A. S. Dunn

IPCG

Vol. 20, No. 2

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

IPCG

INTERNATIONAL POLYMER COLLOIDS GROUP

OCTOBER,1989

VOLUME 20

NUMBER 2

NEWSLETTER

INDEX

FROM THE EDITOR'S DESK

Personal

First,news of two of our founding members: Ron Ottewill was awarded an OBE (Order of the British Empire) in EIIR's Birthday Honours List. Heartiest congratulations, Ron. I hope it will be Sir Ron, Lord Ron or even St Ron next time! Bob Fitch will be retiring from SC Johnson at the end of the year.This will allow Bob to spend more time with his family and to "smell the flowers". He will, of course, continue his research interests in polymer colloids and establish an active consulting programme from his home base in Racine. All members will wish Bob a long and happy retirement.

Finn Hansen has left Dyno to take up a new Chair in Colloid and Surface Chemistry at the University of Oslo.Our best wishes go to Finn in his new venture.

Some members may be unaware that Mrs Jean Proctor, who so diligently sends out the contribution reminder notices, has recently been widowed. I am sure that all members will join in sending our condolences to Jean.

Minutes of the 1989 General Meeting

Minutes of the General Meeting held in New Hampshire are attached (with gateful thanks to Bob Gilbert). The following were invited to membership: Dr Leonardo Rios (Universidad Autonoma de Mexico), Dr Anton (Ton) German (Technical University, Eindhoven), Dr Jaroslav Barton (Slovak Academy of Science,Bratislava) and Dr Klaus Tauer (DDR Academy of Science,Teltow). Acceptances have been received from Drs German and Barton, both of whom are warmly welcomed to membership of the Group.

Conferences

1990 will be a busy year for meetings (see next page).Included here is information on the symposium honoring John Vanderhoff ,which is part of the 64th Colloid and Surface Science Symposium, as well as the MACRO 90 meeting to be held in Montreal.

Contributions

Sandy Dunn has sent in an interesting account of the papers presented at Polymer Latex III, where John Vanderhoff was the Keynote Speaker. A contribution from Dr Yeliseyeva has been held over due to late arrival.

Next Newsletter

Please forward your contributions to me by **30 April,1990.**

D.H.Napper
Editor

CONFERENCE SCHEDULE

1990

Conference	Location	Dates
199th ACS National Meeting	Boston	22-27 April
21st Emulsion Polymers Short Course	Lehigh Uni	4-20 June
8th Intnl Symposium on Surfactants	Gainesville	10-15 June
Vanderhoff Symposium	Lehigh Uni	18-20 June
33rd IUPAC Polymers (MACRO 90)	Montreal	8-13 July
200th ACS National Meeting	Washington	26-31 Aug
Faraday Discussion 'Colloid Stability'	Bristol	11-13 Sept

1991

Conference	Location	Dates
201st ACS National Meeting (Prep,Props& Applics of Latices)	Atlanta	14-19 April
7th Intnl Conf Colloid Surfaces	Compiegne	7-12 July
Polymer Microspheres	Japan	24-27 Oct

International Polymer Colloid Group

Minutes of Meeting
Proctor Academy, New Hampshire
July 12 1989

The meeting was chaired by Professor Piirma.

NATO Meeting

(a) Professor Ottewill reported that the publication from the NATO meeting will be in two volumes, both to appear in several months.
(b) The committee will send a sympathy card to Jean Proctor after the loss of her husband.
(c) The group is financially sound after the NATO meeting, thanks to the efforts of the Organizing Committee.

Newsletter

Professor Gilbert is to check the mailing procedure with Professor Napper. It was decided that the North American mailing is to be continued to be handled by Dr Fitch. The European mailing is to be handled by Dr Pichot (since Dr Donners will no longer be active in the group). Dr Sperry (Rohm & Haas) offered to do the North American distribution, and Professor Napper will organise which of the various possibilities will be implemented.

Forthcoming conferences

(a) Dr Bassett has been elected Chairman for the 1993 Gordon Conference.
(b) The 64th Colloid and Surface Science Symposium will be held at Lehigh June 18-20 1990. The enclosed outline was supplied by Professor El-Aasser for inclusion in the Newsletter.
(c) Dr van de Ven and Dr Waters are organizing a Symposium as part of the IUPAC polymer meeting in Montréal, July 9-13 1990. There will be a two-day session on polymer colloids. The topics will be: Kinetics and Morphology; Polymer Adsorption; Characterization; and Emulsion and Dispersion Polymerization.
(d) There will be a Faraday Discussion, September 10-12 1990, on Colloidal Dispersions (flyer attached).
(e) There will be a meeting, April 14-19 1991, on Preparation, Properties and Application of Polymeric Latexes, organized by Professor El-Aasser as part of the ACS meeting in Atlanta.
(f) The 1991 Polymer Colloids Gordon Conference will be chaired by Professor El-Aasser. It was decided that it would be held on the week of the 4th of July, at Tilton (if available). Bookings are to be made as soon as possible.
(g) The 7th International Conference on Surface and Colloid Science will be held July 7-12 at Compiègne (France). See attached flyer.
(h) Profesor Nomura is organizing an international meeting on Polymeric Microspheres, Oct 24-27 October 1991 in Japan, with the co-sponsorship of the EPI (Lehigh University), McMaster University and the Laboratoire des Matériaux Organiques.
(i) The IUPAC Polymer 91 meeting will be held February ?-? in Melbourne, Australia.
(j) Some possibilities were discussed for the next NATO meeting. 1994 was suggested as a suitable time. It was decided that Dr Asuà will check availablity of suitable regions in Spain, and Dr Costas Kiparissides to do the same for Greece.

New members

(a) Dr Joosten from DSM will replace Dr Donners (subject to agreement by these people).
(b) Dr Riess (Mulhouse) has already accepted membership.

(c) It was agreed that the following should be invited to join: Dr L Rios (Universidad Autonoma de Mexico), Prof A German (Eindhoven), Dr K Tauer (Teltow) and Dr J Bartoň (Bratislava).
(d) The Group is now growing significantly. To ensure that only active members remain in it, the Secretary is to send a Response Sheet once a year to all members, and to cull those not responding (say) for two years. This is in addition to the non-contribution rule.

Action Sheet

1. Ottewill to send sympathy card to Jean Proctor on behalf of group.
2. Gilbert and Napper to confirm new arrangements for mailing Newsletter, subject to confirmation that Donners will no longer be able to do European distribution. Napper to write to Donners, Fitch and Sperry.
3. Napper to include enclosed Symposium, Conference and Discussion outlines in Newsletter.
4. El-Aasser and Piirma to book Tilton for next Gordon Conference.
5. Asuà to check conference venue availablity. El-Aasser to request Kiparissides to do the same for Greece.
6. Napper to write to new nominees for membership asking them to join the Group.
7. Napper to make Response Sheet for automatic mailing to members.

CALL FOR PAPERS
and
PRE-REGISTRATION MATERIAL

64th Colloid and Surface Science Symposium

and

Nucleation Symposium

JUNE 18, 19, 20, 1990

TO BE HELD AT:

LEHIGH UNIVERSITY
BETHLEHEM, PENNSYLVANIA

The Colloid and Surface Chemistry Division of the American Chemical Society holds a special summer symposium each year which is known as the Colloid and Surface Science Symposium. The 64th Symposium will be hosted by Lehigh University on June 18-20, 1990. This Symposium continues a tradition to hold such a meeting on the Lehigh campus every decade, i.e., 1960, 1970, 1980, and 1990. Continuing with the same format as past meetings, the 1990 Symposium will feature plenary lectures, an extensive technical program, exhibits from leading instrument suppliers and book publishers, and a variety of social activities.

SYMPOSIUM LOCATION

Bethlehem is located in the heart of the Lehigh Valley about 50 miles north of Philadelphia and 60 miles west of New York City. It is easily accessible by plane via the ABE (Allentown-Bethlehem-Easton) Airport; by car via the east-west Route 78 (22) and the north-south Northeast Turnpike Extension and Routes 309 and 378; and by bus from New York City (Port Authority Terminal).

PLENARY LECTURE

The first plenary lecture will be given by Dr. P. G. de Gennes, College de France, Paris. Dr. de Gennes' talk is entitled, **"Flexible Polymers at Polymer Interfaces"**. Dr. de Gennes is internationally recognized for his contributions in the field of polymers. The second plenary lecture will be by the winner of the Victor K. LaMer Award.

TECHNICAL PROGRAM

The two themes for the Symposium are: Polymer Surfaces and Interfaces, and Catalysis. Eleven symposia have been selected, each one will be lead by a keynote speaker, (see program for details). The Nucleation Symposium will be held concurrently with the Colloid and Surface Science Symposium.

GRADUATE STUDENT PARTICIPATION

In an effort to increase graduate student attendance, partial travel grants will be provided. Students who are interested in receiving a grant will be expected to actively participate in the meeting by either presenting a paper or a poster. The deadlines for submission of paper/poster abstracts are listed on the Call For Papers.

SPECIAL EVENTS AND EXHIBITS

The following special events are scheduled: a welcoming reception on the evening of June 17 and a mixer on Monday, June 18 (both of which will be held in Rathbone Hall). The Symposium Banquet will be held on Tuesday, June 19 in Stabler Arena. Bus transportation will be provided. The Instrument and Book Exhibits will be on display throughout the Symposium in Rathbone Hall.

ADDITIONAL QUESTIONS

M. S. El-Aasser
Emulsion Polymers Institute
Lehigh University
111 Research Dr.
Bethlehem, PA 18015

Phone: 215-758-3590
Fax #: 215-758-5423

Bethlehem, PA 18015
Phone: 215-758-3082
Fax #: 215-758-5423

Pre-registration Deadline: May 15, 1990

Emulsion Polymers Institute
Lehigh University
111 Research Drive
Bethlehem, PA 18015

NON-PROFIT ORG.
U.S. POSTAGE
PAID
BETHLEHEM, PA
Permit No. 230

TECHNICAL PROGRAM

The 1990 Symposium will honor three distinguished scientists; two of these are members of the Lehigh faculty, Dr. Frederick M. Fowkes and Dr. Henry Leidheiser, Jr., the third is Dr. Irvin M. Krieger from Case Western Reserve. All of these individuals have contributed significantly to the field of colloid and surface chemistry.

Symposium Honoring Henry Leidheiser, Jr.
Substrate/Polymer Interface: Chemistry and Structure

Chairpersons:

Richard Granata
Sinclair Laboratory #7
Lehigh University
Bethlehem, PA 18015
215-758-3574

Ray Dickie
Ford Motor Company
E3198, P. O. Box 2053
Dearborn, MI 48121
313-337-4059

Keynote Speaker: ***F. James Boerio,*** *University of Cincinnati*
"Molecular Structure of Polymer-Metal Interfaces"

In Honor of the 75th Birthday of Frederick M. Fowkes
Acid-Base Interactions: Relevance to Adhesion Science and Technology

Chairpersons:

Kashmiri Mittal
IBM
500 Columbus Ave.
Thornwood, NY 10594
914-742-5747

Herbert R. Anderson, Jr.
IBM
East Fishkill Facility
Hopewood Jct., NY 12533-0999
914-894-3036

Keynote Speaker: ***William B. Jensen,*** *University of Cincinnati*

Symposium Honoring Irvin M. Krieger
Rheology of Concentrated Dispersions and Associative Thickeners

Chairpersons:

Cesar Silebi
Dept. of Chemical Eng.
Lehigh University
111 Research Drive
Bethlehem, PA 18015
215-758-4267

William B. Russel
Dept. of Chemical Eng.
Princeton University
Olden Street
Princeton, NJ 08544-5263
609-452-4590

Keynote Speaker: ***Jim Goodwin,*** *University of Bristol*

Organic Thin Films

Chairpersons:

Steven L. Regen
Dept. of Chemistry
Seeley Mudd Bldg. #6
Lehigh University
Bethlehem, PA 18015
215-758-4842

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

Keynote Speaker: ***Stewart Rice,*** *University of Chicago*
"Theoretical and Experimental Studies of the Structure of Langmuir Monolayers"

Catalysis/Surface Sciences

Catalysis by Membrane and Colloidal Systems

Chairpersons:

Kamil Klier
Dept. of Chemistry
Seeley Mudd Bldg. #6
Lehigh University
Bethlehem, PA 18015
215-758-3577

Russell R. Chianelli
Corporate Research Labs
Exxon Research and Eng. Co.
Clinton Twp., Rte. 22 E
Annandale, NJ 08801
201-730-2563

Keynote Speaker: To Be Announced

Molecular Design of Metal Oxide Catalysts

Chairpersons:

Israel E. Wachs
Dept. of Chemical Eng.
Lehigh University
111 Research Drive
Bethlehem, PA 18015
215-758-4274

Lawrence L. Murrell
Engelhard Corporation
Speciality Chemical Div.
Menlo Park, CN-28
Edison, NJ 08818
201-321-5274

Keynote Speaker: ***Jerzy Haber,*** *Polish Academy of Science*
"Molecular Design of Metal Oxides"

Monolayers and Thin Polymeric Films in Electronics

Chairpersons:

Ralph J. Jaccodine
Sherman Fairchild Lab. #161
Lehigh University
Bethlehem, PA 18015
215-758-4409

Ike Durn
Sinclair Laboratory #7
Lehigh University
Bethlehem, PA 18015
215-758-3570

C.P. Wong
AT&T Bell Labs
Engineering Research Center
P. O. Box 900
Princeton, NJ 08540
609-639-2579

Keynote Speaker: ***David Allara,*** *The Pennsylvania State University*
"Bonding and Structure of Organic Groups at Metal and Metal Oxide Interfaces"

Adhesion of Proteins and Cells to Particles/Surfaces

Chairpersons:

Janice A. Phillips
Dept. of Chemical Eng.
Lehigh University
111 Research Drive
Bethlehem, PA 18015
215-758-4258

Daniel A. Hammer
School of Chemical Eng.
Cornell University
Olin Hall
Ithaca, NY 14583-5201
607-255-8656

Keynote Speaker: ***Evan A. Evans,*** *University of British Columbia*
"Fracture of Agglutinin Attachments Between Membranes: A Random Process of Material Failure"

Polymer Colloids

Chairpersons:

Mohamed S. El-Aasser
Dept. of Chemical Eng.
Lehigh University
111 Research Drive
Bethlehem, PA 18015
215-758-3590

E. David Sudol
Emulsion Polymers Institute
Lehigh University
111 Research Drive
Bethlehem, PA 18015
215-758-3602

Gary Poehlein
School of Chemical Engineering
Georgia Institute of Technology
Atlanta, GA 30332-0265
404-894-3090

Keynote Speaker: ***Donald H. Napper,*** *University of Sydney*
"The Formation and Growth of Polymer Colloids: A Contemporary Perspective"

Colloidal and Surface Chemistry of Coals

Chairpersons:

John W. Larsen
Dept. of Chemistry
Seeley Mudd Bldg. #6
Lehigh University
Bethlehem, PA 18015
215-758-3489

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

Keynote Speaker: ***Om Mahajan,*** *Amoco Research Center*
"CO_2 Surface Area of Coals: A Twenty-Five Year Paradox"

New Surface Analysis Techniques/Advances in Electron Spectroscopy

Chairpersons:

Gary W. Simmons
Sinclair Laboratory #7
Lehigh University
Bethlehem, PA 18015
215-758-3570

Lennie Klebanoff
Sinclair Laboratory #7
Lehigh Unviersity
Bethlehem, PA 18015
215-758-3592

Keynote Speaker: ***Theodore E. Madey,*** *Rutgers University*
"Characterization of Adsorbed Molecules Using Stimulated Desorption of Positive and Negative Ions"

General Papers

Chairpersons:

Nato Micale
Sinclair Laboratory #7
Lehigh University
Bethlehem, PA 18015
215-758-3596

Philip Pendleton
Olin Hunt
201 Roosevelt Place
Palisades Park, NJ 07650
201-585-5821

Nucleation Symposium

Chairperson:

Joseph L. Katz
Dept. of Chemical Eng.
The Johns Hopkins University
Baltimore, MD 21218
301-338-8484

Keynote Speaker: ***Paul Wagner,*** *University of Vienna*
"Nucleation Experiments"

MEETING

64TH COLLOID AND SU

JUNE

Participants may pre-register by co
May 15th. The registration fee covers
registering by May 15th will receive an
a campus map. Other registration mat
upon arrival.

