraray Co., Ltd., Kurashiki, Okayama)

308 Relations between microgel surface functionality and physical properties of the microgel containing film; F.Sakurai & O. Ohe (Nippon Oil & Fats Co., Paint Research Lab.)

309 Composite PVC-based latices with MMA, ST shell monomers; S. Omi et al. (Tokyo Univ. of Agriculture & Technology, Koganei, Tokyo), A. Nakano et al. (Nippon Zeon Co., Ltd. Kawasaki, Kanagawa)

310 Polymer monomolecular particles; J. Kumaki (Plastic Labs. Toray Industries Inc. 9-1, Ooe, Minato-ku, Nagoya, Aichi 455-91)

313 The synthesis of core-corona type microgel by using the block copolymer micelle in selective solvent; T. Fukutomi et al. (Tokyo Institute of Technology, Ookayama, Meguro-ku, 152)

314 The synthesis of microsphere and its use to modify the surface of membrane; T. Fukutomi et al. (Tokyo Institute of Technology, Ookayama, Meguro-ku, Tokyo 152)

315 Studies on Heterogeneous structure of seeded emulsion particles; S. Izumoto et al. (Daicel Chemical Industries, Ltd., Research Center, 1239 Shinzaike, Aboshi-ku, Himeji, 671-12)

316 Preparation of multi-layered fine particles and their characteristics; S. Kawase et al. (Soken Chemical & Engineering Co., Ltd)

317 Preparation of latex-silica composite particles by heterocoagulation; K. Furusawa (Univ. of Tsukuba, Tsukuba, Ibaraki) C. Anzai (Hoechst Gosei K. K., Tokyo)

318 Study of Morphology by blend; M. Sekiya et al. (R&D Center, Nippon Zeon Co., Ltd.)

319 Morphological studies on lod-like poly(tetrafluoroethylene) particles; T. Shimizu et al. (Daikin Industries Co., Ltd., Osaka 566)

320 Synthesis of anomalous polymer microspheres by seeded emulsion polymerization method; M. Okubo et al. (Dept. of Industrial Chemistry, Kobe Univ. Rokko, Nada, Kobe 657)

MORPHOLOGY OF CO-POLYMER COLLOIDAL PARTICLES

G.A. Bootle, J.E. Lye and R.H. Ottewill,*
School of Chemistry
University of Bristol
U.K.

Polymer colloid particles prepared using a single monomer can be described as homogeneous in a broad sense. When a mixture of monomers are used, however, the co-polymer particles formed can have various types of morphologies which qualitatively might be described as "core-shell" or "currant bun". With this more complex morphology a need arises for methods of determining the type of particle structure formed and then controlling it. Thus a point of fundamental interest is to understand the factors which lead to various types of particle morphology.

In recent years we have examined, in particular, the use of small angle neutron scattering and electron microscopy as methods likely to probe the particle structure. The former technique depends upon measuring the intensity of neutrons scattered at small angles, θ, to the direction of the incident beam. For elastic scattering this defines the scattering vector as,

$$Q = 4\pi \sin(\theta/2)/\lambda$$

where λ is the wavelength of the incident beam. For a single homogeneous spherical particle of radius R the scattered intensity at a particular value of Q is given by,

$$I(Q) = A(\rho_p - \rho_m)^2 N_p V_p^2 P(Q)$$

where A = an instrumental constant, N_p = the number of particles per unit volume, V_p = the volume of each particle and P(Q) is the particle form factor, in this case for spheres. ρ_p is the coherent scattering length of the particle and ρ_m that of the medium. These quantities are directly related to the scattering properties of atomic nuclei and hence there is a major difference in the scattering of neutrons by hydrogen and deuterium and hence between H_2O and D_2O and between hydrogenated and deuterated polymers.

For the case of core-shell morphology the scattering can be represented as being that of a concentric shell of one polymer over a core of another, as shown schematically in Figure 1.

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* to present lecture

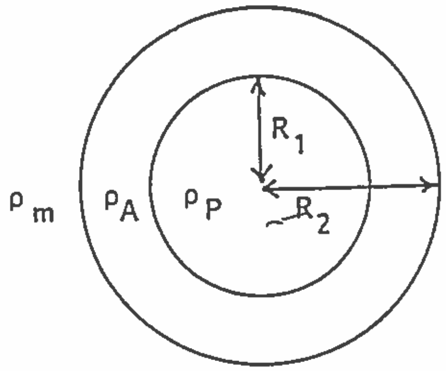

Figure 1: Spherical core particle, radius R_1, neutron scattering length density, ρ_p, with a concentric shell of neutron scattering length, ρ_A, in a medium of scattering length density, ρ_m. Total particle radius, R_2.

In this case there is interference between the beams scattered from the core and those scattered from the shell which leads to substantial changes in the scattering patterns as the medium is changed from H_2O to D_2O. Theoretical plots illustrating this are shown in Figure 2, and some experimental results for d-polystyrene - polyacrylonitrile particles are shown in Figure 3. The trends in both the theoretical and experimental curves are very similar, suggesting that the particles had a core-shell morphology.

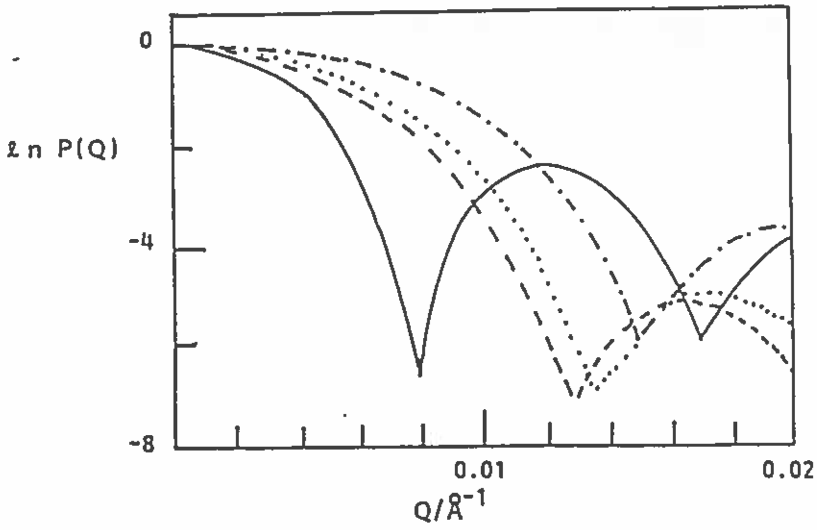

Figure 2: Computed scattering curves for a concentric sphere with a core of d-polystyrene, radius 330 Å and $\rho_p = 6.47 \times 10^{10}$ cm^{-2}, and a shell of polyacrylonitrile, thickness 50 Å and $\rho_A = 2.27 \times 10^{10}$ cm^{-2} in various media: – – –, $\rho_m = -0.56 \times 10^{10}$ cm^{-2}; ······, $\rho_m = 2.64 \times 10^{10}$ cm^{-2}; –·–·–, $\rho_m = 4.17 \times 10^{10}$ cm^{-2}; ———, $\rho_m = 6.00 \times 10^{10}$ cm^{-2}.

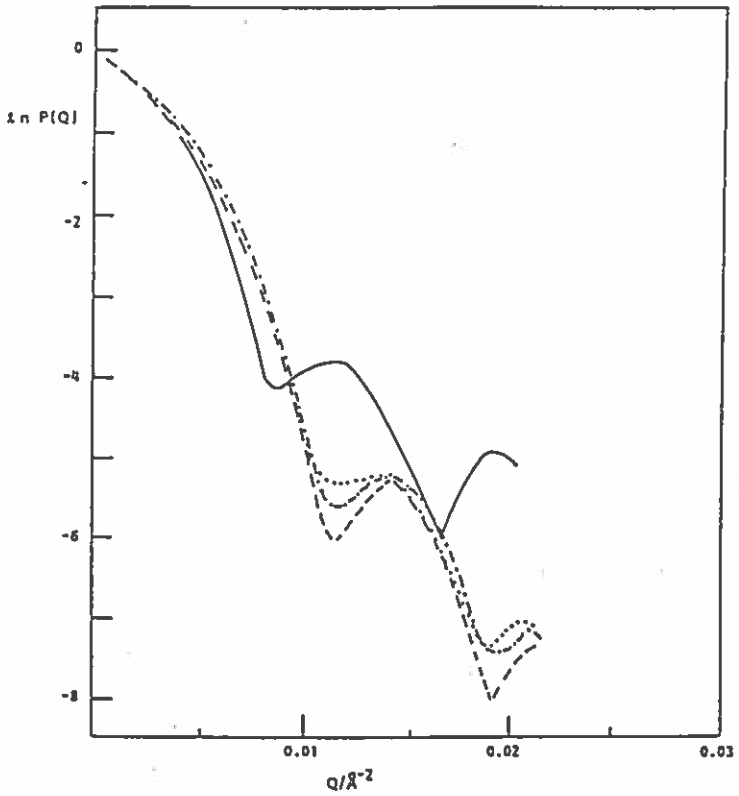

Figure 3: Experimental curves obtained on d-PS:PAN (80:20) latices in various H_2O:D_2O mixtures: ······, H_2O (ρ_m = -0.56 x 10^{10} cm^{-2}); -·-·-, 28% D_2O (ρ_m = 1.40 x 10^{10} cm^{-2}); - - - , 68% D_2O (ρ_m = 4.17 x 10^{10} cm^{-2}); ———, 94% D_2O (ρ_m = 6.00 x 10^{10} cm^{-2}).

Analysis of these data gave the final composition of the particles as 84% deuterated polystyrene and 16% polyacrylonitrile which compared with the initial monomer ratio of 80% d-styrene and 20% acrylonitrile. A fit to the experimental scattering data suggested a core particle with a radius of 46 nm with a shell of thickness 5 nm.

An alternative method of obtaining information about the structure is to take the Fourier transform of the scattered intensity. This gives the density distribution, P(r), as a function of distance r, i.e. the distribution in real space terms. An example is given in Figure 4. For investigations in H_2O the scattering is dominated by the deuterated material and the curve obtained under the conditions suggests spherical geometry. In D_2O, however, the deuterated polystyrene is similar in scattering length to the medium and hence the scattering is dominated by the polyacrylonitrile. Under these conditions the size of the particle has increased giving a strong indication that the polyacrylonitrile is on the outside of the particle. The dip in the middle of the curve suggests that the boundary between the core of d-polystyrene and polyacrylonitrile is not sharp but there is interdiffusion between the two polymers.

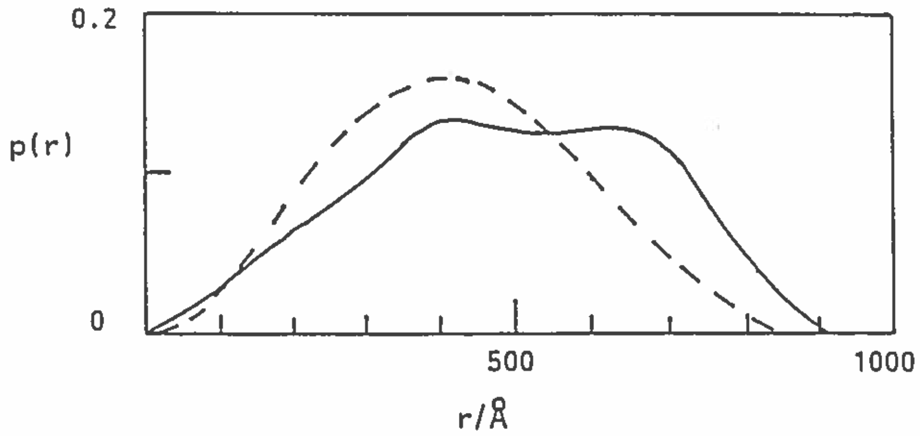

Figure 9: p(r) against r for a copolymer latex (d-PS:PAN, 80:20); – – –, H_2O; ——, in D_2O.

Polymer latices have been prepared using mixed monomer systems, namely, acrylonitrile and styrene, acrylonitrile and deuterostyrene and styrene and deuterostyrene. The use of small angle neutron scattering on these systems will be described. In addition, the application of electron microscopy will be briefly described.

Contribution to Polymer Colloid Newsletter

R. PELTON AND A.E. HAMIELEC

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A comparison of chain length distributions of polymers terminally and randomly anchored to a solid/solution interface.

by Robert H. Pelton

Expressions were derived for the length distributions of polymer chains anchored to a surface by a single point. Two cases were considered. The first case was the formation of two attached chains by the attachment of a precursor (unattached) polymer at a randomly distributed position along the backbone. The second case was the attachment of precursor by end groups. These results are relevant to the properties of the stabilizing layer on latexes produced by nonaqueous dispersion polymerization.