The Symposium Registration Desk
Hall, starting Saturday, June 16 from 7
3:00 p.m. to 10:00 p.m.; Monday, Tuesd
to 4:00 p.m. Housing registration will

Name ______________________
(Please Print or Type) Last

Organization ______________________

Address ______________________

____
City St

Daytime Phone ( ) ______________________

Pre-registration (before/after)
(Please circle the fee)
Members
Nonmembers
Students
Banquet

Meal Tickets (non-refundable)*:
(Please check appropriate boxes)

June

Breakfast: $4.00/day
Lunch: $5.75/day
(Soup, salad and deli bar only)

Total Number of Breakfast Tic
Total Number of Luncheon Tic
REGISTRATION FEE
MEAL TICKETS
BANQUET
TOTAL AMOUNT DUE:

*A limited number of meal tickets will be a
Participants are strongly encouraged to

Checks should be drawn on a United
from a non-U.S. bank, in any currency, w
fee must be included with the registrati

Enclosed is check or money order paya

in the amount of ______________________

BILL MY ☐ VISA ☐ MASTE

Account No. ______________________

____
Sig

REFUND POLICY: After June 1st, th
deducted for cancellation.

MEETING REGISTRATION

64TH COLLOID AND SURFACE SCIENCE SYMPOSIUM

JUNE 18 - 20, 1990

Participants may pre-register by completing the enclosed form and returning it by May 15th. The registration fee covers the Book of Abstracts and the mixers. Those registering by May 15th will receive an acknowledgment by mail, which will include a campus map. Other registration materials can be picked up at the registration desk upon arrival.

The Symposium Registration Desk will be located in the main lobby of Rathbone Hall, starting Saturday, June 16 from 7:00 p.m. to 9:00 p.m., on Sunday, June 17 from 3:00 p.m. to 10:00 p.m., Monday, Tuesday, and Wednesday June 18-20 from 8:00 a.m. to 4:00 p.m. Housing registration will also be done at this site.

Name ______________________________
(Please Print or Type) Last First MI

Organization ______________________________

Address ______________________________

____
City State Zip Country

Daytime Phone ( ) ______________________________

Pre-registration (before/after) (Please circle the fee)	May 15th/After
Members	$100.00/$125.00
Nonmembers	$100.00/$135.00
Students	$ 25.00/$ 25.00
Banquet	$ 40.00

Meal Tickets (non-refundable)*:
(Please check appropriate boxes)

		June 18	June 19	June 20
Breakfast:	$4.00/day	☐	☐	☐
Lunch:	$5.75/day	☐	☐	☐

(Soup, salad and deli bar only)

Total Number of Breakfast Tickets ________

Total Number of Luncheon Tickets ________

REGISTRATION FEE $ ____________

MEAL TICKETS $ ____________

BANQUET $ ____________

TOTAL AMOUNT DUE: $ ____________

*A limited number of meal tickets will be available during the on-site registration period. Participants are strongly encouraged to purchase their meal tickets in advance.

Checks should be drawn on a United States bank in U.S. dollars. Checks drawn from a non-U.S. bank, in any currency, will be charged a $50.00 processing fee. This fee must be included with the registration fee.

Enclosed is check or money order payable to LEHIGH UNIVERSITY

in the amount of ______________________________

BILL MY ☐ VISA ☐ MASTERCARD ☐ Exp. Date ________

Account No. ______________________________

____
Signature

REFUND POLICY: After June 1st, there will be a processing charge of $25.00 deducted for cancellation.

HOUSING REGISTRATION

UNIVERSITY ACCOMMODATIONS

University Residence Halls are available within two to three blocks of the conference site. University accommodations provide daily maid service, linens and towels, and a "light" continental breakfast.

Housing Registration will be held in conjunction with the Meeting's Registration at Rathbone Hall. Check-In Time is 2:00 p.m. and Check-Out Time is 12:00 Noon. Early and late arrivals will be able to check in at the Conference Service Desk in Brodhead House from 6:00 a.m. to 10:00 p.m. daily.

Air Conditioned Three Bedroom Apartments:

Two Persons per Apartment*	$28.25/night	☐
Three Persons per Apartment*	$28.25/night	☐
Four Persons per Apartment**	$24.25/night	☐

* Each individual will have a private bedroom. ** More than one person in a bedroom.

Air Conditioned Traditional Residence Hall:

Multiple	$21.25/night	☐	Single	$27.25/night	☐

Non-Air Conditioned Traditional Residence Hall:

FANS WILL BE PROVIDED FOR EACH ROOM.

Multiple	$19.00/night	☐	Single	$26.25/night	☐

Please check the appropriate box which indicates the accommodation you would prefer. *Rooms will be assigned on a First Come-First Serve basis.* A 10% fee will be charged for dormitory cancellations after June 1st; 50% fee after June 17th.

Name ______________________________
(Please print or type) Last First MI

Organization ______________________________

Address ______________________________

____
City State Zip Country

Daytime Phone ( ) ______________________________

Arrival Date ____________ Departure Date ____________

Total Number of Nights ______________________________

Pre-Arranged Roommate: ______________________________
Name

Please Check: ☐ Male ☐ Female ☐ Smoking ☐ Nonsmoking
☐ Wheelchair Accessible

Checks should be drawn on a United States bank in U.S. dollars. Checks drawn from a non-U.S. bank, in any currency, will be charged a $50.00 processing fee. This fee must be included with the housing fee.

Enclosed is a check or money order payable to:
LEHIGH UNIVERSITY in the amount of ______________

BILL MY ☐ VISA ☐ MASTERCARD Exp. Date ________

Account No. ______________________________

____
Signature

HOTEL/MOTEL OPTION:

Blocks of rooms have been reserved at a local hotel and three motels. Hotel/motel reservations should be made by contacting the hotel/motel directly. Rooms will be held until May 15, 1990 only.

Hotel Bethlehem: Two miles from campus. (215-867-3711)
Holiday Inn: Six miles from campus. (215-866-5800)
Comfort Inn: Nine miles from campus. (215-865-6300)
Sheraton Jet Port: Nine miles from campus. (215-266-1000)

When making your reservations be sure to mention that you are attending the Symposium.

64TH COLLOID AND SURFACE SCIENCE SYMPOSIUM

CALL FOR PAPERS

Those wishing to submit a paper should send a 200 word abstract listing the title and author(s), to M. S. El-Aasser by *December 1, 1989. ACS abstract forms will be provided to each author and must be returned to the session chairperson no later than January 15, 1990.* Papers excluded from any symposium may be given in the general session if the author agrees. It is recommended that anyone wishing to submit a paper contact the appropriate session chairperson at the earliest practical time and advise him/her of your intention.

There will be a poster session. Poster abstracts are to be sent to M. S. El-Aasser by *December 1, 1989.* The poster format will be provided after an abstract has been accepted.

________ I plan to attend the Symposium and to present a paper.

________ I plan to attend the Symposium and to present a poster.

________ I plan to apply for a Graduate Student Travel Grant.

Session Title ______________________________
(Please print or type)

____

Title of Paper/Poster ______________________________

____

____

Author (s) ______________________________

____

____

Name ______________________________

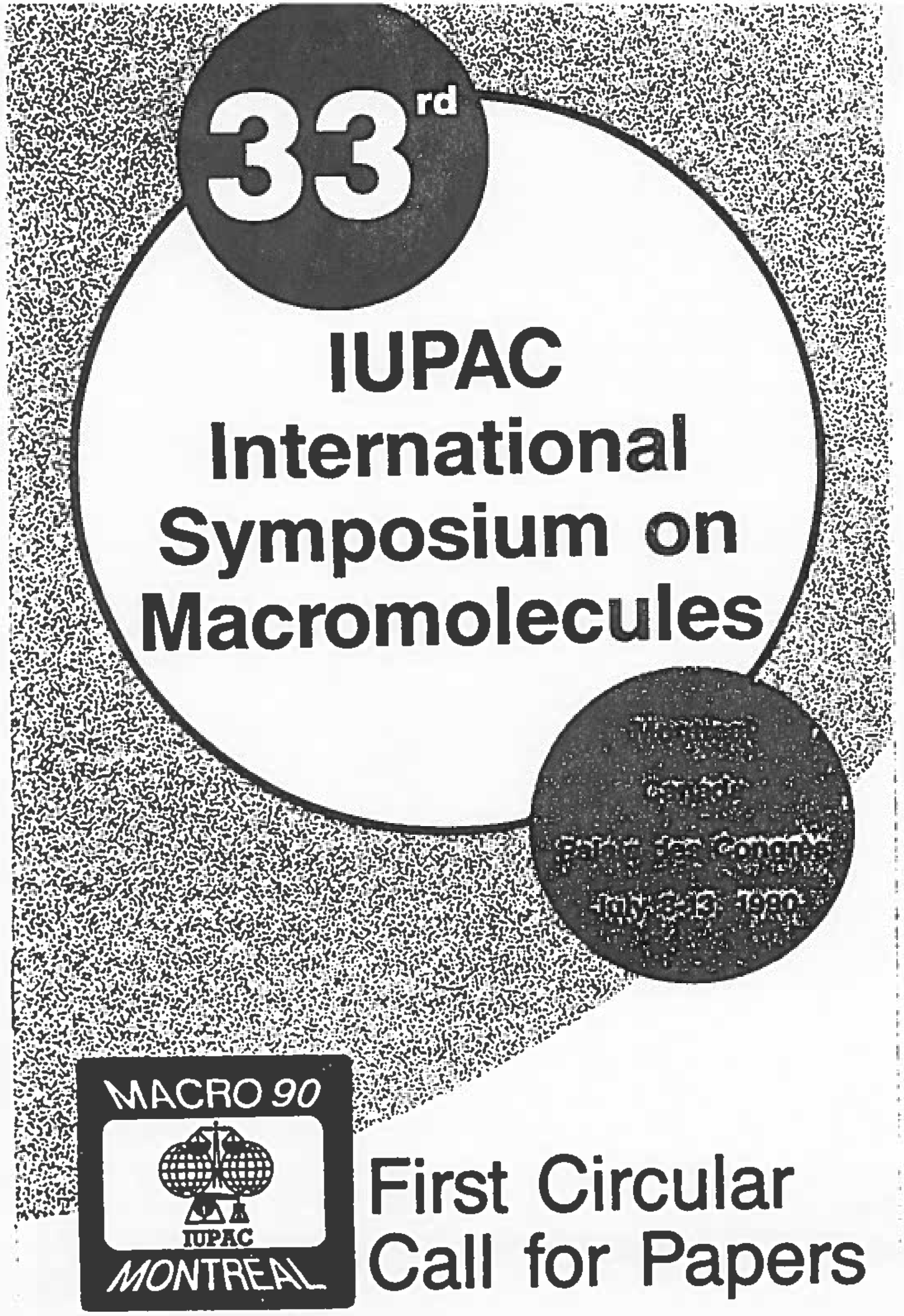
Address ______________________________

____

____

____

Daytime Phone ( ) ______________________________



33rd

IUPAC
International
Symposium on
Macromolecules

Montreal
Canada
Palais des Congrès
July 8-13, 1990

MACRO 90
IUPAC
MONTREAL

First Circular
Call for Papers

2.5 POLYMER COLLOIDS Van de Ven (Canada), Waters (UK)

Emulsion and Dispersion Polymerization, Characterization of Polymer Colloids, Interfacial Properties of Polymers, Composite Particles

El-Aasser (USA), Ottewill (UK), Pelton (Canada), Rowell (USA), Stenius (Sweden), Winnik (Canada)

2.6 ENVIRONMENTAL DEGRADATION
Carlsson (Canada), Billingham (UK)

Polymer Degradation, Prevention, Biodeterioration, Plastic Waste Management, Environmental Effects on Organic Composites, Performance of Polymer Blends and Alloys

Albertsson (Sweden), Day (Canada), George (Australia), Huang (USA), Pearce (USA), Scott (UK), Teyssié (Belgium), Wiles (Canada)

2.7 THERMAL PROPERTIES Wunderlich (USA), Richardson (UK)

The Glass Transition, The Thermal Functions, Thermal Characterization of Modern Macromolecules, General Topics Session

2.8 RHEOLOGY Carreau (Canada), Meissner (Switzerland)

Rheology of Polymer Solutions in Novel Applications, Rheology of Liquid Crystalline Polymers

DeKee (Canada), Soane (USA)

2.9 SURFACE AND INTERFACIAL PHENOMENA
Meier (USA), Higgins (UK)

Polymer Surfaces, Polymer/Polymer Interfaces, Polymers Absorbed on Surfaces, Polymer Modification of Interfaces

2.10 SYNTHESIS & CATALYSIS
Rempel (Canada), Kaminsky (FRG)

Polymer Synthesis, Chemical Modification of Polymers

Grubbs (USA), Mohammadi (Canada)

General Information

The 33rd IUPAC International Symposium on Macromolecules will be held from July 8-13, 1990, at the Palais des Congrès in Montreal, Canada.

All those who plan to attend the Symposium are kindly requested to return the form at the end of this circular by **November 1, 1989**. More detailed information on the scientific program, advance registration, hotel reservations, social activities, and other aspects of the conference will be given in the second circular.

The deadline for advance registration will be April 15, 1990. The registration fees (in Canadian dollars) are given below. IUPAC Affiliate Members are entitled to a 10% reduction.

	Before April 15, 1990	After April 15, 1990
Full Registration	$ 400	$ 450
Student Registration	$ 100	$ 130
Accompanying Persons	$ 50	$ 50

Presentations

Seven plenary lectures of one hour each are scheduled for the conference, as well as over 50 invited lectures. More than 1000 contributed papers will be accepted for either oral or poster presentation.

Each oral presentation will be allotted 30 minutes, including discussion. Those wishing to present a paper must indicate their intention by returning the form at the end of this circular to the Conference Secretariat before **November 1, 1989**. A complete abstract, which will be included in the preprint booklet, will be required by **January 15, 1990**. A camera-ready form will be provided for this purpose.

Exhibition

MACRO 90 will also include a technical exhibition. Those interested in preparing a booth are requested to return the form at the end of this circular by **November 1, 1989**.

Passports and Visas

A valid passport is sufficient for entering Canada from many countries, but in some cases a visa is also necessary. Those planning to attend the Symposium should verify whether a visa is required and if so, make the necessary arrangements.

IUPAC sponsorship implies that entry visas will be granted to all bona fide chemists provided application is made not less than three months in advance. If a visa is not granted one month before the meeting, the IUPAC Secretariat should be notified without delay by the applicant.

Currency

The current exchange rate for the Canadian dollar with respect to the US dollar is $1.00 (US) = $1.19 (Canadian). US dollars are accepted in most stores, restaurants, etc., but other foreign currencies should be converted into Canadian dollars. The business hours of currency exchange offices are limited, so it is advised that travellers arriving from overseas bring some Canadian currency or travellers' cheques with them.

Climate

In July it is warm in Montreal, with a typical maximum daytime temperature of 26°C (79°F) and a nighttime low of 16°C (61°F).

Transportation

Flights from Canada and the United States arrive at Montreal's Dorval Airport. The trip to downtown may be made by Aerocar bus service ($7.00 per person), taxi (about $20.00), or limousine service ($24.00).

Flights from overseas land at Mirabel Airport, about 50 km (30 mi) north of the city. Aerocar bus service is available from there to downtown for $9.00 per person. Limousine or taxi service (about $40.00) is also available.

Prices quoted are based on 1989 rates.