For an ideal condensation polymer (eg. polydimethylsiloxane) the distribution of tail lengths (assuming no adsorption) for random attachment at one point is:

$$Ng_x = \sum_{j=x}^{j=\infty} p^{(j-1)} (1-p)(1/j) \qquad [1]$$

where Ng_x is the number fraction of tails of length x
p is the degree of condensation of graft precursor

The corresponding average degree of polymerization of the grafted tails, DP_{gn}, is related to the degree of polymerization of precursor, DP_n, by the following relation

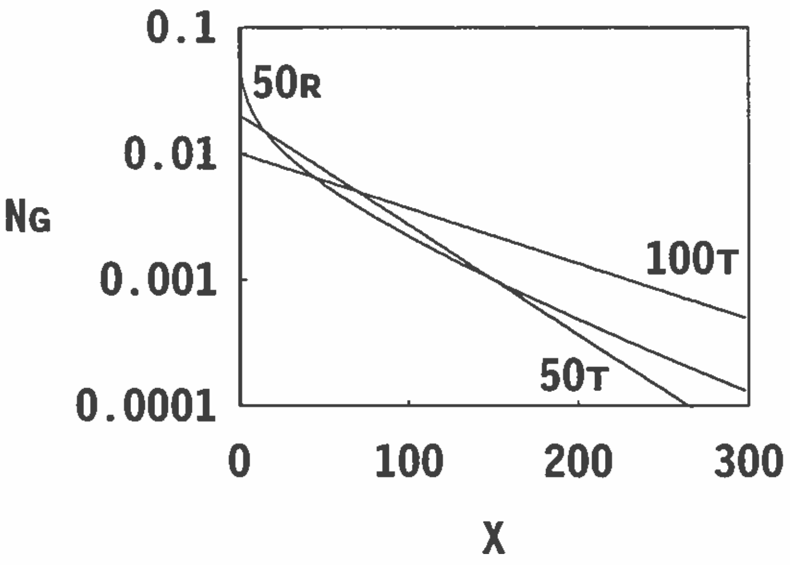
$$DP_{gn} = \frac{DP_n + 1}{2} \simeq \frac{DP_n}{2} \qquad [2]$$

For an ideal condensation polymer, $DP_n = 1/(1-p)$ and this becomes

$$DP_{gn} = \frac{1}{2(1-p)} \qquad [3]$$

For a terminally attached chain $DP_{gn} = DP_n$. These relationships have relevance to sterically stabilized systems in which the stabilizer chain is attached by only one point.

Figure Number fraction distribution of chain lengths. The numbers beside the curves indicates the number average degree of polymerization, DP_{gn}. R denotes randomly grafted precursor polymer whereas T denotes terminally anchored chains.



NON-AQUEOUS DISPERSION POLYMERIZATION OF SILICONE STABILIZED PMMA.

R.H. Pelton, M.A. Brook, and A. Osterroth

The polymerization of methyl methacrylate in heptane in the presence of polydimethylsiloxane (PDMS) and vinyl terminated polydimethylsiloxane (PDMS-V) was systematically investigated. The siloxane is thought to be grafted onto the surface of the PMMA particles thus giving steric stabilization.

At a constant silicone weight concentration, the minimum degree of silicone polymerization, DP_n, for stable latex was between 378 and 847 for PDMS and between 10 and 17 for PDMS-V. The following conclusions are based on arguments presented in a manuscript submitted to Journal of Colloid and Interface Science.

The lowest DP_n of PDMS-V for stable latex (between 10-17) was determined by the minimum thickness of the steric barrier for stable latex. If too thin, van der Waals forces cause latex aggregation. By contrast, the lower PDMS DP for stable latex (between 378 and 847) reflected the minimum latex particle surface area covered per grafted silicone chain. These differences arise from the higher grafting efficiency of the vinyl terminated silicones.

MECHANISMS AND KINETICS OF THE SUSPENSION POLYMERIZATION OF VINYL CHLORIDE AT HIGH CONVERSIONS - EFFECT OF MONOMER CONCENTRATION, TEMPERATURE PROGRAMMING AND n-BUTANE LEVEL ON KINETICS AND PROPERTIES OF PVC

T.Y. Xie, A.E. Hamielec, P.E. Wood and D.R. Woods

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ABSTRACT:

The suspension polymerization of vinyl chloride is a typical heterogeneous process due to the very low solubility of polyvinylchloride in its monomer. The polymerization occurs in two phases - monomer and polymer - rich phases until a critical conversion at which point the monomer-rich phase is consumed. Thereafter, the polymerization proceeds in a single phase. A comprehensive kinetic model which accounts for radicals transfer between phases initiator and monomer partition in the phases (monomer, polymer and gas) has been developed based on the elementary reactions which have recently been identified as likely by C^{13}-NMR. This model can be used for the entire conversion range for the suspension or bulk polymerization of vinyl chloride. A series of experiments on suspension polymerization of vinyl chloride in a 5-litre reactor have been carried out, which include batch, semi-batch polymerization with temperature programming at high conversions. The conversions were measured by n-butane tracer technique. The diffusion controlled reactions in the polymer phase, particularly at high conversions, were investigated. Comparisons between kinetic model predictions and experimental data will be made. The effect of monomer concentration, temperature programming and n-butane level at high conversions on the polymerization rate, molecular weight development and thermal stability of PVC will be discussed. A strategy to improve the thermal stability of rigid grade PVC will be suggested.

NETWORK FORMATION IN FREE RADICAL POLYMERIZATION

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ABSTRACT:

A kinetic model for network formation in free radical copolymerization of vinyl and divinyl monomers is proposed. Since network formation in free radical polymerization is a non-equilibrium process, namely, it is kinetically controlled, the history of the generated network structure must be considered. In free radical polymerization, each primary polymer molecule experiences a different history of crosslinking and cyclization and, therefore, a polymer network possesses "a crosslinking density distribution". The variance of this distribution becomes significant when the polymerization conditions deviate from Flory's simplifying assumptions. The concept of crosslinking density distribution makes it possible to generalize Flory's theory of network formation. Also to be discussed is the formation mechanism of spatially inhomogeneous networks.

SUSPENSION POLYMERIZATION OF STYRENE - AN EVALUATION OF BIFUNCTIONAL INITIATORS

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McMaster University,
Hamilton, Ontario, Canada L8S 4L7

ABSTRACT:

Three symmetrical bifunctional initiators were evaluated experimentally for the bulk polymerization of styrene over wide ranges of concentration and temperatures to obtain a product with the molecular weight characteristics of expandable polystyrene (EPS). Reductions in reaction time of up to 75% (compared to the traditional use of monofunctional initiators) were achieved with bifunctional initiators obtaining the same levels of conversion and essentially the same molecular weights. It was found that almost insignificant broadening of the molecular weight distribution occurs at high polymerization rates with bifunctional initiators.

A reaction mechanism is proposed for the bifunctional system and the kinetic model derived was solved using the method of moments. A computer simulation program was developed and its predictions are in very good agreement with experimental data. Diffusion-controlled termination and propagation were modelled using the free volume theory.

A 1-gallon pilot-plant suspension polymerization reactor was scaled-down to obtain the desired mean particle size (MPS) with the traditional suspension process. Previously-simulated short-cycle runs with bifunctional initiators, at polymerization temperatures below and above Tg, were performed without noticeable effects on the suspension stability, MPS or particle size distribution (PSD).