Correspondence

All correspondence concerning the Symposium should be addressed to:

IUPAC M. Secretariat
Dept. of Chem. E g, McGill University
348 ity St.
Montrea :, Canada
7

Telephon) 398-7487

Facsimil 398-6678

Location

Montreal has become known around the world through events such as Expo '67, the 1976 Olympic Games, the world-renowned Botanical Gardens, its International Film and Jazz Festivals, International Marathon, and the Formula I Grand Prix.

Whether you are coming from another part of Canada, the United States, or anywhere around the globe, Montreal, with two major airports, is easy to reach. Dorval Airport takes care of North America, including direct flights to some 30 cities in the U.S. Mirabel Airport handles the remaining international routes. Montreal also has the advantage of being an inland port and is on line with major railways and roadways. It is a city full of life where pleasure may be found in even the most simple task, such as finding the right restaurant in a city known for its fine and varied cuisine.

Montreal enjoys the reputation of being one of the world's truly cosmopolitan cities, combining the quaint elegance of Europe with the comfortable familiarity of North America. There is a rich cultural life: the Montreal Symphony Orchestra, a permanent opera, twenty professional dance and theatre companies, and several museums. During the summer, sports fans will appreciate the Montreal Expos baseball club.

In another vein, Montreal is a commercial and industrial metropolis with a community of specialists working in intellectual research. There are four universities: Concordia, McGill, Université de Montréal, and Université du Québec. Montreal universities have always been particularly active in polymer research. In addition, the city has very dynamic medical, industrial, electrical, and aeronautic sectors.

Montreal is also within easy travelling distance of other cities such as Ottawa (200 km), Quebec City (260 km), Toronto (540 km), and New York (650 km).

History

Discovered and claimed for France by Jacques Cartier in 1534, Quebec was the source of much of the exploration that took place in the following years. French explorers headed west from Montreal into the wilderness that would become Canada in 1867. Vast areas were also opened up in the U.S. — New York by Champlain, the Mississippi by Marquette and Jolliet, Louisiana by LaSalle, Montana by the La Vérendrye family. Today, people in many corners of the continent trace their roots back to Quebec.

When Cartier arrived in Montreal in 1535, he found an Indian settlement of 3,500 called Hochelaga. The actual founding of the city by Paul de Chomedey, Sieur de Maisonneuve, dates from 1642. In the 18th century, Montreal became a fur-trading capital; in the 19th century, a financial capital. Today it is a multicultural city of 2,500,000 that has retained its French heritage and charm.

Convention Centre

The Palais des Congrès was designed to be functional as well as aesthetic. Because of the simplicity of its architectural design, clear directions, and wide hallways, it is easy to find your way around the Convention Centre — or your way to it. Located in downtown Montreal, it is close to most major hotels and attractions. You can just as easily find your way by taxi, bus, or car — there is parking either at the Convention Centre itself or in the vicinity. The Centre is also connected by an indoor passage to the Place d'Armes metro station.

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POLYMER LATEX III

The Plastics and Rubber Institute's 3rd International Conference on POLYMER LATEX was held 27-29 June 1989 at a new venue, the Institution of Marine Engineers' City Conference Centre near Aldgate in the City of London. There were 139 participants of whom 62 were from overseas. This provides a 200 seat Lecture Theatre with the facility of catering for 125 for lunch in adjacent rooms which was very suitable for the requirements of this meeting.

The PRI publishes extended preprints of the papers to be presented at its conferences from the authors' camera-ready copy in an A5 format book of which copies are available separately afterwards. The preprint book for 'POLYMER LATEX III' cost £20 + £3.50 postage. The preprint books for POLYMER LATEX (1978) at £10, EMULSION POLYMERS (1982) £15, and POLYMER LATEX II (1985) £20 are also still available from the Plastics and Rubber Institute, 11 Hobart Place, London, SW1W OHL. Telephone 01-245 9555 Telex 915719 PRIUK G Fax: 01-823 1379 and are desirable acquisitions for Polymer Colloid libraries because definitive versions of the papers tend to be published only in a minority of cases. The 'Polymer Latex' Conferences cover both synthetic latices and natural rubber latex.

John Vanderhoff's keynote address was on 'Practical Aspects of Emulsion Polymerisation'. He highlighted the progress which has been made in selecting emulsifiers for use in commercial emulsion polymerisations. When residual monomer was to be removed by steam-stripping alkyl sulphate emulsifiers which had been sufficient to keep the latex stable during polymerisation would fail because of hydrolysis necessitating the addition of an alkyl sulphonate emulsifier. Then addition of a non-ionic emulsifer as a post-stabiliser was essential to give the latex sufficient stability to mechanical shear. The finished latex could contain about 5% emulsifier making it liable to foam badly and rendering films formed from the latex water-sensitive with poor adhesion. Polymeric emulsifiers which could overcome these difficulties had been developed during the last decade but only commercialised recently. They had been developed from latices stabilised by use of functional comonomers by determining the composition of the copolymer prepared in situ and adsorbed on the surface of the latex particles and preparing a similar copolymer for use as an emulsifier in a separate reaction.

David Lange represented Georgia Tech. The problem of oscillations during emulsion polymerisation in a CSTR system could be eliminated by use of a Tubular pre-reactor to generate a large number of seed particles initially. Steady-state age distribution analysis of a seed-fed CSTR provides a method for evaluating the radical desorption parameter which is important when a relatively water-soluble comonomer such as acrylonitrile or methyl acrylate is used.

I presented results which have already been noted in earlier issues of this 'Newsletter' indicating that while the micellar nucleation of latex particles must now be considered doubtful even in the case of styrene (and it is certainly not applicable to more water-soluble monomers), it is applicable to the less water-soluble p-tert butyl styrene for which 'emulsifier-free' emulsion polymerisation is impossible and for which limited coalescence of latex particles is not a factor at 60 °C.

P.A.Weerts represented the large new group working on emulsion polymerisation at the Eindhoven University of Technology led by J.L.M. van der Loos and A.L.German discussing the emulsion polymerisation of butadiene. He concluded that the efficiency of both water-soluble (persulphate and azobiscyanopentanoic acid) and water-insoluble (AIBN) initiators in nucleating latex particles was low. Using dresinate 214 as emulsifier, particle size measurements showed the occurrence of extensive particle coalescence at all emulsifier concentrations below 6.5% in the water phase (c.m.c. 0.12%). The order of particle number and polymerisation rate in emulsifier concentration differ showing the average number of radicals per particle to be a function of particle size. The emulsifier exponent was found to increase with ionic strength indicating an increasing degree of coalescence. Constant Interval II rates were observed despite the lack of constancy of latex particle number. Case I kinetics were being observed with radical exit from particles attributable to transfer to monomer rather than mercaptan.

Victoria Dimonie (Lehigh) compared 'Dowfax' 8174 (a predominately C_{12} dialkylated diphenyl ether disulphonate) as emulsifier in the copolymerisation of styrene and butadiene or butadiene and acrylonitrile with sodium dodecyl sulphate. The 'Dowfax' surfactants (which differ in the nature of the alkyl substituents) are widely used industrially because of their electrolyte tolerance and stability to acids and alkalis but they are a mixture of homologues rather than pure compounds. She had reported in the Lyon Symposium that the critcal factor determining the particle size obtained in the styrene-butadiene emulsion copolymerisation was the adsorption energy of the surfactant at the particle/water interface. The higher the adsorption energy, the larger the interfacial area which can be stabilised by a given amount of surfactant so that a larger number of smaller particles is produced.

Akron was represented by Gary Jialanella who discussed the use of a copolymer of polymethyl methacrylate and hydroxypropyl methacrylate on to which polyoxymethylene branches had been grafted as emulsifier in the emulsion polymerisation of methyl methacrylate. With a supposedly optimum hydrophobe/hydrophile ratio of 0.4 an emulsifier concentration of 2.5 % on the aqueous phase (20% on monomer) was found to effect good stabilisation. Varying the backbone molecular weight between 4000 and 20 000 with the branch molecular weights at 2000 was found to have no effect. One molecule of the polymeric surfactant with the largest backbone had the same effect as five molecules with the smallest backbone. But the emulsifer was less effective when the molecular weight of the branches was reduced below 2000. Increasing the number of grafted side-chains improved the emulsifier. The graft copolymers were vastly more effective than the same concentrations of polyoxyethylenes of the same molecular weight alone.

Christian Pichot reported on the copolymerisation of small quantities of N-methylol acrylamide with butyl acrylate and styrene or butyl acrylate and methyl methacrylate to obtain a film-forming latex which can be cross-linked by heating when formaldehyde is eliminated to form methylene bridges from the methylol groups. In agreement with H.Kawaguchi et al. (J.Appl.Polym.Sci. 26 (1981) 1649) it was confirmed that the N-methylol acrylamide polymerises rapidly at the beginning and end of the reaction but that its polymerisation stops between these stages whilst the bulk of the hydrophobic monomers reacts. This is because, once latex particles are formed, they capture all the initiator radicals formed from persulphate in the aqueous phase.

It was found that most of the poly(N-methylol acrylamide) was grafted to or strongly adsorbed on the exterior of the latex particles and that the difference in particle diameters as measured by Dynamic Light Scattering and Transmission Electron Microscopy could be used to measure the thickness of the polymethylol acrylamide layer which collapses when the dispersion medium is removed. ^{13}C n.m.r. of the latex comprises a high resolution spectrum due to the polymethylol acrylamide on the surface of the particles superimposed on a broad line spectrum attributable to the core copolymer. Soap titration using sodium dodecyl sulphate showed that the molecular area occupied by this surfactant was much higher on the terpolymer than on a similar copolymer latex without the methylol acrylamide. Very little water-soluble polymethylol acrylamide homopolymer was produced: too much of this homopolymer will flocculate the latex.

D.T.Wu of DuPont's Marshall Laboratory in Philadelphia discussed the use of dynamic light scattering to investigate the conformations adopted by steric stabilisers in different solvents which could affect the rheology of the dispersions and the properties of coatings formed from them as well as the stability of the dispersion. The hydrodynamic layer thickness is determined from the difference in particle diameters determined by dynamic light scattering with and without the steric stabiliser but it is important that the particles be monodisperse if the conversion from diffusion coefficient (which is what DLS actually measures) to diameter is not to be invalidated. Silica particles were used to ensure absence of swelling in the organic solvents used. The steric stabiliser also needs to be monodisperse so that the chain length of the polymer on the surface of the particles can be known. Alkyl methacrylate stabiliser were synthesised by group transfer polymerisation with some triethoxy silyl propyl methacrylate added prior to termination to provide an anchor group. Using polybutyl methacrylate $\bar{M}_n$ = 30 000 grafted on to 194 nm diameter silica particles, the tickness of the hydrodynamic layer was found to vary with solvent quality from 10 nm in isopropanol to 20 nm in ethyl acetate all the solvents being better than θ-solvents giving stable dispersions. Intrinsic viscosity measurements show that the configuration of the steric stabiliser is not that of a random coil but that the polymer is more or less extended according to the quality of the solvent.

A second contribution from L.M.O. Vernaison was given by B.Dumont following up the work of K. Kato et al. (Coll. Polym.Sci. 264 (1986) 737. 265 (1987) 950) on the use of the amphoteric N,N-dimethy-n-Lauryl betaine as an emulsifier which permits the preparation of concentrated monodisperse latices with a particle size in the 50-100 nm range. The sulphobetaines used in this work gave higher critical coagulation concentrations against sodium and magnesium ions than were obtained with sodium dodecyl sulphate.

D. Kranz (Atochem) reported on the location of the carboxyl groups and the stability of carboxylated styrene-butadiene latices which are widely used for carpet backing, paper coating, and in non-woven fabrics. Copolymerisation with acrylic acid produces more acid groups on the surface than does methacrylic acid. In different recipes (which are not disclosed) it was found that between 1 and 43 % of the carboxylated co-monomer finished up in the aqueous phase as a water soluble polymer, 10 to 65 % of the carboxyl groups were in the interior of the latex particles causing an increase in glass transition temperature of up to 20° and 34 to 68% were on the surface of the particles.

D.V.Keight (ICI, Runcorn) discussed the persulphate/metabisulphite initiator system which is not thoroughly understood despite having been widely used for over 40 years. Such suggestions as to the mechanism of the reaction which have appeared in the literature appear to be inadequate. There was an inverse relationship between polymer molecular weight and particle stability: there are more surface sulphonate groups when the polymer molecular weight is low.

Richard Lynn (Department of Pharmaceutical Sciences, University of Nottingham) gave an account of the surface chemical analysis of polymer latex particles using X-ray Photoelectron Spectroscopy (at the University of Surrey) and Secondary Ion Mass Spectrometry (at UMIST). However the results obtained do not, as yet, appear to provide much additional information except that it has been possible to detect residual surfactant on the surface of a latex which had been subjected to rigorous cleaning procedures.

Peter Lovell (Materials Science Centre, UMIST) described the preparation of 'onion-skin' particles by emulsion polymerisation which had alternating rubbery and glassy layers for use in toughening polymethyl methacrylate. There was a market for a tough thermoplastic which would be cheaper than polycarbonate. Although such materials were patented as long ago as 1973 they have not attracted much attention in the scientific literature hitherto. Rubbery seed particles of crosslinked poly(n-butyl acrylate)-co-styrene were overcoated with crosslinked glassy poly(methyl methacrylate)-co-(ethyl acrylate) followed by a second rubbery layer and a final thin glassy layer. The outside glassy layer is essential to prevent coalescence when the latex is coagulated to isolate the particles. Crosslinking is necessary to ensure that the particles retain their integrity during melt processing. The cross-linking agen also achieves grafting across the interfaces. Blending of these particle with polymethyl methacrylate greatly enhances the toughness of the polymethyl methacrylate without significant reduction in transparency and with only a moderate reduction in modulus.

Something altogether different was described by A.Fiorillo of Morton Thiokol: a mixture of an aqueous polysuphide dispersion with a vinyl acrylic latex to give a film-forming composition which was very effective in preventing the leakage of radon gas from the underlying rock into houses which was now believed to be a major cause of lung cancer in areas at risk (e.g. Cornwall) second only to smoking.

John Hearn (Trent Polytechnic) spoke on the use of surfactant-free latices to prepare films through which the permeability of nitrophenol or aniline and its derivatives could be studied and compared with similar results on solvent cast films. The effect of the presence of surfactants on the results could then also be studied.

Stranded in Kingston by the one-day rail strike on the day he has due to speak, Mel Croucher nevertheless gave a brilliant presentation on the following day not only of his own paper on the use of non-aqueous latices as liquid developers for xerography to produce coloured copies but also of the contribution of his Turkish co-worker Professor Pekcan despite the fact that he had seen Pekcan's text for the first time only two days previously.

Most of the remaining papers were concerned with natural rubber latices which would probably be of lesser interest to members of the Polymer Colloids Group although of equal or greater interest to many of the Conference participants.

33rd IUPAC INTERNATIONAL SYMPOSIUM ON MACROMOLECULES
July 8-13, 1990

SYMPOSIUM 2.5: POLYMER COLLOIDS

Symposium Chairman:
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SESSION TITLES	SESSION CHAIRMAN	SESSION CO-CHAIRMAN	INVITED SPEAKERS
Emulsion and Dispersion Polymerization	Prof. M. El-Aasser Emulsion Polymer Institute Lehigh University Bethlehem, PA 18105, USA	Prof. R. Pelton Dept. Chem. Eng. McMaster University Hamilton, Ontario	Prof. R. Ottewill
Characterization of Polymer Colloids	Prof. P. Stenius Ytkemiska Institute Box 5607 S-114 86 Stockholm, Sweden	Prof. M. Winnik Dept. of Chemistry U of Toronto Toronto, Ontario	Prof. R. Rowell
Interfacial Properties of Polymers	Prof. R. Ottewill Dept. Physical Chemistry Univ. of Bristol Bristol, U.K.	Prof. T. van de Ven	Prof. P. Stenius
Composite Particles	Prof. R. Rowell Dept. of Chemsitry U. of Massachusetts Amherst, Mass. 01003, USA	Dr. J. Waters	Prof. M. El-Aasser

15/03/89

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

Simulation of the Latex Particle Morphology.