RADICAL TRAPPING AND TERMINATION IN FREE-RADICAL POLYMERIZATION OF METHYL METHACRYLATE

S. Zhu, Y. Tian, A.E. Hamielec and D.R. Eaton*

Institute for Polymer Production Technology,
Department of Chemical Engineering,
McMaster University,
Hamilton, Ontario, Canada L8S 4L7

ABSTRACT:

Post-effect measurements of radical concentrations for bulk free-radical polymerization of methyl methacrylate (MMA) at 25°C with 5.0 wt% 2,2'-azobis [2-methyl-propionitrile] (AIBN) initiated by ultra-violet light (UV) were made using an on-line ESR spectrometer. Number-average termination rate constants were therefrom directly measured using radical decay rates. It was found that these termination rate constants decrease significantly in the post-effect period at high conversions. These observations are in disagreement with the concept of termination by propagation-diffusion which was expected to be the dominant mode of termination at these high conversion levels. It was also found that a fraction of the radicals are trapped during the course of polymerization. In other words, there exist two radical populations in the reacting mass: free radicals and trapped radicals. The former are in the liquid state (as indicated by 13-line ESR spectra) while the latter are in the solid state (9-line spectra). These two radical populations have very different reactivities in both propagation and termination reactions. Our data show that there is no minimum value of the termination rate constant for the long-lived trapped radicals. The trapped radical fractions measured directly herein suggest that heterogeneity in the polymerization medium can have a significant effect, and must be properly accounted for when making an analysis of the kinetics of polymerization.

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*Department of Chemistry, McMaster University

COPOLYMERIZATION OF METHYL METHACRYLATE / ETHYLENE GLYCOL DIMETHACRYLATE - MEASUREMENT OF RADICAL CONCENTRATIONS BY ESR

S. Zhu, Y. Tian, A.E. Hamielec and D.R. Eaton*

Institute for Polymer Production Technology,
Department of Chemical Engineering,
McMaster University,
Hamilton, Ontario, Canada L8S 4L7

ABSTRACT:

Stable free radicals at high concentration levels are formed during the free-radical copolymerization of MMA/EGDMA (during the course of polymerization radical concentrations can vary from 10^{-7} to 10^{-3} molar). Radical centres situated on polymer chains in a 3-dimensional crosslinked network have little mobility. Online ESR (Bruker ER-100D) was used to monitor radical concentrations during the course of polymerization. Both 13-line and 9-line spectra (and composite spectra) were observed. The 9-line spectra are normally obtained for radicals trapped in the solid state. Implications of these measurements for a more comprehensive understanding of high conversion kinetics will be discussed.

*Department of Chemistry, McMaster University

Contribution to Polymer Colloids Group Newsletter

from the University of Akron
I. Piirma

The use of amphipathic block and graft copolymers as stabilizers in colloidal dispersions has received significant attention in both the academic and the industrial arenas. However, few studies have focused on the effects of structural variations of the amphipathic materials on particle stabilization and polymerization kinetics.

Synthesis and Application in Emulsion Polymerization of Polymeric Surfactants Containing Polyoxyethylene as the Hydrophile

Reported by G. L. Jialanella

One aspect of the current study involved the synthesis of an amphipathic graft copolymer, poly(methyl methacrylate-co-2-hydroxypropyl methacrylate-g-oxyethylene), for use in the emulsion polymerization of methyl methacrylate. The stabilizing effectiveness of this graft copolymer was studied as a function of its chemical structure. These experiments were conducted by altering the molecular weight of the backbone copolymer and the polyoxyethylene graft moieties and by varying the weight ratio of the graft moieties to the backbone copolymer. It was found that when the molecular weight of the backbone was within the investigated range of $4x10^3$g/mol to $2x10^4$g/mol, stable emulsion polymerizations of methyl methacrylate were possible. Effective stabilization also occurred when the graft moieties possessed a molecular weight of either $2x10^3$g/mol or $5x10^3$g/mol.

Another aspect of this study was to evaluate the stabilizing effectiveness of well-defined block copolymers, poly(styrene-b-oxyethylene), in the emulsion polymerization of styrene. The hydrophobic portion (polystyrene block) of this amphipathic block copolymer functioned very efficiently as an anchor group when its molecular weight was approximately $1x10^3$g/mol, but an improvement was not observed by increasing the molecular weight. The stabilizing effectiveness of the block copolymer was found to be independent of the molecular weight of the hydrophilic block (polyoxyethylene block) within the range of $3x10^3$g/mol to $9x10^3$g/mol: Latices exhibited the same number of particles and the same particle size. However, the stabilizing effectiveness was dependent on the weight ratio of the two blocks, the hydrophilic/hydrophobic ratio. Block copolymers with a polyoxyethylene amount of 75% to 90% by weight, effectively stabilized emulsion polymerizations of styrene.

Synthesis of PMMA-b-PEO Copolymers and Their Application as Stabilizers in the Emulsion Polymerization of Methyl Methacrylate

Reported by Wen-Lin Wu

Diblock PMMA-b-PEO copolymers were prepared from esterification between PMMA and PEO blocks according to the following steps:

(1) a carboxylic acid terminated PMMA was made by reacting MMA/BPO/3-mercaptopropionic acid;
(2) the PMMA was treated with thionyl chloride to generate acid chloride end group;
(3) the functionalized PMMA was coupled with poly(ethylene glycol methyl ether) in the presence of triethylamine.

Subsequently, these diblock copolymers were used as sole stabilizers in the emulsion polymerization of MMA. Preliminary results on the kinetics and colloidal properties are shown in Table 1. More systematic studies will be carried out on the relationship between the structure of PMMA-b-PEO copolymers and their corresponding colloidal properties in the emulsion polymerization.

Table 1. Emulsion Polymerization of MMA using PMMA-b-PEO as Stabilizers at 45°C

Structure of PMMA-b-PEO		Rate of Polymerization	Particle Size	Number of Particles
MW(PMMA)	MW(PEO)	$R_p x10^4$(Mol/L-Sec)	Dz(nm)	$Nx10^{-16}(L^{-1})$
500	750	0.9	213	1.7
500	2000	1.5	103	14.7
500	5000	2.4	116	10.3

CONTRIBUTION TO POLYMER COLLOID GROUP NEWSLETTER

FROM

LABORATOIRE DES MATERIAUX ORGANIQUES (CNRS/LYON)
(SUBMITTED BY C.PICHOT)

KINETIC STUDIES IN EMULSION POLYMERIZATION OF 2-ETHYL -HEXYL ACRYLATE

(T.DESROCHES)

In this work,the main objective is to understand the polymerization mechanism which occurs during the emulsion polymerization of the 2-ethyl-hexyl acrylate , a monomer with a very low solubility in water and which homopolymer displays a very low Tg.The mechanism of particle formation is currently studying during the interval I of the process , in the presence of a surfactant (SDS,below and above the CMC) by following the variation of the PSD vs.conversion .It is intended to explain the behavior of this monomer during emulsion polymerization through the determination of kinetic parameters and also by studying the transport of this monomer in the aqueous phase and the stability of the corresponding latex particles.