(José C. de la Cal, Rosa Urzay, Aranzazu Zamora, Jacqueline Forcada and José M. Asua)

A model has been developed for the simulation of the formation of the polymer particle morphology under conditions in which the new polymer chains are compatible with the polymer previously formed. The model involves the calculation of the monomer gradients within the particles due to discrepancies in thermodynamic interactions between the monomer and the different polymers present in each part of the polymer particle. In addition, the distribution of free radicals in the latex particle is taken into account. This distribution results from the anchoring of the hydrophilic end-group of the growing polymer chain on the surface of the particle. The profile of concentration of free radicals in the polymer particles is calculated taking into account the following events: i) Entry in the polymer particle of an oligoradical from the aqueous phase and subsequent anchoring on the surface of the polymer particle; ii) Growing of the polymer chain inside the particle until a transfer reaction occurs; iii) Diffusion of the generated monomeric-unit free radical until it reaches the surface of the polymer particle and desorbs or undergoes a propagation reaction. In this case, diffusion stops and a new polymer chain begins to grow. In order to simulate these processes a Monte Carlo approach was used. The model was applied to the simulation of the polymerization of vinyl acetate on a heterogeneous butyl acrylate-vinyl acetate copolymer seed. Both

Interval II and Interval III were considered taking into account the changes in particle size occurring during these intervals. Figure 1 presents the time evolution of the morphology of a 30 nm seed particle. It was found that the development of the particle morphology was mainly due to the profile of concentration of radicals in the particle. On the other hand, the effect of the monomer-polymer thermodynamic interactions on the particle morphology was found to be negligible. However, it has to be pointed out that this is because, for the system studied, the interaction parameters of vinyl acetate with polyvinyl acetate and polybutyl acrylate are nearly identical.

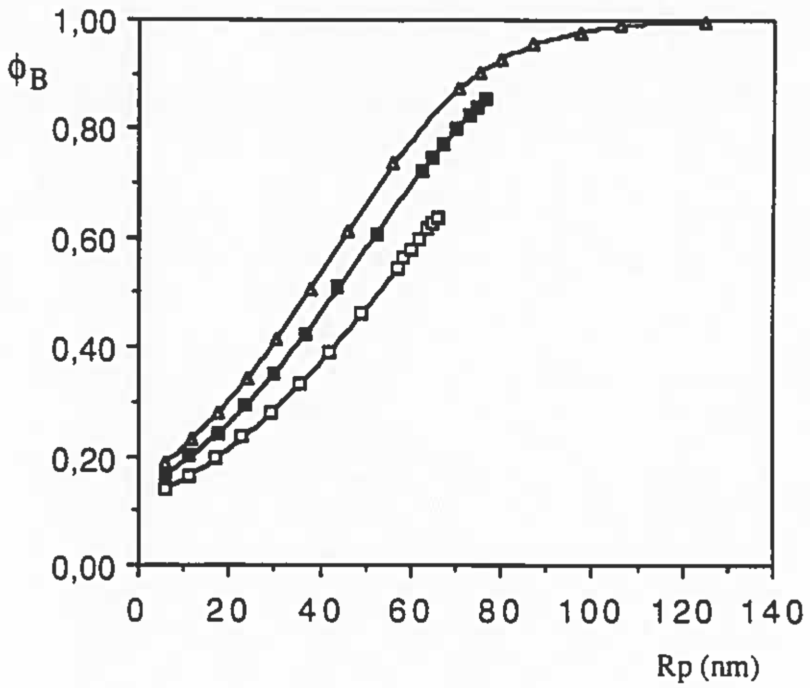


Figure 1.- Time evolution of the polymer particle morphology.
r_o = 30 nm ; □ t = 5 min ; ■ t = 10 min ; △ t = 105 min.
ϕ_B : volume fraction of polyvinyl acetate.

Accepted for publication in J. Polym. Sci., Polym. Chem. Ed.

Modeling of Unseeded Emulsion Copolymerization of Styrene and Methyl Methacrilate

(J. Forcada and J.M. Asúa)

A mathematical model for the unseeded emulsion copolymerization of styrene and methyl methacrylate has been developed. This model, which includes a new rate coefficient for radical desorption, was used to analyze the effect of the styrene/methyl methacrylate molar ratio in the initial charge on the number of particles, overall conversion and copolymer composition. It was found that the number of particles increased with the methyl methacrylate content and that a drift of the copolymer composition resulted during the polymerization of styrene/methyl methacrylate molar ratios other than 50/50. Good agreement between experimental results and model predictions was achieved.

Accepted for publication in J. Polym. Sci., Polym. Chem. Ed.

NOVEL AZO INITIATOR/STABILISERS FOR AQUEOUS EMULSION POLYMERISATION REACTIONS.

I. PREPARATION, DECOMPOSITION KINETICS AND SOLUTION PROPERTIES

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

At the Gordon Research Conference on Polymer Colloids held in July of this year, I presented a paper which summarised an investigation we completed a few years ago into the preparation and properties of a novel series of non-ionic azo initiators which are water-soluble and surface-active. As such, they are capable of functioning as colloid stabilisers for the latex which forms as an aqueous emulsion polymerisation reaction proceeds, and so they are suitable for the initiation of aqueous emulsion polymerisation reactions in the absence of other colloid stabilisers. This investigation has hitherto remained unpublished, except for two contributions to the Polymer Colloid Group Newsletter. A surprising (to me at any rate!) degree of interest was shown in these initiators, both during and after the presentation at the Gordon Research Conference. Several requests for further information were received. Although it is certainly our intention to publish this work in detail in an appropriate journal in due course, the pressure of other commitments is such that it will be some time before anything appears in print. I have therefore undertaken to make some information available by way of two further contributions to the Polymer Colloid Group Newsletter.

The initiator/stabilisers we have investigated are the di-esters of 4,4'-azobis-4-cyanopentanoic acid (4,4'-AB-4-CPA) and a range of fatty-alcohol ethoxylates based upon a mixture of cetyl and oleyl alcohols. The esterification reaction is carried out by reacting the diacid chloride of 4,4'-AB-4-CPA with the fatty-alcohol ethoxylate. It is presumed that esterification takes place *via* the terminal hydroxyl group of the fatty-alcohol ethoxylate. The starting materials for the preparation of these initiator/stabilisers are (1) a range of the fatty-alcohol ethoxylates, and (2) 4,4'-AB-4-CPA. The fatty-alcohol ethoxylates we used are commercial materials (the "Texofor A" series supplied by ABM Chemicals). They were used as received. The 4,4'-AB-4-CPA can either be purchased as such or prepared by a procedure in which 1 mole of sodium cyanide and 0.5 mole of hydrazine sulphate are dissolved in 500 cm^3 of water at 50°C, and to this solution is added over a period of 30 minutes a solution of 1 mole of laevulinic acid and 1 mole of sodium hydroxide in 200 cm^3 of water. The solution is stirred vigorously, and bromine added until the solution is deep yellow in colour. The excess bromine is removed by adding sodium hydrogen sulphite until the colour is white/pale yellow. The white solid which precipitates is collected and washed once with iced water. The yield is *ca.* 40%. The diacid chloride of 4,4'-AB-4-CPA can be prepared by reacting 0.1 mole of 4,4'-AB-4-CPA with 0.3 mole of phosphorus pentachloride in 300 cm^3 of benzene. The mixture is allowed to stand in an ice bath for 30 minutes, and then for 2 hours at room temperature. The solution is filtered and dried using a rotary evaporator. The product is a pale-yellow solid. It is washed twice with a 1:3 mixture of diethyl ether and hexane. The residue is then dissolved in the minimum volume of dichlorohexane, and the diacid chloride precipitated by adding hexane. The product is a white solid of pungent odour. The yield is *ca.* 65%. The product has been characterised by elemental analysis, infrared spectroscopy, ^{13}C NMR spectroscopy, and mass spectroscopy. The characterisation data for the batches of compound subsequently used to prepare the derivatives of the fatty-alcohol ethoxylates are consistent with the compound having been the expected diacid chloride of 4,4'-AB-4-CPA. However, it should be noted that sometimes we obtained products which appeared to differ significantly from the expected diacid chloride, and which yielded derivatives with aliphatic alcohols which had unexpected properties. We do not at present have a plausible explanation for the formation of two different products on different occasions under virtually identical reaction conditions, although we have investigated this problem in some detail and have had discussions with organic chemists.

The initiator/stabilisers are then prepared by reacting 1 mole of the diacid chloride with 2 moles of fatty-alcohol ethoxylate and 2 moles of triethylamine in 300 cm^3 of toluene at room temperature for one hour. A precipitate of triethylammonium chloride forms almost immediately. This precipitate is removed by filtration, and the desired derivatives isolated by evaporating the toluene at 35°C using a rotary evaporator. The derivatives are obtained as white waxes in near-theoretical yield. We have used them without further purification. The infrared spectra of compounds obtained by reacting the diacid chloride of 4,4'-AB-4-CPA with hydroxy compounds are consistent with those compounds being the expected esters of 4,4'-AB-4-CPA.

Initiators based upon ethoxylates which contain 10 mols of ethylene oxide or less appear to be at most only very sparingly soluble in water. Initiators based upon ethoxylates which contain 14 or more mols of ethylene oxide are soluble in water at ambient temperatures, although, as expected, they show a cloud-point transition as the temperature of the aqueous solution is raised. The temperature of the cloud point increases as the degree of ethoxylation increases, being *ca.* 55°C for the 14-mole ethoxylate ester and > 80°C for the 45- and 60-mole ethoxylate esters. The initiators from the higher ethoxylates are able to reduce the surface free energy of water to *ca.* 46 mJ cm^{-2}. However, whereas the curves of surface free energy *v.* concentration for the parent ethoxylates are such that it is possible to estimate critical micelle concentrations from them, this is not so for the ester derivatives.

The ultraviolet absorption spectra of the fatty-alcohol ethoxylate derivatives are consistent with them being the expected azo compounds. The kinetics of the thermal decomposition of these derivatives in water have been determined by following the decrease in the intensity of the ultraviolet absorption at 350 nm. The initial concentration of azo groups was determined from the absorption after heating the solution at 70°C until the absorption underwent no further change. Satisfactory first-order plots for the decomposition were obtained for each of the derivatives at all the temperatures investigated. Typical results (for the derivative obtained from the 30-mole ethoxylate) are as follows:

temperature/°C	k_d/s^{-1}
50	3.24×10^{-6}
60	1.02×10^{-5}
65	1.80×10^{-5}
70	3.09×10^{-5}

In all cases, satisfactory Arrhenius plots for log k_d *v.* T^{-1} were obtained, at least over a limited range of temperature. From these Arrhenius plots, the following activation energies were calculated:

derivative from 24-mole ethoxylate : 164 kJ mol^{-1}
derivative from 30-mole ethoxylate : 132 kJ mol^{-1}
derivative from 45-mole ethoxylate : 105 kJ mol^{-1}
derivative from 60-mole ethoxylate : 135 kJ mol^{-1}

Both the k_d-values and the energies of activation are broadly as expected for azo initiators, but the variation of energy of activation with ethylene oxide rank is unexpected, and is greater than can reasonably be attributed to experimental error.

POLYMER COLLOID GROUP NEWLETTER

Contribution from the Institut Charles Sadron (CRM-EAHP)
6, rue Boussingault, 67083 Strasbourg Cédex

by

Françoise CANDAU

POLYMERIZATION IN MICROEMULSIONS : I. FORMULATION AND STRUCTURAL PROPERTIES OF MICROEMULSIONS CONTAINING A CATIONIC MONOMER

(in collaboration with P. Buchert).

Microemulsions are attractive media for polymerization reactions. However, the formulation of polymerizable microemulsions is subject to severe constraints, due in large part to the high surfactant level (≃ 10%) needed for achieving their thermodynamic stability. This fact, together with the requirement of high polymer contents in most applications raises the problem of specific monomer-surfactant interactions, which generally tend to destabilize the dispersion or to produce ill-defined products. In a recent series of papers (1,2), we have developed a method for preparing microemulsions based on acrylamide and/or sodium acrylate, which led after polymerization to very stable and clear inverse microlatexes. The purpose of the present investigation was to extend the process to the polymerization of a cationic monomer, a methacryloyloxyethyltrimethylammonium chloride (MADQUAT), used in numerous applications as thickener, dispersant or flocculant. To optimize the procedure, we have used an approach similar to the so-called CER (Cohesive Energy Ratio) concept developed by Beerbower and Hill (3) for the stability of classical emulsions. The basic assumption of this approach is that the partial solubility parameters of oils (δ_0^2) and lipophiles (δ_L^2) as well as those of water (δ_ω^2) and hydrophiles (δ_H^2) are perfectly matched. When these conditions are met, one gets the following relationship

$$HLB_0 = 20\ \delta_L^2\ (K + \delta_L^2) \qquad (1)$$

where HLB_0 is the optimum HLB when $\delta_L^2 = \delta_0^2$ and K is a constant defined by

$$K = R_0\ \delta_H^2\ d_L/d_H \qquad (2)$$

R_0 is the ratio of the cohesive energies of lipophile for oil and hydrophile for water and d_L, d_H the density of the lipophile and hydrophile respectively. By using these criteria, general rules of selection for a good chemical match between oils and nonionic surfactants have been established. The cationic water-soluble monomer plays an important role in the formulation, owing to its amphiphilic and electrolytic character, as confirmed by surface tension (Fig.1) and turbidimetry experiments. As a cosurfactant, it enhances considerably the microemulsion domain and as an electrolyte, it salts-out the surfactant. These effects taken together control the structural properties of the microemulsions. The optimal conditions correspond to bicontinuous microemulsions characterized by interconnected oily and aqueous domains. These microemulsions form in an HLB range (HLB ≃ 12-13) much higher than would be expected in the absence of monomer.
A typical polymerization recipe is the following : cyclohexane : 37.5% ; MADQUAT : 25% ; water : 25% ; nonionic surfactants (HLB = 12.9): 12.5%.

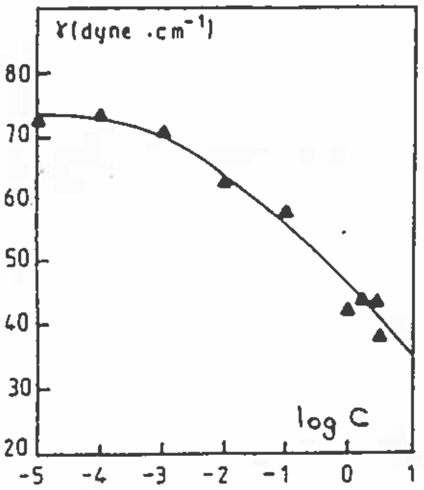


Figure 1.: Surface tension versus MADQUAT molar concentration in water.

The effect of monomer in polymerizable microemulsions could be quantitatively expressed from the CER concept. The Beerbower and Hill approach assumes a perfect chemical match between hydrophile and water. Addition of monomer obviously modifies the matching, since it affects the value of $\delta_w^2 - \delta_H^2$ included in the constant K used in the evaluation of optimum HLB (see Eq.2).

The partial solubility parameters of the aqueous phase δ_{aq}^2 (i.e. water + monomer) have been evaluated from the $\gamma = f[\text{MADQUAT}]$ measurements reported in Fig.1 and from the following relationship.

$$\gamma = 0.0715\, V^{1/3}\, (\delta_d^2 + 0.632\, \delta_p^2 + 0.632\, \delta_h^2) \qquad (3)$$

which relates the solubility parameters of many liquids (including water) to their surface tensions (4). In Eq.(3), the subscripts d, p and h refer to the London dispersion forces, Keesom polar forces and hydrogen-bonding forces respectively. The pseudo-constant K and the corresponding HLB_0 have been thus recalculated for each given composition of the aqueous phase. It could be shown that increasing the monomer content in the starting microemulsion amounts to increasing the HLB_0 by several units (Figure 2). In spite of some approximations implied in the calculations, this approach seems quite satisfactory in predicting the unexpectedly high HLB values required for these polymerizable microemulsions.