SWELLING OF POLYBUTADIENE FILMS AND LATEXES BY STYRENE-ACRYLONITRILE MONOMERS

(P.MATHEY)

Studies on swelling by styrene/acrylonitrile mixtures have been investigated at different temperatures in the presence of either polybutadiene fims cast from latexes or polybutadiene latex particles.The influence of crosslinking density of particles has been shown with pure monomers according to the FLORY equations.Monomers mixed in various proportions were found to exhibit their own behavior ,depending on the relative concentration of the two monomers.The evaluation of diffusion coefficient for styrene and acrylonitrile in films evidenced the importance of temperature , comonomer mixture composition and crosslinking density of latex particles

FILM FORMATION STUDIES ON STYRENE-BUTYL ACRYLATE COPOLYMER LATEXES

(L.RIOS-C.GRAILLAT-Y.CHEVALIER)

This work was investigated during the sabbatical year of L.RIOS (UNAM -MEXICO)in the lab and it was mainly devoted to the influence of particle morphology in styrene-butyl acrylate copolymer latexes(with and without methacrylic acid) on the film formation process and dynamic mechanical properties of ultimate films. A series of latexes were prepared using various polymerization pathways with N.N dimethyl dodecyl ammonio propane sulfonate (NC 12) as emulsifier (so as to make sure to obtain monodisperse and small particle size in the range 50-200 nm).

The film formation phenomena are currently investigated by SANS (with B.CABANE- CEA-SACLAY) with a view to following the ordering of particles during the water evaporation and coalescence.Preliminary results show that the effect of surface coverage is an important parameter in the film structure during the drying process.In collaboration with J-Y.CAVAILLE (GEMPPM, INSA-LYON), the mechanical behavior of these films is studied by dynamic mechanical spectrometry (MECHANALYSER) in order to provide information on the film morphology.

COLLOIDAL PROPERTIES OF ZWITTERIONIC-STABILIZED POLYSTYRENE LATEXES

(B.DUMONT- C.GRAILLAT-P.DEPRAETERE)

Further work has been investigated on these latex systems in order to have a better understanding on the mode of action on various amphoteric - sulfobetaine surfactants when used either as emulsifier in emulsion polymerization or as poststabilizer of latexes .Different colloid polystyrene latexes have been prepared with varying the particle size and the surface charge density ; their stability against electrolyte and electrophoretic mobility have been examined as a function of the type of emulsifier(with reference to the SDS) and pH .Viscosity and viscoelastic measurements are currently performed on these latexes covered to saturation with the three emulsifiers , at various solids content and ionic strength.

SOFTWARE FOR DATA ACQUISITION AND TREATMENT:HYDRODYNAMIC CHROMATOGRAPHY ANALYSIS .(A.REVILLON-J.F.GUILLAND-C.GRAILLAT)

An original software (written in Turbo Pascal 4.0)has been developed for data acquisition and treatment in HDC to transform and to correct chromatograms in particle diameter distributions(D(v)). It is able to perform useful computations with high capacity and high velocity compatible with HDC requirements. Effect of calibration errors on diameter have been investigated ; number and weight average sizes have been derived through choices of different n values of the response factor ($H = N^*D^n$). Application to measurements of particle diameter of various latexes have been carried out using open capillary and packed columns.

RECENT PAPERS

*Structure properties relationships in styrene-butyl acrylate emulsion copolymers
I) Synthesis and characterization of latexes(in press POLYMER)
A.Crus,L.Rios,C.Monnet,B.Shlund,J.Guillot,C.Pichot

II) Viscoelastic properties of latex films .experimentalresults and simulation(in press POLYMER)
B.Shlund,J.Guillot,C.Pichot,A.Cruz

*Dielectric properties of cleaned and monodisperse polystyrene latexes in microwaves
(F.Henry,C.Pichot,A.Kamel,M.S El Aasser)
Colloid and Polymer Sci. 267:48 (1989)

*Study of the polymer coalescence by dielectric measurements at microwave frequency - feasibility of the method
(F.Henry,F.Cansell,J.L. Guillaume,C.Pichot)
Colloid and Polymer Sci. 267:167 (1989)

Contribution to the Polymer Colloids Group Newsletter
Spring 1989

H. THYEBAULT and G. RIESS
Ecole Nationale Supérieure de Chimie de Mulhouse (France)

The goal of Hervé THYEBAULT's thesis was to study the preparation of ABS resins by emulsion polymerization and to design a new agglomeration process for latex particles by using block copolymers based on poly(ethylene oxide).

A large variety of polybutadiene, polystyrene and acrylic latices have been synthesized by emulsion polymerization in which polystyrene-poly (ethylene oxide) di- and triblock copolymers PS-PEO and PEO-PS-PEO were used as emulsifiers.

The influence of the different reaction parameters, especially that of the block copolymers (influence of structure, molecular weight and composition) acting as emulsifiers, has been examined with respect to the polymerization kinetics and to the particle size of the latex. It could for instance be shown that triblock copolymers PEO-PS-PEO lead to smaller latex particles than a diblock copolymer PS-PEO of same composition and same molecular weight. At constant molecular weight of the copolymer, the particle size of the latex decreases with increasing PEO content.

Such "hairy latices", having on their surface PEO chains ($\overline{M}_n$ between 1,800 and 37,000), are able to agglomerate in a controlled manner anionic latices, by forming a complex between PEO and the anionic soap. The agglomeration process has been studied in detail for polybutadiene latices, stabilized with potassium laurate, which can be agglomerated with the "PEO hairy seed latices". The size of the polybutadiene latex could be increased by a factor of 6 to 8 and depending on the ratio polybutadiene latex/seed latex, it was possible to obtain either monomodal or bimodal distributions for the final latex.

ABS resins have been prepared and characterized by using such agglomerated polybutadiene latices.

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The Influence of Associating Polymer on the Physical Properties of Dispersions

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Novel rheological modifiers, associative thickeners comprised of water-soluble polymers with 1-2 wt% linear alkane grafts (10-20 carbons), impart complex equilibrium phase behavior to coatings and even simple latex dispersions. The hydrophobic groups in these thickeners associate inter- and intra-molecularly, and adsorb reversibly onto the hydrophobic surface of latex particles. Previous theoretical treatment of these systems was limited to the effects of the hydrophobes on volume restriction flocculation. (Santore et al.) Experiments were conducted with monodisperse polymethyl methacrylate polybutyl acrylate copolymer latices and two types of hydrophobically modified polymer: polyethylene oxide (40-80K MW) (PEO) from Rohm and Haas, and hydroxyethyl cellulose (200-300MW) (HEC) from Hercules. Prior to the addition of polymer, latex dispersions formulated to a pH of 9 with ammonia and an appropriate ionic strength using $(NH_4)_2SO_4$, contained a strong but short-range electrostatic interparticle repulsion preventing flocculation into the Van der Waals minima, but allowing close enough particle spacing to probe the effects of the polymer. Different concentrations of polymer solution were added to samples of this dispersion, mixed and allowed to separate for several months. In most cases, phase separation became apparent several minutes after mixing, as a soap scum-like film was left on the vials after agitation. Because the density of the latices is so close to that of water, several months were needed for the floccs to settle and form a sediment. After a sufficient equilibration period, samples of the sediment and serum from each vial were analyzed for particle content, using hydrodynamic chromatography, and the results plotted as phase diagrams.

Figure 1 illustrates the volume restriction flocculation that occurs when the polymer's adsorption to the latices is negligible, as established by Sperry and Gast. Here, a phase separation results when unmodified HEC is added to dispersions initially containing 10% by volume 0.024 (__) and 0.089 (_ _ _) μm latices. The horizontal axis shows the amount of polymer added to the dispersion, while the vertical axis maps the particle content of the resulting phases. The points represent data from our experiments, while the lines indicate our interpretation of the phase boundary. (The smaller points show the initial compositions of various samples, not all of which contain enough polymer to induce phase separation.) The large particles can sustain up to 0.13 wt% HEC before the dispersion becomes unstable, separating into a dense opalescent sediment of 60% solids and a light phase containing very few particles. The 0.089 μm particles undergo a fluid-fluid phase transition at somewhat higher polymer concentrations than needed to induce the fluid-solid separation of the 0.24 μm particles. In vials containing the separated 0.089 μm particles, both phases flowed as the vial was tipped; neither phase was opalescent.

When HEC contains hydrophobic grafts, the dispersion is no longer susceptible to volume restriction flocculation. With concentrations up to 0.6 wt% HEC containing up to 1.0 wt% C_{12} arms or 0.4 wt% C_{16} arms, dispersions appear stable for one year or longer. Greater hydrophobe content, such as 1.5 wt% C_{12} groups or 0.6 wt% C_{16} groups along the HEC backbone induces separation into a gummy sediment and a watery serum in dispersions of 0.24, 0.089, and 0.068 μm latices. This separation occurs at very low polymer concentrations, 0.01wt% HEC, and is apparent at all higher concentrations, up to 0.5 wt%, beyond which we had solubility problems with some of our solutions.

End-modified PEO, though more soluble than C_{16}-HEC, exhibited similar trends in phase separation. Figure 2 illustrates the phase envelope for hydrophobically modified PEO in dispersions of 0.068 (_ _ _) and 0.24 (____) μm latices. The large particles undergo separations at very low (0.003 wt%) PEO concentrations into a dense opalescent sediment of 60% solids and a light phase containing a few vol % particles. At higher polymer concentrations, the sediment appears flaky, not opalescent, with 45-50% solids, and the light phase is clear. This is likely a kinetic effect, as we again observe dense opalescent sediments with 0.8 wt% PEO, just prior to restabilization. (Hence, our sketch of the phase boundary indicates 60% solids by volume from 0.01-1% PEO, and 0.24μm latices). Similar separation and restabilization phenomena are observed with smaller particles which undergo a fluid-fluid transition covering a much smaller two-phase region. Preliminary rheological studies show the restabilized dispersion to be a true fluid.

The concentration dependence of these phase transitions leads us to two mechanisms for phase separation. The well-understood volume restriction flocculation mechanism (figure 1) is driven by the osmotic force of the polymer coils on the particles. Replotting unmodified HEC concentration as dimensionless osmotic pressure (with ρ, the coil number density, R_g, its radius of gyration, and a, the particle diameter) in figure 3A shows that phase separation by volume restriction flocculation requires an O(1) dimensionless osmotic pressure. In figure 3B, the PEO concentration is scaled similarly; however, separation occurs with osmotic pressures not high enough to squeeze the particles together by volume restriction flocculation. A second mechanism, likely bridging, is responsible for the separation of the polymer with significant hydrophobic modification. Not shown in figure 3 is the boundaries for the heavily C_{12} and C_{16} modified HEC which separated at dimensionless osmotic pressure of O(.1), also consistent with this hypothesis.

To summarize, hydrophobically modified polymer can induce several types of equilibrium phase behavior, depending on the strength of the hydrophobic association. With negligible attraction between polymer and particles, volume restriction flocculation results at moderate polymer concentrations. With low but significant modification, the dispersion is stable against volume restriction flocculation at polymer concentrations where unmodified chains would induce volume restriction flocculation. Finally, strongly modified polymer can induce bridging flocculation at low (0.001 wt%) polymer concentrations, but the system restabilizes as the polymer solution becomes concentrated (0(1 wt%)). The nature of the transition, i.e. fluid-solid or fluid-fluid depends on the particle/polymer size ratio, with large particles giving fluid-solid transitions, as indicated by the opalescence.

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Gast, A. P., Russel, W. B., and Hall, C. K., *J. Coll. Int. Sci.* 109, 161 (1986).

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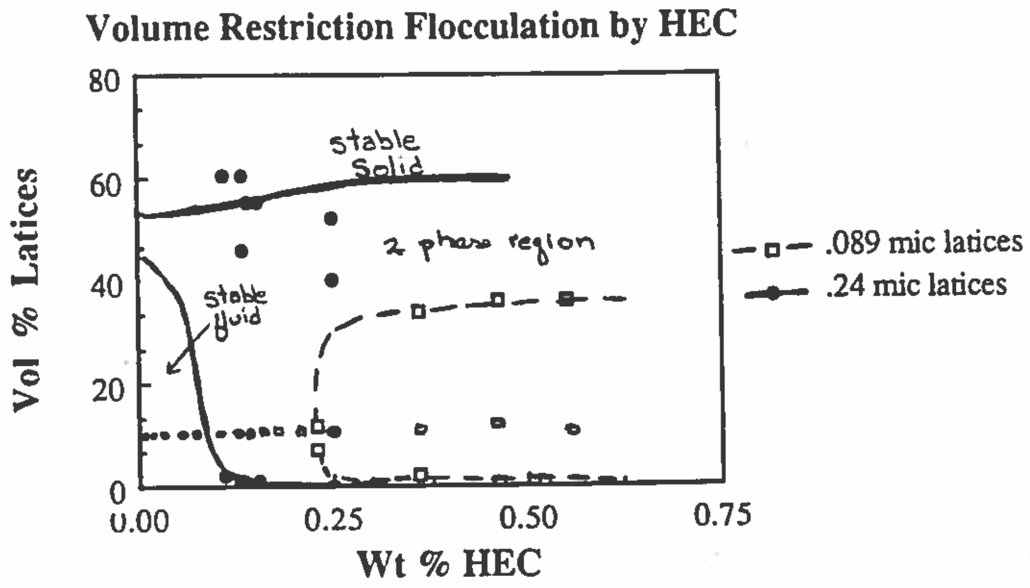

Figure 1. Volume Restriction flocculation upon addition of unmodified HEC to .24 and .089 mm latices.