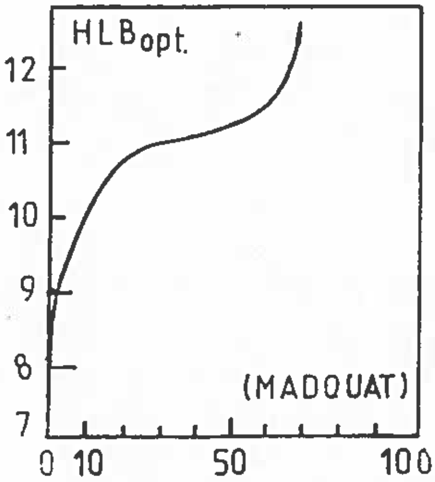


Figure 2. : Calculated curve of optimum HLB versus MADQUAT weight percentage.

The optimal conditions reported here are the same as those needed to promote clear and stable microlatexes after polymerization. The properties and characteristics of the latexes and polymers formed by this process will be given in a future report.

References.

1) Candau, F., Zekhnini, Z., and Durand, J.P., J. Colloid Interface Sci., 114, 398 (1986).

2) Holtzscherer, C., and Candau, F., J. Colloid Interface Sci., 125, 97 (1988).

3) Beerbower, A., and Hill, M.W., in "Mc Cutcheon's Detergents and Emulsifiers Annual" (Allured Publ.Co., Ridgewood) pp.223, N.J. 07450, 1971.

4) Beerbower, A., J. Colloid Interface Sci., 35, 126 (1971).

Recent Publications.

1) Kinetics of Photopolymerization of Acrylamide in AOT Reverse Micelles, M.T. Carver, U. Dreyer, R. Knoesel, F. Candau and R.M. Fitch, J. Polym. Sci. Part A, 27, 2161 (1989).

2) Effect of Solution Components on the Termination Mechanism in Acrylamide Microemulsion Polymerization,
M.T. Carver, F. Candau and R.M. Fitch, J. Polym. Sci. Part A, 27, 2179 (1989).

3) Percolation and Particle Nucleation in Inverse Microemulsion Polymerization,
M.T. Carver, E. Hirsch, J.C. Wittmann, R.M. Fitch and F. Candau, J. Phys. Chem., 93, 4867 (1989).

EFFECT OF POLYMERIZATION SURFACTANT AND ADDED SURFACTANTS ON THE VISCOSITY OF ACRYLIC LATEXES

By James S. Dodge, The B. F. Goodrich Co.
P. O. Box 122, Avon Lake, Ohio 44012, U.S.A

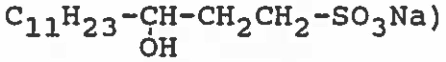
(This summarizes a paper given at the Polymer Colloids Gordon Conference, July 1989. The paper has not yet been submitted for publication.)

When caustic, ammonia, organic amine or other base is added to a carboxylated latex, the viscosity of the latex may increase substantially with increasing pH. Some authors, including both Verbrugge and Bassett and Hoy, have presented evidence that this is attributable to swelling of the particles. For some compositions, we have obtained data which indicate that water-soluble polymer plays a major role in the viscosity increase. Furthermore, the type of surfactant present, if any, both during polymerization and added later, has a major influence in the magnitude of the viscosity developed.

For latexes made by polymerizing ethyl acrylate (EA) with minor amounts of acrylic acid (AA) and N-methylol acrylamide (NMA), the viscosity developed at high pH depends partially on particle swelling and to a major amount on water-soluble polymer. When alpha olefin sulfonate (AOS) is used as the polymerization surfactant, chain transfer to surfactant occurs, apparently to give lower molecular weight of water-soluble polymer, and lower viscosity at high pH, than when sodium lauryl sulfate (SLS) is used. (AOS is a mixture of compounds, predominantly the sodium salts of alkenyl sulfonates and hydroxyalkane sulfonates, as shown below:

$$C_{11}H_{23}-CH=CH-CH_2-SO_3Na$$

and



$$C_{11}H_{23}-\underset{OH}{CH}-CH_2CH_2-SO_3Na)$$

Conductometric titration provides confirmation that AOS is a chain transfer agent, providing additional strong acid groups on the surfaces of latex particles. Added SLS can significantly increase the viscosity at high pH; SLS solubilizes polymers of this type. By contrast, AOS does not solubilize such polymers to the extent that SLS does. Added nonionic surfactant containing PEO chains can decrease the viscosity at high pH by complexing with SLS. The formation of a PEO-SLS complex appears to prevent or drastically decrease polymer solubilization by SLS. Use of a water-phase polymerization inhibitor (hydroxyl amine sulfate) can significantly decrease the extent of water-soluble polymer for these compositions and, hence, the extent of viscosity increase at high pH. For a more hydrophobic polymer composition (n-BA instead of EA), the viscosity developed at high pH is lower by a factor of 100 and the extent of solubilization of polymer by SLS apparently is much lower. For a slightly different hydrophilic polymer composition, (substituting additional AA for the NMA), the extent of polymer swelling is substantially increased and the viscosity developed is correspondingly larger.

Contribution to the Polymer Colloids Group Newsletter

M.S. El-Aasser, A. Klein, C.A. Silebi, J.W. Vanderhoff
E.S. Daniels, V.L. Dimonie, O.L. Shaffer, and E.D. Sudol

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The titles of our current research projects are given in the enclosed Contents of our Graduate Research Progress Reports, No. 32, July 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. Preparation and Characterization of Acrylate Latexes Prepared with Itaconic Acid

(Michele Lock)

Itaconic acid, a dicarboxylated vinyl monomer, was studied in terms of its influence on various parameters in emulsion copolymerization with n-butyl and methyl acrylate. The primary factors examined were final monomer conversion levels, particle size trends and differences between batch and semicontinuous latex preparation.

It was found that itaconic acid caused an induced decomposition of potassium persulfate, which resulted in a lowering of the initiator efficiency. Therefore, the water-soluble azo initiator 4,4'-azobis(4-cyanopentanoic acid) was chosen for use throughout the majority of this study.

A mechanism was developed to explain why the amount of itaconic acid present in a recipe caused the lowering of both the final itaconic and acrylate conversion levels in batch latexes. Although the carboxylated monomer essentially did not affect the rates of acrylate conversion during the middle stage of emulsion copolymerization, its presence was found to slow down the rates in the final stage. This occurs due to the favorable probability of copolymer oligomeric radical capture by growing particles during the middle stage of conversion. However, during the final stage, the radical flux into the particles decreases due to the unfavorable probability of capture of polar oligomeric radicals consisting mainly of itaconic acid, so that both types of monomers find it difficult to convert.

Adding tetrahydrofuran to the latex recipe showed that the monomer conversion levels reached during the final stage could be increased. This came about due to this solvent's ability to increase the concentrations of the acrylate monomers in the aqueous phase. Consequently, copolymer oligomeric radicals were formed for a longer period of time, which led to more itaconic acid being converted as well as maintaining the radical flux into the particles so that more acrylate monomer could be polymerized.

In regards to particle size, the trend seen was one of larger size when itaconic acid was present in a latex. This was found to be a result of a lowered number of particles being nucleated in the initial stage of emulsion copolymerization, thus causing the final particle sizes to be larger. Itaconic acid did not cause coalescence of particles during the course of polymerization.

Semicontinuous preparation resulted in monodisperse latexes when itaconic acid was present in the recipe, demonstrating the beneficial effect of the monomer in keeping secondary particles from forming during the monomer addition period. These latexes exhibited higher final acrylate conversion levels along with lower final itaconic acid conversion levels, compared to batch latexes, which was related to the tendency of forming copolymer oligomeric radicals when adding the monomers semicontinuously.

2. Synthesis of Monodisperse Porous Polymer Particles

(Chieh-Min Cheng)

The seeded emulsion polymerization technique was used to synthesize 10μm diameter monodisperse porous polymer particles. Linear polymer (polystyrene seed) or a mixture of linear polymer and solvent or nonsolvent were used as inert diluents. By the addition of solvent together with a mixture of styrene and divinylbenzene into swellable, monodisperse polystyrene seed latex particles, a porous structure is obtained by removal of the diluents following polymerization. The monodispersity was maintained during this process. The pore diameters of the resulting macroporous polymer particles were on the order of 1,000 Å with specific surface areas up to 300 m^2/g.

The pores of the macroporous polymer particles consist of the spaces between microspheres and macrospheres (agglomerates) inside the polymer particles. Nitrogen adsorption-desorption isotherms indicate that there are no pores in the microporous and transitional regions. These measurements also indicate that the surface area of the porous polymer particles indeed consist of those microspheres inside the particles.

The physical properties of the porous polymer particles are governed by various synthesis parameters, such as: (1) crosslink density; (2) type and amount of solvent; (3) amount of linear polymer; (4) nature of the polymer seed particles; (5) initiator concentration; and (6) reaction temperature. The specific surface area is strongly dependent on the overall divinylbenzene content of the particles. Pore size can be controlled by the molecular weight of the linear polymer. If a polymer seed with a low degree of crosslinking is used the surface area and pore size are reduced. Also, the precipitating ability of nonsolvent is dependent on its molecular size and solubility parameter.

In the study of pore structure development, it was found that the pore stability is dependent on the nature of the extraction solvent as well as the crosslinking density.

3. Preparation and Application of Hollow Polymer Particles
(Jong M. Park)

A multistage emulsion polymerization technique was used to prepare hollow polymer particles. The concentric core-shell composite latex particles, comprised of highly carboxylated polymer cores (e.g., copolymer of 70/30 mol% of methyl methacrylate/methacrylic acid) and rigid polymer shells (e.g., polystyrene), were treated with a volatile base at a temperature near the T_g of the shell polymer. Under these conditions the particles are swollen with the aqueous solution and subsequently air voids are generated upon cooling and drying. The sizes of the voids and the overall particles were controlled by varying the size of the alkali-swellable seed particles and the stage ratio in the subsequent core-shell polymerization stage, respectively.

Model hollow polymer particles with void diameters ranging from 130 to 780 nm were prepared by both surfactant-free and conventional emulsion polymerization and used to make microvoid-containing films. The light scattering efficiency of these microvoid coatings was examined using a Cary 2300 spectrophotometer over the wavelength range of 400 to 800 nm. It was found that there is no significant scattering dependency of the microvoids over the void volume concentration of 2 - 14%. The Kubelka-Munk scattering coefficient (S/mil/unit concentration) is plotted against the void diameter in Figure 1. A maximum scattering coefficient of 9.7/mil/unit concentration is observed at a void diameter of 280 nm, which is in good agreement with the theoretical value computed by Ross [J. Paint Tech., 43(563), 50 (1971), who modified the Mie theory by including the effect of multiple scattering and the internal surface reflectance. He computed a maximum scattering coefficient of 10.2/mil/unit concentration at a void diameter of 230 nm.

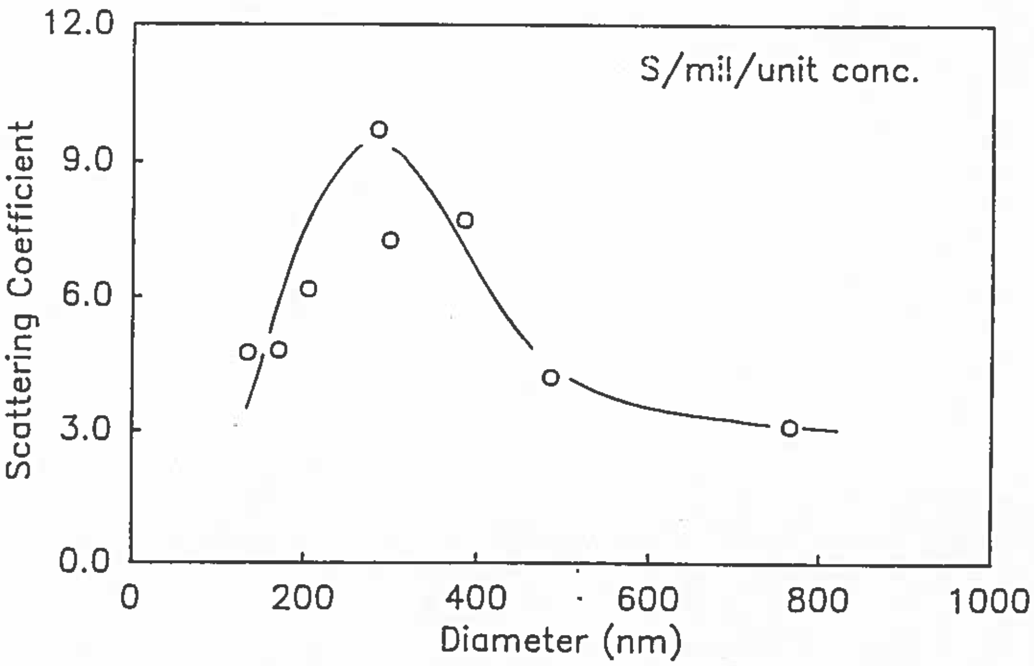

Figure 1: Kubelka-Munk Scattering Coefficient as a Function of Void Diameter.

4. Inverse Emulsion Polymerization of Acrylamide in a Tubular Reactor

(Tom Bash)

Inverse emulsion polymerization of acrylamide was successfully completed in a tubular reactor. The latexes produced were free of coagulum, had high molecular weights, and the kinetics were in general characteristic of a batch reactor. This was anticipated because the flowing emulsion in the tube was broken up into short segments by injecting nitrogen bubbles into the tube, thus each emulsion segment acted as a small batch reactor as it traveled the length of the tube.

The kinetics of inverse emulsion polymerization in the tube were found to be a strong function of the emulsifier used. The surfactant selected for use in the tubular reactor was Tetronic 1102 (an ethylene diamine tetra-N-substituted with polyoxypropylene -polyoxyethylene; BASF Wyandotte Corporation) which was shown to yield inverse emulsions in a xylenes continuous phase of exceptional stability. However, the original batch of this surfactant degraded, apparently by oxidation of the tertiary carbons in the polyoxypropylene chain segments. The degradation became noticeable in the reduced stability of freshly prepared inverse emulsions. Subsequent batches of Tetronic 1102 behaved differently from the original batch in terms of emulsion stability, polymerization kinetics, and other properties when the emulsifier was characterized.

Polymerizations were carried out in the tubular reactor at a temperature of 51.5°C using the same recipe except for different batches of Tetronic 1102, and the results are plotted in Figure 1. Lot WSA1 8021 11104 is the batch supplied in 1989, Lot DEUA 52172 F is the batch supplied in 1986, and Lot DCOA 52172 H is the original batch of Tetronic 1102. It is clear from Figure 1 that Lot DEUA 52172 F (supplied in 1986) inhibits the kinetics in comparison to the lot supplied in 1989. It can also be seen that the kinetics using this latest batch appear to be an extension of the early work with the original batch of Tetronic 1102 before degradation resulted in unstable emulsions.

A mathematical model for inverse emulsion polymerization in a tubular reactor which takes into account the principal microscopic phenomena believed to occur has been developed and used to determine some kinetic parameters through a least squares approach. The model has been applied to an experimental study of interparticle monomer transport from droplets to particles, and the results indicate that monomer transport does not occur at a rate significant enough to affect the kinetics.

The steady-state data (using the batch of Tetronic 1102 supplied in 1989) was analyzed with the model using parameters corresponding to $\bar{n}$=0.08 determined from a least-squares analysis of the model to experimental conversion, molecular weight, and particle size data. Figure 2 shows the experimental steady-state conversion time data along with the simulation using the best fit parameters. Residence time has been non-dimensionalized and normalized such that τ=1 corresponds to 30 minutes. The agreement between the experimental data points and the model simulation is excellent, indicating that the model does a good job of describing the kinetics for this system.

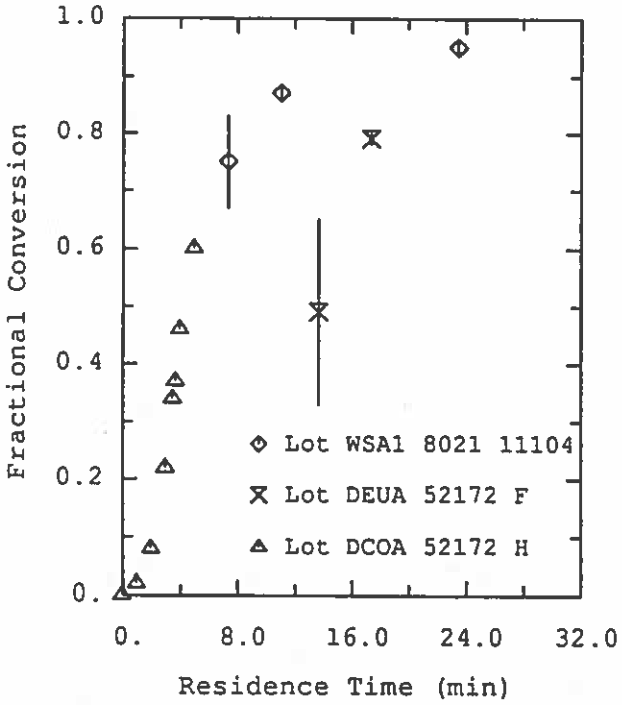

Figure 1: Steady-State Conversion versus Residence Time at 51.5°C for the Different Batches of Tetronic 1102.

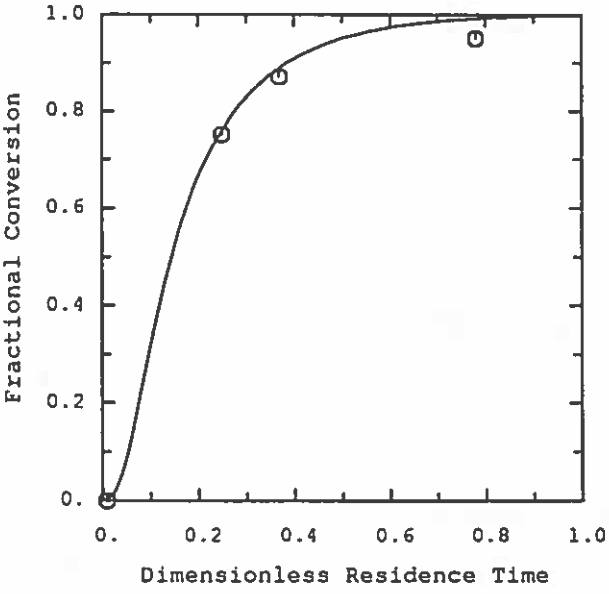

Figure 2: Steady-State Conversion versus Dimensionless Residence Time; Points Represent Experimental Data and Solid Line the Simulation.

Papers Recently Presented

The following papers were presented at the Fall Meeting of the Polymeric Materials Science and Engineering Division of the ACS at Miami Beach, Florida, September 1989.

"Steady Shear and Linear Viscoelastic Material Properties of Associative Thickener Solutions", R.D. Jenkins, C.A. Silebi, and M.S. El-Aasser.

"Characterization of Film Formation from Latex Particles via Small-Angle Neutron Scattering", J.N. Yoo, L.H. Sperling, and A. Klein.

"Theoretical and Experimental Study of Capillary Hydrodynamic Fractionation (CHDF)", C.A. Silebi and J.G. DosRamos.

"Size Analysis of Submicrometer Particles by Capillary Hydrodynamic Fractionation (CHDF), J.G. DosRamos and C.A. Silebi.

"Comparison Between Capillary Hydrodynamic Fractionation and More Standard Methods of Particle Size Analysis: Peak Separation and Broadening", J.G. DosRamos and C.A. Silebi.

Recent Publications

"Interparticle Monomer Transport in Miniemulsions", V.S. Rodriguez, J. Delgado, C.A. Silebi and M.S. El-Aasser, I&EC Research, 28, 65 (1989).

"Microemulsion Polymerization of Styrene", J.S. Guo, M.S. El-Aasser, and J.W. Vanderhoff, in *Polymer Association Structures, Microemulsions and Liquid Crystals*, M.A. El-Nokaly, Ed., ACS Symposium Series No. 384, Washington, D.C.. 1989, pp. 86-99.

"Dynamic Modeling and State Estimation for an Emulsion Copolymerization Reactor", J. Dimitratos, C. Georgakis, M.S. El-Aasser and A. Klein, Computers Chem. Engrg., 13 (1/2), 21 (1989).

"Axial Dispersion of Submicron Particles in Capillary Hydrodynamic Fractionation", C.A. Silebi and J.G. DosRamos, AIChE Journal, 35(8), 1351 (1989).

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

"Development of Graduate Core-Shell Supramolecular Structure in Polystyrene Latexes via Small-Angle Neutron Scattering", Ph.D. Dissertation by Se-In Yuang.

"The Grafting Reactions of Poly(Vinyl Alcohol) During the Emulsion Copolymerization of Poly(Vinyl Acetate-Co-Butyl Acrylate)", Ph.D. Dissertation by Neal J. Earhart.

"Particle Morphology in Seeded Composite Latexes", M.S. Report by Yi-Cherng Chen.

"Semicontinuous Polymerization Utilizing Miniemulsions", M.S. Report by Phan L. Tang.

Copies of the Abstracts are available upon request.

The Emulsion Polymers Institute's 21st Annual Short Course "Advances in Emulsion Polymerization and Latex Technology" will be held at Lehigh on June 4-8, 1990. The European Short Course will be given August 20-24, 1990.

Don't forget the 64th National Colloid and Surface Science Symposium being held at Lehigh on June 18-20, 1990. Contact Mohamed El-Aasser if you require further information.

EMULSION POLYMERS INSTITUTE
Lehigh University

Graduate Research Progress Reports
No. 32 July 1989

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A NOVEL STANDARD INSTRUMENT FOR SURFACE TENSION MEASUREMENTS USING COMPUTER IMAGE ANALYSIS OF A PENDANT DROP

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ABSTRACT

A new method has been developed for the determination of surface and interfacial tensions from primary drop shape data. In addition wetting angles of sessile drops may be determined. The method has been built around a commercial pendant drop instrument and an IBM compatibel PC with a frame grabber card. In order to discriminate the drop profile, a filter routine using local threshold and interpolation technique combined with an edge-tracing algorithm has been developed. The program for calculation of surface tension is divided into two parts. The first part is based on the traditional optical method which uses inflection of the drop profile. By means of several polynomial interpolations and curve fitting of theoretical profiles, the form factor ß and surface tension v is determined. The second part of the calculation utilizes the above values as a first estimate and then performs a further optimalization of v by comparison of experimental and theoretical Young-Laplace profiles. With a PC AT with a 80287 mathematical coprocessor the measurements take about 5 seconds and the accuracy is typically 0.01 - 0.03 mN/m for a wide range of known liquides.

EXPERIMENTAL

A block diagram of the apparatus for pendant drop surface tension measurements appears in Figure 1. All parts are commercially available.

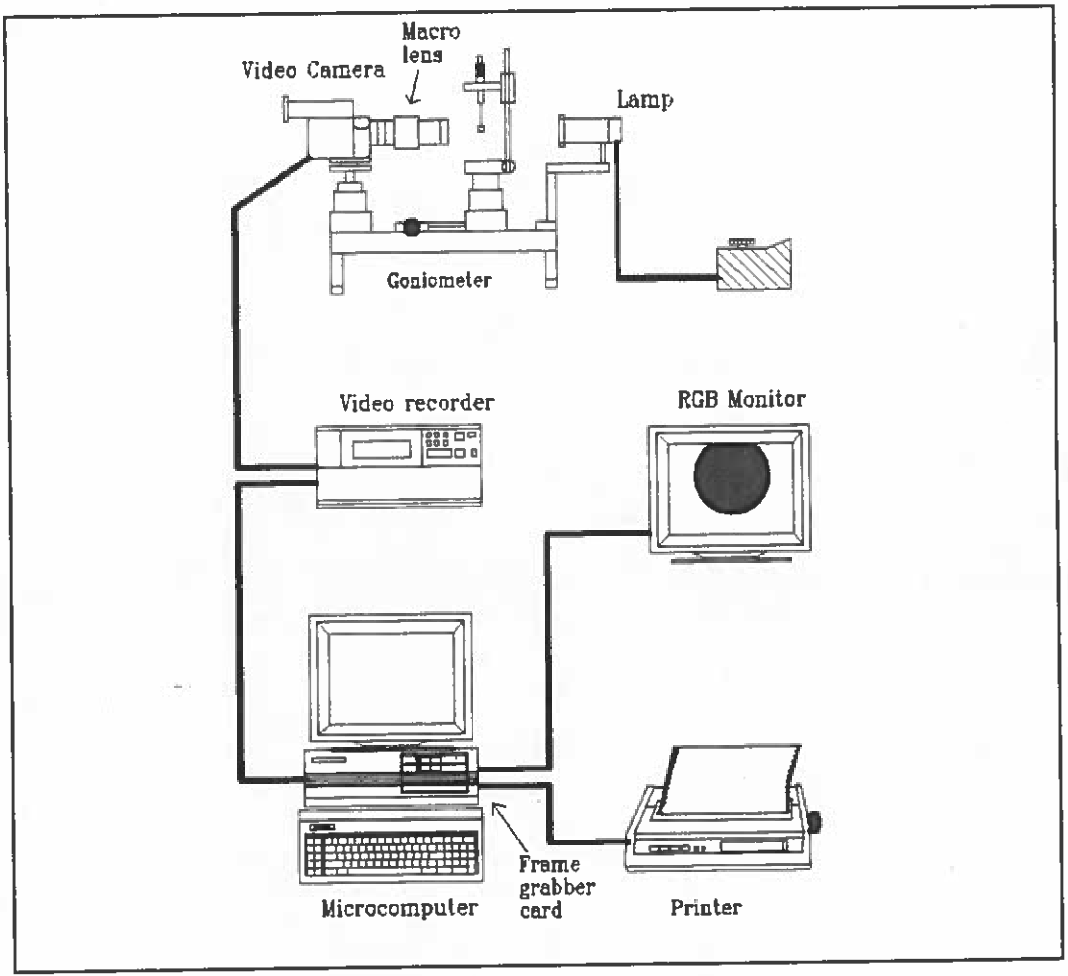

Figure 1.

Schematic setup of the instrument.

Because of the general applicability of the filter routines, it was found useful to include measurement of contact angles in the same instrument. While this is a relatively trivial task, at least with respect to the pure optical measurement, a video-enhanced method is both faster and more accurate. Also the instrument need not be dismanteled in order to measure both surface tension and contact angle in the same experimetal setup.

RESULTS

Comparison of litterature data and measured values of interfacial tension. Method 1 are values calculated from initial size parameters. Method 2 are values from the fitting of full profile data. Standard deviation is calculated from 10 consequitive measurements on the same drop.

Type of liquid	Litterature (mN/m)	Method 1 v (mN/m)	Method 1 Sdev (mN/m)	Method 2 v (mN/m)	Method 2 Sdev (mN/m)
Water (20°C)	72.75	71.4	0.2	71.76	0.02
Formamide	58.2	59.0	0.3	59.05	0.03
Sulfuric acid	55.1	55.1	0.1	57.73	0.01
Ethylene glycol	47.7	46.8	0.1	47.46	0.01
Aniline	42.9	42.8	0.1	41.77	0.02
Pyridine	38.0	36.6	0.2	36.52	0.01
Dimethyl formamide	37.7	35.8	0.2	36.23	0.01
Ethyl benzene	29.20	28.6	0.2	28.21	0.06
2-Ethoxy ethanol	30.0	27.8	0.2	28.58	0.05
Toluene	28.5	28.6	0.2	28.77	0.02
Tetrachlormethane	26.95	27.2	0.1	26.14	0.04
Cyclohexane	25.5	25.1	0.2	24.31	0.05
Hexane	18.43	19.6	0.3	17.72	0.04

This paper was presented at the 10th Scandinavian Synposium on Surface Chemistry, and will be published in the proceedings.

The authors are planning to make the computer program commercially available.

September 26, 1989

CONTRIBUTION TO THE INTERNATIONAL POLYMER COLLOIDS GROUP NEWSLETTER

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

A paper entitled "NMR Linewidth Study of Latex Structure" has been submitted to Colloid & Polymer Science for publication. Its abstract is as follows:

NMR LINEWIDTH STUDY OF LATEX STRUCTURE

C. J. McDonald*, P. B. Smith, D. I. Lee, J. A. Roper, J. G. Galloway

The structure of latex particles with two polymer phases has been investigated by measuring the temperature dependence of the carbon magnetic resonance (CMR) peak linewidths. Interpenetrating polymer networks (IPN) were formed by a continuous-addition process in which a crosslinked seed particle was the site for formation of a linear second-stage polymer. The morphology was controlled by the level of crosslinking in the seed stage. The two polymers of the composite particle differ in their glass-transition temperatures by 100°C. By heating the particles to 50°C above the glass-transition temperature of the softer polymer, which formed the continuous network phase of this composite, it was possible to observe its CMR spectrum independently of the other polymer. The temperature dependence of the linewidth varied with the structure of the network. This was characterized by limiting linewidth behavior at both low and high temperature, which systematically varied as a function of the degree of mixing of the two phases. Differential scanning calorimetry and electron microscopy corroborated the morphology change observed with the linewidth data. The influence of a diluent, present during formation of the network stage, was also examined with this CMR approach.

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School of Chemistry

Polymer Colloids at the University of Sydney

Reporter: D.H. Napper

The occurrence of compositional inhomogeneities in growing latex particles can be of central importance in emulsion copolymerizations. Clever manipulation of the processes that govern the growth of the particles can allow the spatial distribution of the inhomogeneities to be tailor-made to satisfy specific end-use demands. The occurrence of local inhomogeneities in emulsion homopolymerizations is less well-documented and less well-understood.

Grancio and Williams endeavoured to study this phenomenon in seeded styrene emulsion polymerizations by using small amounts of butadiene, which can be stained for electron microscopy, as a trace. Examination of sectioned particles suggested the occurrence of core-shell morphology, with the new polymer being located near to the surface of the particles. This was postulated to result from the formation of a monomer rich shell adjacent to the interface. The latter was argued to be a consequence of the diminished polymer segment density in the interfacial region, resulting from the geometric constraints that the impenetrable interface places on the polymer conformation (an interfacial excluded volume effect). More recently, Sperling and coworkers have used neutron scattering to determine the spatial distribution of deuterium labelled styrene after polymerization in unlabelled latex particles. The scattering was interpreted as showing the existence of core-shell morphology in the final product under appropriate conditions.

Lau and co-workers at Rohm and Haas have also interpreted their ESR results as evidence for inhomogeneities in emulsion polymerizing systems. They measured the value of the propagation rate coefficient (k_p) for methyl methacrylate at high weight fractions of polymer and found that its value was dependent upon the latex particle size. Variations as large as a factor of 5 were reported, the smaller values of k_p being observed in the larger particles.

Martin Mills and Bob Gilbert in the Sydney Group have tackled theoretically the generation of heterogenities in seeded emulsion homopolymerizations by solving the appropriate reaction/diffusion equations for an entering flux of free radicals that remain anchored at the interface. The results show that significant spatial inhomogeneities may arise at high weight fractions of polymer ($w_p>0.9$) and for large particles (e.g., radius = 250 nm, say); small particles do not, however, give rise to significant inhomogeneities. These calculations support the notion that the observed lowering of k_p for methyl methacrylate as a result of increasing the particle size arises from the existence of monomer concentration gradients within the larger polymerizing latex particles at higher weight fractions of polymer. At these high weight fractions of polymer, the concentration of monomer at the polymerizing free radical sites cannot be replenished sufficiently rapidly by diffusion to prevent a drop in monomer concentration, thus causing the k_p measured via the rate of polymerization and ESR to appear to be lower than that observed at smaller particle sizes when significant monomer gradients are absent. The theory does not predict inhomogeneities to the same extent as is apparently observed by neutron scattering. The cause of this discrepancy may arise *inter alia* from the neglect in the theoretical development of the interfacial excluded volume effect mentioned above and/or possible phase separation effects in the experiments arising from the incompatability of proto – and deuterated polymers.