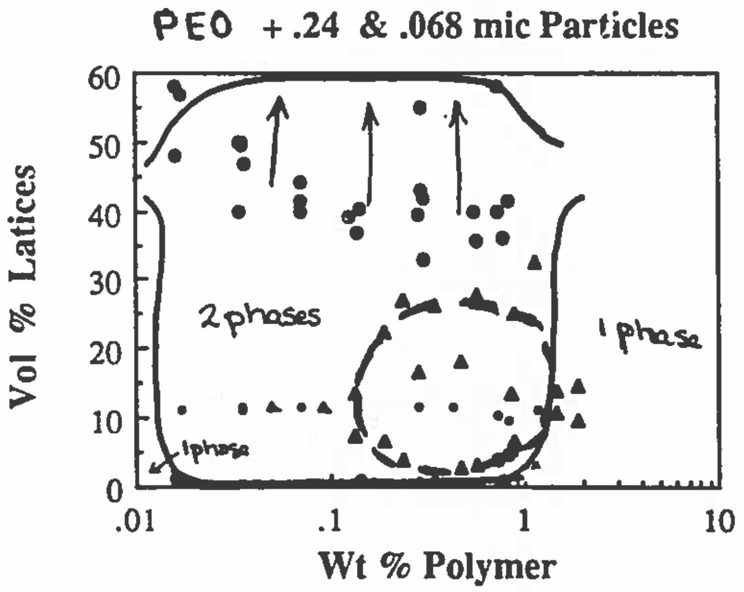

Figure 2. Flocculation and Restabilization upon addition of end-modified PEO to .24 and .068 mm latices.

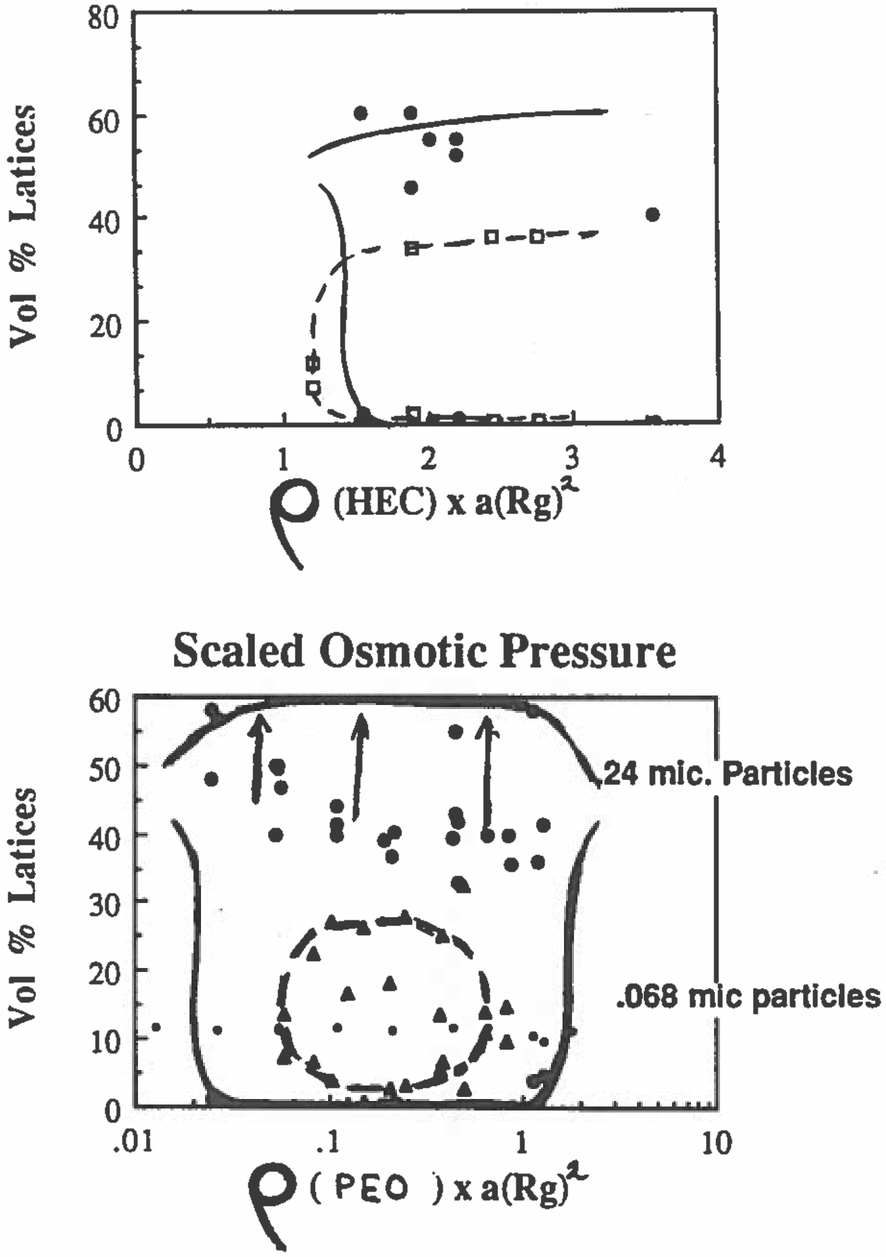

Figure 3. A) Volume restriction with unmodified HEC
B) Bridging flocculation with end-modified PEO
Polymer concentrations represented as dimensionless osmotic pressure.

Contribution to the Polymer Colloid Newsletter, submitted by A. Vrij

A LIGHT SCATTERING CONTRAST VARIATION STUDY ON NON-AQUEOUS SUSPENSIONS OF COATED SILICA SPHERES.

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ABSTRACT

Light scattering contrast variation is applied to recently developed suspensions of homogeneous and inhomogeneous silica spheres in non-aqueous solvent mixtures. The results are explained with contrast variation theory which we extend for the scattering of large, inhomogeneous spheres at finite wave vectors. Further, the influence of polydispersity at various wave vectors is investigated for dilute dispersions and also for a concentrated (nearly crystallizing) sol.

Will appear in J. Colloid and Interface Sci.

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Contribution to Polymer Colloids Group Newsletter
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Submitted by T.G.M. van de Ven

The following are abstracts of papers which are presently submitted or in press.

TRANSIENT LIGHT SCATTERING OF SUSPENSIONS OF CHARGED NONSPHERICAL PARTICLES SUBJECTED TO AN ELECTRIC FIELD (K.M. Baloch and T.G.M. van de Ven).