CONTRIBUTION TO POLYMER COLLOID NEWSLETTER

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POLY(NIPAM) LATEXES - BETTER PARTICLES AND ELECTROPHORESIS

Previously we have shown that monodisperse latexes can be prepared by the persulfate initiated, surfactant free polymerization of N-isopropylacrylamide crosslinked with methylenebisacrylamide (R.H. Pelton, H.M. Pelton, A. Morfesis and R.L. Rowell, "Particle Sizes and Electrophoretic Mobilities of poly(N-isopropylacrylamide) Latex" Langmuir, 5, 816-8 (1989).). These latexes are highly swollen in water at room temperature whereas above 32 °C, the LCST of poly(NIPAM), they shrink by a factor of 2 with a correspondingly large increase in electrophoretic mobility.

Latex Preparation

The surfactant free latexes were rather large and not extremely monodisperse. Recently we have produced much smaller latexes by polymerizing in the presence of SDS at 1/20 of the CMC. Very uniform particle sizes distributions with diameters roughly half of the surfactant free case were obtained. Unlike hydrophobic latex, the SDS was easily removed by serum replacement at room temperature.

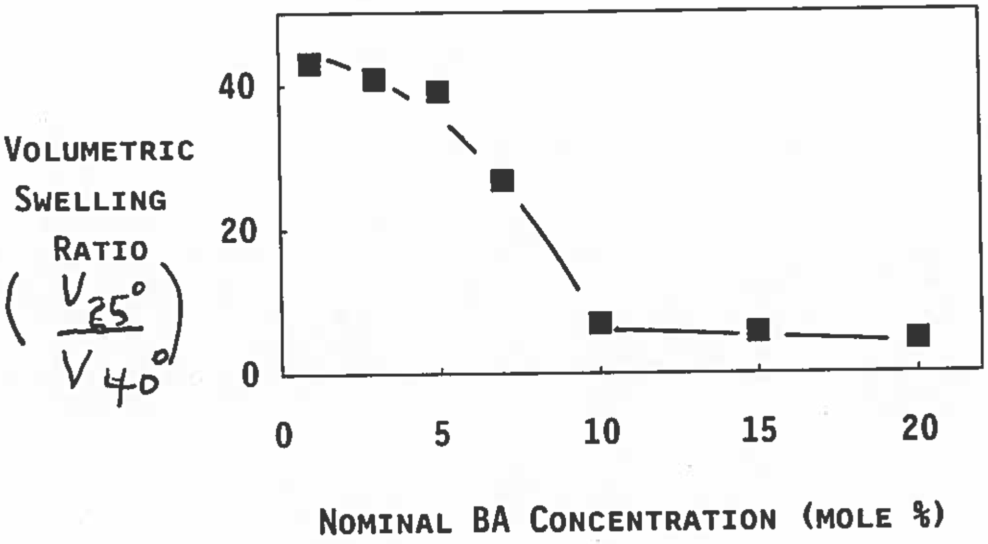
Swelling ratios, determined from dynamic light scattering, are shown as a function of nominal cross-link density in Figure 1. Obviously, more cross-linking leads to less swelling. Particles could not be prepared at methylene bisacrylamide concentrations lower or higher than shown in Figure 1. The lower limit is simply due to the fact that linear poly(NIPAM) dissolves in water at room temperature. The upper limit is more difficult to understand. Our working hypothesis is that with high methylene bisacrylamide, the sulfate groups from the persulfate are buried in the particles preventing sufficient surface charge density for colloidal stabilization.

In another project we have begun to measure the polymerization kinetics.

Electrophoresis

We have measured the electrophoretic mobility of one the poly(NIPAM) latex at 40 °C (contracted) as a function the concentration of KCl and the results are shown in Figure 2. Unlike many sulfate stabilized hydrophobic latexes there is no maximum in the mobility ionic strength curve.

Figure 1



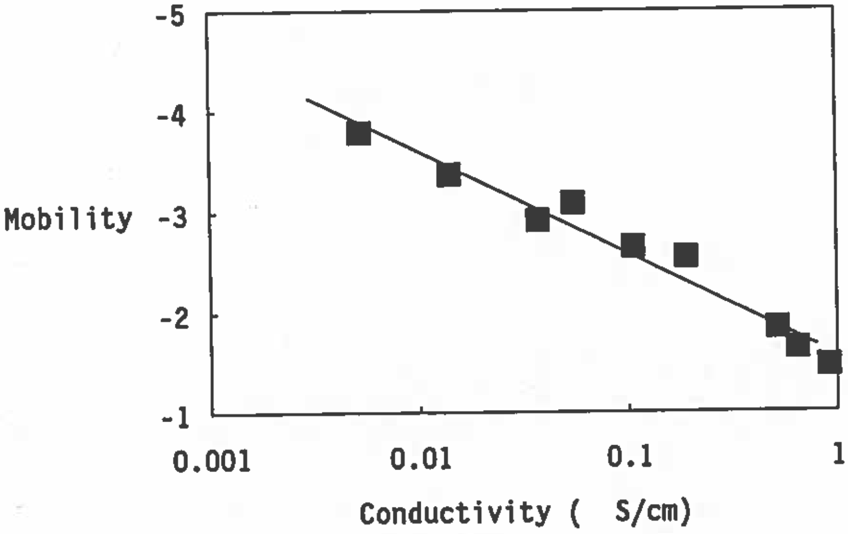


Figure 2

CONTRIBUTION TO POLYMER COLLOID GROUP NEWSLETTER
FROM
LABORATOIRE DES MATERIAUX ORGANIQUES (CNRS-LYON)
SUBMITTED BY C.PICHOT

Study of polymer latex coalescence by dielectric measurement in microwave domain-Influence of latex characteristics.F.Cansell, F.Henry, C.Pichot. Jal of Applied Polymer Science (in press)

The coalescence process of polymer latex particles has been investigated by following simultaneous weight losses and dielectric constants variations during water evaporation in a latex , deposited as a film in a resonant cavity at microwave frequency(5 GHz) and under controlled humidity and temperature .Various styrene-butyl acrylate emulsion copolymers were examined so as to differentiate the behaviors of film-forming or non film-forming latexes.In the latter ones, both flocculation and maximum packing points were clearly evidenced , whereas only the first point was shown in the former ones. The effect of other colloidal parameters (particle size distribution, surface charge density, particle diameter, ionic strength) have also been studied. It is found that the influence of the last three parameters is reflective of the latex stability and can be well detected by dielectric measurement. Such a method appears to be reliable for studying the film forming process of latexes having different colloidal characteristics.

Thermomechanical properties of film-forming functionalized emulsion polymers(L.Rios,M.Hidalgo,J.Y.Cavaille(GEMPPM-INSA))

Two-step polystyrene(PS) (I)polybutyl acrylate(pba)(II) emulsion polymers have been functionalized by addition of methacrylic acid(MA) during the second stage of polymerization.Films were cast from these latexes in order to investigate their thermomechanical behavior.Small quantities of MA were found to strongly affect the reaction mechanism in comparison to the non-functionalized systems.The same effect was observed concerning the thermomechanical properties of original matured fims and annealed ones. Some interesting relations were established between the particle structure in the latexes and the mechanical properties of the corresponding films.The effect of other functional nonionic monomers on a PBA matrix is currently being studied.

Synthesis and characterization of styrene/butyl acrylate latexes functionalized with methyl acrylamido glycolate methyl ether(MAGME) or with glycidyl methacrylate (MAG)-relationships between particle morphology and film properties (S.Magnet,J.Guillot)

Styrene/butyl acrylate lattices have been functionnalized by copolymerization with 1°) Methyl acrylamido glycolate methyl ether(MAGME) and 2°) glycidyl methacrylate (MAG).

Kinetic parameters such as polymerization rate constants, reactivity ratios and partition coefficients have been determined. The kinetics of polymerization as well as the microstructure and the glass transition of terpolymers have been studied with the help of simulation programs.

The morphology of S/ABu/MAG latex particles can be controlled by selecting the polymerization pathway. Core functionnalized particles, homogeneously functionnalized particles and surface reactive particles have been synthesized. Room temperature crosslinked films were obtained by drying off these lattices in the presence of Diamino hexane. Their mechanical properties are dependent on the localisation of the reactive monomer inside particles.

Characterization of acrylic latexes functionalized by N-methylol acrylamide:C.Bonardi,Ph.Christou,Llauro-Darricades,J.Guillot, A.Guyot, C.Pichot - Abstract of a paper published in Polymer Latex III Preprints-London (editor: PRI) . June 1989

N-methylol Acrylamide (NMA) has been copolymerized as a third monomer with butylacrylate (BA) and either styrene (S) or methylmethacrylate (MMA). The individual consumption of each monomer is estimated either from elemental and IR analysis of polymer samples taken at various polymerization time, or from GC polymer analysis of the residual monomers. Water soluble polymers containing mainly NMA units were separated after centrifugation and characterized by NMR analysis and size exclusion chromatography. These water soluble polymers are mainly produced at the end of the polymerization process. The NMA contents of the copolymer particles is very low, whatever is the mode of introduction of the NMA monomer (either at the beginning in a batch process or near the end in a shot process). The NMA units are located around the particles, as a hairy shell of grafted or strongly adsorbed polymers. That result is deduced either directly from ^{13}C NMR analysis of the cleaned latex where only the highly mobile interfacial layer is observed with high resolution, or undirectly from the difference of size between the light scattering and transmission microscopic measurement of the size. The measurement of the area covered by sodium dodecyl sulfate onto latex particles (soap titration method) also gives evidence for the location of NMA units around the particles.

Newsletter Contribution
From The University of Akron

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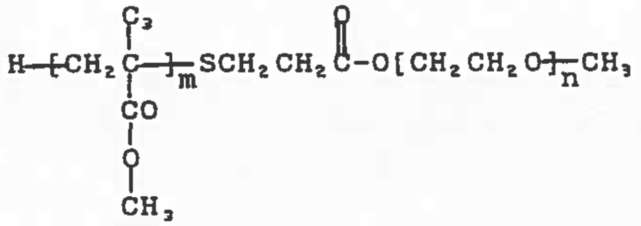
1. Use of a Water-Soluble Polyester as Stabilizer in the Emulsion Polymerization of Styrene by Tammy McCartney

A water-soluble polyester surfactant was synthesized from polyoxyethylene (MW = 200 g/mol), dimethyl 5-sulfoisophthalate, sodium salt and phthalic anhydride for use as a polymeric stabilizer in the emulsion polymerization of styrene. The surfactant concentration was varied from 5% to 60% based on monomer. The initiator used was potassium persulfate at a concentration of 1% based on monomer. Unstable latices which partially coagulated during polymerization were obtained for surfactant concentrations below 20%. At concentrations above 20% the rate of polymerization is essentially constant with surfactant concentration. The rate of polymerization, R_p is 2.52×10^{-4} ℓ/mol·sec using 20% surfactant and plateaus at 2.75×10^{-4} ℓ/mol·sec for concentrations from 30 to 60%. Although the rate is essentially unaffected by changes in surfactant concentration, the final particle size (measured with a Malvern Autosizer IIC at 65-75% conversion) varies from 76 nm at 20% surfactant to 52 nm at 60% surfactant. The number of particles, N, respectively from 3.8×10^{14} to 10.5 particles/cm^3 aqueous phase. The exponential dependence of N on surfactant concentration is $N \propto [S]^{0.31}$.

The molecular structure of the surfactant is such that sufficient anchoring moieties are lacking; therefore, it is possible that a depletion stabilization mechanism is operative in this system.

2. Synthesis of PMMA-b-PEO Diblock Copolymers and Their Application as Stabilizers in Emulsion Polymerization by Wen-Lin Wu

Diblock PMMA-b-PEO copolymers in this study were made by coupling carboxylated PMMA blocks and hydroxyl PEO blocks. The structure of these diblock copolymers is shown below,



$$H{-}\!\!\left[CH_2\overset{C_3}{\underset{\substack{CO\\|\\O\\|\\CH_3}}{C}}\right]_m\!SCH_2CH_2\overset{O}{\overset{\|}{C}}{-}O[CH_2CH_2O]_n\,CH_3$$

where m and n are varied in order to change the Hydrophile-Lipophile Ratios of the resulting copolymers.

Emulsion polymerizations of MMA using these diblock copolymers as stabilizers were carried out to elucidate the effect of stabilizer structure on the rate of the polymerization and the colloidal stabilities of the resulting PMMA latices. The results indicated that a change of the molecular weight of PMMA block from 500 to 1100, 1700, 2300, and 3800 while keeping that of PEO block molecular weight at 5000, the rate of polymerization and number of particles was maximized at the block combination of PMMA (1700)-b-PEO (5000) with styrene and vinyl acetate as the monomers using the same diblock copolymers as stabilizers. It was found that polystyrene latices were well stabilized only by the following two copolymers: PMMA(500)-b-PEO(750) and PMMA(1100-b-PEO(2000). However, poly(vinyl acetate) latices were easily stabilized by the use of all of the PMMA-b-PEO diblock copolymers.

3. The Use of Polystyrene-block-polyoxyethylene as a Stabilizer in the Emulsion Polymerization of Styrene by G. L. Jialanella

The effect of varying the structure of polystyrene-block-polyoxyethylene on the emulsion polymerization of styrene was studied. The first molecular parameter investigated was the molecular weight of the polystyrene block (anchor group). It was found that the molecular weight of the anchor group did not have to exceed 1000 g/mol. Effective attachment of the block copolymer to the colloidal particles occurred when the molecular weight of the anchor group was equal to this value. Moreover, there was no benefit to increase the molecular weight of the anchor group beyond this value. When the molecular weight of the anchor was increased above 1000 g/mol without a corresponding increase in the molecular weight of the stabilizing block, there was a decrease in the stabilizing effectiveness of the block copolymer.

The molecular weight of the polyoxyethylene portion of the block copolymer was found not to influence the stabilizing capability of the block copolymer within the range of 3000 g/mol to 9000 g/mol. In all cases, high stability was observed as reflected by the polymerization rate and particle size.

The stabilizing effectiveness of the block copolymers was found to be dependent on its hydrophilic/hydrophobic balance. When hydrophilic/hydrophobic balance was less than a ratio of 3/1, the stability of the emulsion polymerization was poor. However, the stabilizing effectiveness was independent of this ratio when the ratio was equal to or greater than 3/1. In these cases, high stability was observed as reflected by the polymerization rate, particle size.

Table XIX

Emulsion Polymerization of Styrene Using Polystyrene-Block-Polyoxyethylene as the Stabilizer

	Block $\bar{M}_n$(g/mol)		Hydrophilic/ Hydrophobic	R_px 10^4	D_z^*
#	PSt	POE	Ratio	(mol/L s)	(nm)
1	7000	4000	7/4	No pzn.	
2	4000	4000	1/1	0.2	259**
3	1000	3000	3/1	3.1	84
4	1000	5000	5/1	3.4	82
5	1000	9000	9/1	3.9	84

* - Obtained from Dynamic Light Scattering

** - Latex coagulated at 31.4% conv.

Stabilizer conc. = 18g/;100g monomer (2.7% aq. phase)

Monomer/water = 100/666.67

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FOR AMERICAN CHEMICAL SOCIETY, ANAL. DIV., BOSTON APRIL 1990.