The transient light scattering response of suspensions of nonspherical latex particles to an oscillating electric field has been investigated both theoretically and experimentally. The relaxation times for rotary Brownian motion obtained from transient response times at small fields agree with those obtained from the relaxation after the field has been switched off, indicating that at small fields changes in light scattering are controlled by rotary Brownian motion. At high fields the changes are controlled by the characteristic alignment times of the individual particles, which are found to be a factor of about two larger than predicted, assuming the particles are model spheroids with a constant dielectric constant. Electric double layers surrounding the particles are found to have a profound effect on alignment times for intermediate electrolyte concentrations ($\sim 10^{-4}$ M). For low and high electrolyte concentrations the effect of double layers vanishes. From the response times obtained for various electrolyte solutions used as suspending medium, it is concluded that different cations adsorb to various degrees onto the particles, creating a Stern layer that strongly affects the alignment time. In general, the more ions there are in the Stern layer the shorter is the alignment time, indicating that polarization occurs within this layer. (J. Colloid Interface Sci. (in press)).

KINETICS OF ELECTROSTATICALLY CONTROLLED DEPOSITION OF COLLOIDAL PARTICLES ON SOLID SURFACES IN STAGNATION POINT FLOW (M.Y. Boluk and T.G.M. van de Ven).

The deposition of titanium dioxide (anatase) particles onto cellophane and glass surfaces was studied in an impinging jet cell which provides a well-controlled stagnation point flow.

The DLVO-theory was tested by comparing experimental with calculated results and a fairly good agreement was found. However the experimental critical deposition concentration (CDC) was larger than predicted and depended on the size of ions in solution with $CDC_{Li^+} > CDC_{Na^+} > CDC_{K^+}$ and $CDC_{C_6H_5COO^-} > CDC_{Cl^-}$. The slopes in stability plots were found to be less steep than predicted and to depend on the size of ions as well. These discrepancies between observations and DLVO-theory can be explained by including ion-size effects in the hydrodynamic correction functions which describe hydrodynamic particle-wall interactions. (PhysicoChemical Hydrodynamics (in press)).

EFFECTS OF ELECTROLYTES, POLYMERS AND POLYELECTROLYTES ON PARTICLE DEPOSITION AND DETACHMENT (T.G.M. van de Ven).

In many systems the kinetics of particle deposition can be described by three parameters: the deposition rate constant, k_o, the escape time, τ_{esc}, and the average area blocked per particle, γ, normalized by the projected area of a deposited particle. Theoretically the best understood parameter is k_o, which can be calculated from transport theory. However experimental observations in a confined impinging jet show important deviations from standard theory, for both electrically charged particles and particles coated with polymers or polyelectrolytes. The escape time τ_{esc} depends strongly on the bond strength and the hydrodynamic conditions near the surface. In the absence of polymers τ_{esc} can often be considered constant, while in their presence τ_{esc} is usually a strong function of time. The blocking parameter γ depends mainly on the interaction between freely suspended particles and deposited particles, and is a measure of the stability of the dispersion used in the deposition process, being independent of the nature of the surface. (Colloids and Surfaces (in press)).

PARTICLE TRAJECTORIES NEAR FREELY ROTATING SPHEROIDS IN SIMPLE SHEAR FLOW (J. Petlicki and T.G.M. van de Ven).

Equations to describe the velocity of a spherical particle near a freely rotating spheroid in simple shear flow have been formulated and integrated numerically. Both hydrodynamic and colloidal interactions have been taken into account. Examples are given of trajectories of particles leading to capture in primary or secondary energy minima. (Physico-Chemical Hydrodynamics (in press)).

LIGHT SCATTERING FROM SEMI-DILUTE DISPERSIONS OF NON-SPHERICAL LATEX PARTICLES SUBJECTED TO AN ELECTRIC FIELD (M.K. Baloch and T.G.M. van de Ven).

The intensity of light scattered by non-spherical latex particles suspended in aqueous media was measured as a function of particle volume fraction. It was found that the intensity first increases with concentration and subsequently decreases. The concentration dependence depends strongly on the strength of the applied electric field, as well as on the electrolyte concentration of the medium. Transient light scattering after the onset of an electric field shows a complex behavior, which is due to a complicated dependence of scattering on particle orientation and concentration. A series expansion of the response time and the rotary diffusion constant in terms of particle volume fraction shows that two-particle interactions have a pronounced effect on alignment and relaxation. (J. Colloid Interface Science, submitted for publication).

Catastrophic Shear Thinning in Ordered Latex Suspensions

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The rheological properties of concentrated latex suspensions have been studied using a Bohlin constant stress rheometer. Suspension volume fractions greater than 0.5 were of particular interest. Amphoteric latex particles 250nm in diameter were synthesized and cleaned according to the techniques worked out by Homula and James and Harding and Healy, concentrated to the desired volume fraction and brought to equilibrium with a particular ionic strength through dialysis. We have found that standard, surfactant free latex particles are difficult to work with at volume fractions approaching 0.6 as they show irreversible aggregation in this volume fraction region. The amphoteric lattices of Homula and James were stable and the rheological properties of suspensions with volume fractions of 0.62 were studied for dialysate ionic strengths as high as 0.01M.

The rheological properties of these suspensions showed four characteristic regions if they were ordered (as determined by iridescence of the suspension). Primarily, at low stresses, the suspensions deformed as elastic solids showing complete strain recovery even 10 ks after the stress had been applied. Over a range of stresses, the steady state strain increased in a linear manner with applied stress and could be used to define an elastic modulus. At larger stresses, the recoverable strain was no longer a linear function of stress and complete strain recovery was not achieved upon release of the stress. However, even after 10 ks, a steady state viscosity was not achieved. This is referred to as the elasto-viscous region.

The final two characteristic flow responses observed were of a shear thinning nature. The elasto-viscous region ended over a narrow range of stresses where there was a sharp break in the recoverable strain curve (Fig. 1). For stresses above this value, steady state viscosities were observed in time scales less of than 300 s. These viscosities decreased with increasing stress giving rise to a shear thinning region I. This type of behavior ended abruptly at a stress, τ^* , where the steady state suspension viscosity dropped 1-3 orders of magnitude over a very narrow stress range (Fig. 2). For larger stresses, a second shear thinning region was entered.

For stresses just above τ^*, the suspensions show a metastable viscosity during the approach to a final steady state viscosity. The suspension viscosity is stable at its metastable value is for a period of time before is decays at a characteristic time to a lower steady state value. This characteristic time decreases dramatically as the applied stress is increased. As shown in Figs.

2 and 3, the metastable viscosity follows the upper branch of viscosities in the viscosity, stress curve, and acts to provide a continuous transition between the upper and lower branches in the viscosity, shear rate curves.

These four regions and the transitions between them were observed over a range of volume fractions (0.4 < O <0.62) and for three ionic strengths (10^{-2} , 10^{-3} , 10^{-4} M). In all cases the behavior was similar to that described above. In addition an ordered surfactant free latex at a volume fraction of 0.40 at an ionic strength of 10^{-3} M was found to display the same responses to stress. Changing rheometer tool geometry did not substantially alter characteristic stresses for flow and catastrophic shear thinning. We feel that the observed features are characteristic of the deformation of ordered latex suspensions and are currently analyzing our results in terms of the structures observed in latex suspensions under flow as determined by light and neutron scattering methods.