ELECTROPHORETIC FINGERPRINTING AS A PROBE OF SEPARABLE COLLOIDS. R. L. Rowell, B. J. Marlow, and S.-J. Shiau. Department of Chemistry, University of Massachusetts, Amherst, MA 01003.

In place of the zeta potential, a calculated quantity requiring a model for the structure of the double layer, we prefer the directly measurable electrophoretic mobility. The average electrophoretic mobility may be represented as a function of the characteristic variables pH and $p\lambda$ giving a surface which is quantitated by the electrophoretic fingerprint (EF), a contour plot in the pH-$p\lambda$ domain. The EF is characteristic for a particular surface chemistry and defines a reproducible and stationary state for a stable system. The EF can be used as a probe for *in situ* measurement of colloid stability or for monitoring changes in an interactive system. The pronounced features are the domains of maximum charge, the mobility gradients and the possible presence of an isoelectric line. Recently available computer-controlled automated electrophoretic mobility measuring apparatus is capable of monitoring the fine structure in the EF as well. The fine structure gives the frequency distribution of the electrophoretic mobility at a point in pH-$p\lambda$ space, a spectrum which is also characteristic of the system, and a useful predictor of the properties of stability and separability.

FOR AMERICAN CHEMICAL SOCIETY PMSE DIV., BOSTON, APRIL 1990.

ELECTROPHORETIC FINGERPRINTING FOR SURFACE CHARACTERIZATION OF COLLOIDAL PARTICLES. R. L. Rowell, S.-J. Shiau, and B. J. Marlow, Department of Chemistry, University of Massachusetts, Amherst, MA 01003.

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

Contribution to the Polymer Colloids Group Newsletter
Autumn 1989

Suspension Polymerization of "Water-in-Oil-in Water" Emulsions Stabilized by Polymeric Surfactants - Preparation of White Organic Pigments

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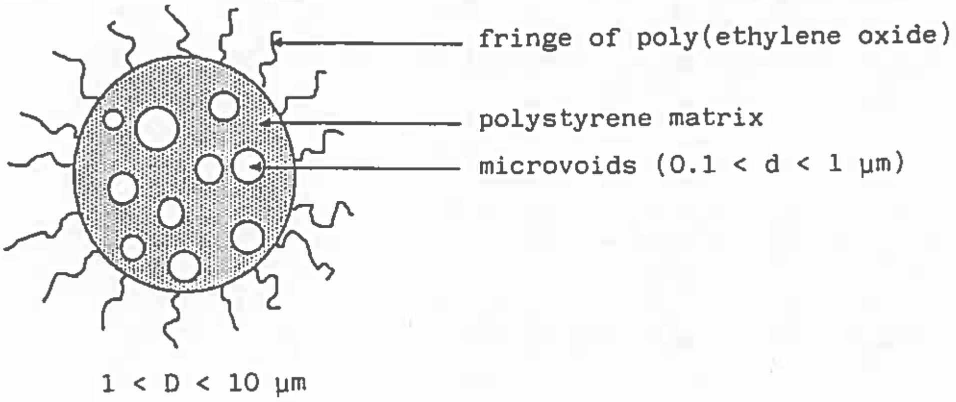
Particles of hydrophobic polymers (unsaturated polyesters) containing voids of 0.1 to 1 µ m scatter light and so have been used for example in paints as a partial replacement for increasingly expensive opacifying agents or matting agents such as titanium dioxide.

In the thesis of H. ADAM (1), we have developed a technique in order to obtain multicellular polystyrene particles in the size range of 1 to 10 µ m. The occlusions (microvoids) have a diameter from 0.1 to 1 µ m. In addition, these polystyrene particles have on their surface a polymeric surfactant, typically a block copolymer like polystyrene-block-poly(ethylene oxide). Such a PS-PEO diblock or PEO-PS-PEO triblock copolymer is anchored in the polystyrene matrix of the particle by its PS segment. The PEO segments of the block copolymer form a fringe on the particle surface which imparts good dispersibility in water as well as compatibility with acrylic polymers of the final paint film.

The schematic structure of such organic white pigments formed by multicellular particles is a follows :



The preparation of these multicellular particles is in 4 steps :

- formation of a water in oil (W/O) emulsion which is stabilized by a PS-POE block copolymer Cop 1 ($\overline{M}_n$ of 20,000 to 60,000 and PEO content of 15 to 40 wt %)

- dispersion in water of this W/O emulsion in order to obtain a multiple emulsion "water in oil in water" [(W/O)/W] ; this multiple emulsion is stabilized by a second block copolymer PS-PEO Cop 2 ($\overline{M}_n$ 3,000 to 75,000 ; PEO content 60 to 80 wt %) which is more hydrophilic than the first one

- suspension polymerization of the (W/O)/W emulsion by using a peroxide as initiator (lauroyl peroxide or preferably cyclohexyl percarbonate)

- purification of the pigment, by washing and centrifugation in order remove the excess of polymeric surfactant and a minor amount of latex of small particle size formed simultaneously in the aqueous phase.

A typical formulation, given here after, shows that the pigment particles can be crosslinked by divinylbenzene (DVB) :

Organic phase

styrene	65 wt %
DVB	20 wt %
polystyrene	5 wt %
Cop PEO-PS-PEO (Cop 1)	5 wt %
(M_n 25,800 ; % PEO : 30 wt %)	
Cyclohexyl percarbonate	5 wt %

W/O emulsion 50 % water / 50 % organic phase

This W/O emulsion is dispersed in an aqueous phase containing :

- 1 % of Cop PEO-PS-PEO (Cop 2)
  ($\overline{M}_n$ 11,000 % PEO 73 wt %)
- 5 to 10 % of PEO homopolymer
  ($\overline{M}_n$ 20,000 to 400,000)
  acting as viscosifier for the aqueous phase.

The volume ratio of the multiple emulsion is typically :

40 % W/O emulsion
60 % aqueous phase (continuous phase).

The polymerization is carried out 60°C for 12 hours.

The multicellular particles obtained by this process have been characterized by :

- their *particle size* ($\overline{D}_n$, $\overline{D}_v$, $\overline{D}_w$ and distribution) as determined by Coulter Counter and electron microscopy
- the *size of the occlusions*
- the *open and closed porosity* as determined by mercury porosimetry and pycnometry.

The existence of the PEO fringe on the particle surface has been proved by formation of an interpolymer complex poly(acrylic acid) - PEO.

Another evidence, which is of practical importance, is the fact the particules after drying can easily be redispersed in water.

Table 1 gives as an example the characteristics of the particles prepared with the above mentioned receipe.

TABLE 1

Exp N°	Viscosifier of the aqueous phase (PEO) $\overline{M}_n$	Viscosifier of the aqueous phase (PEO) wt %	$\overline{D}_v$ μ m	Porosity vol % pores
46	/	/	16.7	44
50	20,000	5	7.6	35
51	20,000	10	3.5	37
52	400,000	5	3.8	38

Organic pigments with the best opacifying properties (particle size $\leqslant$ 10 μm ; occlusion size 0.3-1 μm ; closed porosity $\geqslant$ 25 vol % of the particles) were obtained under the following conditions :

- formation of a W/O emulsion stabilized by 5-10 % Cop 1 ("hydrophobic" PS-POE block copolymer) and where the water phase contains 0.01 to 0.3 mole/l of an électrolyte (e.g. HCl, HCOOH,...) ; this step determines essentially the occlusion size

- formation of the multiple emulsion (W/O:/W in the presence of 1 % Cop 2 ("hydrophilic" PS-PEO block copolymer) and adjusting the particle size by agitation

- polymerization in suspension under static conditions (without agitation) at 60°C in the presence of cyclohehexyl percarbonate ; this type of peroxide, which does not give volatile products by thermal decomposition leads to higher values for the closed porosity of the final particles, than lauroylperoxide.

Table 2 gives as an example the characteristics of the organic pigments obtained under these conditions.

TABLE 2

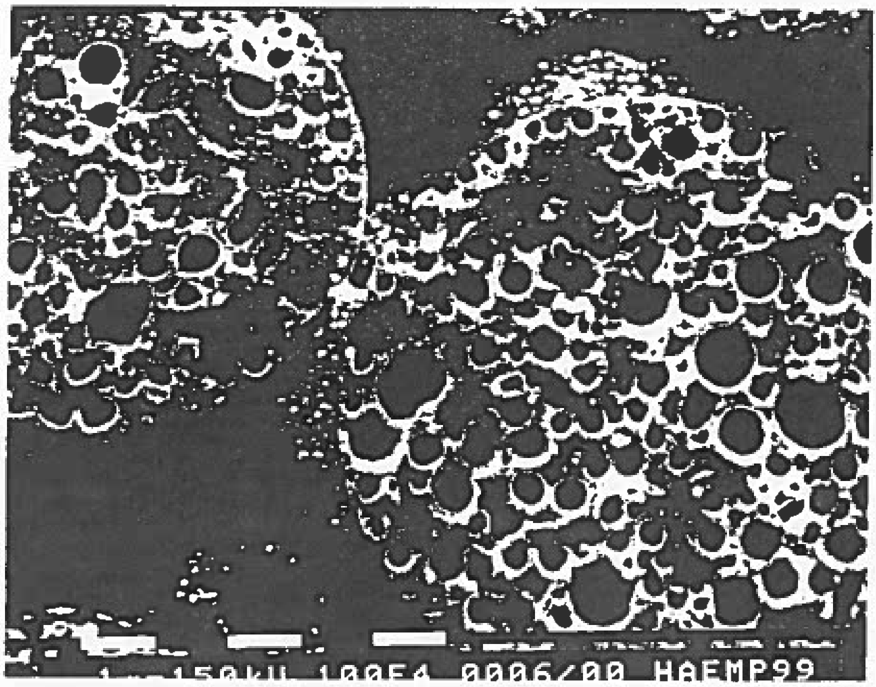
Exp N°	Particle size $\bar{D}_v$ (μm)	Occlusion size		Total porosity % vol	Open porosity % vol	Closed porosity % vol
		$\bar{D}_n$ (μm)	$\bar{D}_v$			
88	7.0	0.3	1.1	55	20	35
99	5.5	0.3	0.6	27	0	27

The microphotograph N° 1, obtained by freeze-fracture, shows the inside morphology of the multicellular particles.

Microphotograph 1

References :

1) H. ADAM Thesis University of Upper Alsace July 17th, 1989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RESEARCH ACTIVITIES

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Recent Publications:

W. B. Russel, D. A. Saville, and W. R. Schowalter, *Colloidal Dispersions*, Cambridge University Press, 1989.

K. E. Davis and W. B. Russel, "Disorder-to-Order Transitions in Settling Suspensions", *Science* **245**, 507 (1989).

Norman J. Wagner and William B. Russel, "Nonequilibrium Statistical Mechanics of Concentrated Colloidal Dispersions: Hard Spheres in Weak Flows with Many-Body Thermodynamic Interactions", *Physica A* **155**, 475 (1989).

Bruce J. Ackerson, C. G. de Kruif, Norman J. Wagner, and William B. Russel, "Comparison of Small Shear Flow Rate -- Small Wave Vector Static Structure Factor Data with Theory", *J. Chem. Phys.* **90**(6), 3250 (1989).

K. E. Davis and W. B. Russel, "Sedimentation of Lyophilic Colloidal Silica Spheres", *Ceramic Transactions* **1**(B), 693 (1989).

Prakash D. Patel and William B. Russel, "An Experimental Study of Aqueous Suspensions Containing Dissolved Polymer. A. Phase Separation", *J. Colloid and Interface Sci.* **131**, 192 (1989).

Prakash D. Patel and William B. Russel, "An Experimental Study of Aqueous Suspensions Containing Dissolved Polymer. B. Rheology", *J. Colloid and Interface Sci.* **131**, 201 (1989).

K. E. Davis and W. B. Russel, "An Asymptotic Description of Transient Settling and Ultrafiltration of Colloidal Dispersions", *Phys. Fluids A* **1**(1), 82 (1989).

"Floc Coagulation in a Shear Field: Kinetics and Floc Structure"

Frank E. Torres
W. B. Russel
W. R. Schowalter

Coagulation in a flowing suspension is governed by the colloidal and hydrodynamic interactions between the aggregating particles and flocs. Beyond the initial particle-particle coagulation step these interactions determine the structure of a floc being formed, and at the same time they depend on the structure of the aggregating flocs. To develop a better understanding of the coagulation process, we have examined both the internal structure and growth rate of flocs formed by rapid shear coagulation of dilute suspensions. Low surface charge polystryrene particles dispersed in 1.00 M NaCl solutions were used to ensure the formation of rigid flocs, and the suspending solvent was 36.00% glycerol by weight to slow the coagulation to convenient rates. Floc sizes were measured by dynamic light scattering, and structure information was extracted from static light scattering spectra covering the domain $0.18 < q^*a < 1.7$, where q is the scattering wave number and a is the individual particle radius. Comparison of the results with results for flocs formed by Brownian coagulation reveals a similar structure for the two modes; in contrast, the growth kinetics for these two modes are inherently different, as expected. To model the growth behavior in a shear flow, we treat a porous floc as a body with a hydrodynamic radius which is less than the capture radius corresponding to floc-floc contact, and we compare predicted kinetics based on this model with data at several shear rates.

THE PHASE BEHAVIOR OF LATICES CONTAINING ASSOCIATIVE THICKENERS

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Theoretical and experimental studies of dispersions containing hydrophobically modified water-soluble polymer, i.e. nonadsorbing chains with alkane grafts that associate among themselves and adsorb reversibly onto latex particles, define the equilibrium phase behavior. Since rheological responses generally reflect the phase behavior for colloidal systems, this represents an important step toward a full understanding of the properties relevant to the formulation of coatings.

Our recent pseudo-one component model for the phase behavior predicts three effects of the associative groups:

(a) suppression of the depletion or volume restriction flocculation encountered with nonadsorbing polymer,

(b) introduction of bridging flocculation with strong stickers and low polymer concentrations, and

(c) restabilization at high polymer concentrations as the particles become fully coated.

Experiments reported in the literature have identified these phenomena, and indeed motivated our theory, but do not delineate the full scope of the phase behavior. Hence we explored more completely the consequences of polymer concentration and the size, number, and placement of the hydrophobes, by adding end-modified poly(ethylene oxide) (Rohm and Haas) and hydroxyethyl cellulose with random grafts along the backbone (Hercules) to stable dispersions of poly(methyl methacrylate/butyl acrylate) copolymer latices (Rohm and Haas) of several different sizes. Although the observations are quite complicated and obscured a bit by slow equilibration of the separated phases, the predicted phase envelopes agree quantitatively for the modified poly(ethylene oxide) and qualitatively for the modified hydroxyethyl cellulose.

Polymer Colloids at the Institute for Surface Chemistry

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At the Institute for Surface Chemistry the following ongoing projects are concerned with polymer colloids

Surface modification with polymerizable surfactants (Eva Sjöblom). In this project, we investigate polymerization in microemulsions and liquid crystalline phases stabilized by polymerizable anionic and cationic surfactants. It has been shown that very small polymer particles can be synthesized by this method. The surface modification of latexes and pigments with polymerizable anionic and cationic surfactants is also being investigated.

Competitive adsorption in water–based paints (Margareta Huldén). The competitive adsorption of surfactants and polymers in systems that may serve as models for water–based paints is investigated. Abstract of a submitted paper on adsorption on TiO_2 is enclosed.

Associative thickeners in water–based paints (Margareta Huldén). In this project, the effect of surfactants on the rheology of latex dispersions containing modified polyurethane etoxylates is investigated. The goal is a better understanding of the interactions of these hydrophobically modified water–soluble polymers in latex and pigment dispersions.

Forces between hydrophilic surfaces (Per Claesson, Björn Bergenståhl). The forces between a number of different surfactant layers (amine oxide, polyetyleneoxide, phosphine oxide and monoglyceride) adsorbed on mica or hydrophobed mica are measured in the surface forces apparatus. Short range repulsive forces that are due to a combination of hydration and steric forces are observed. For the monoglycerides, the forces between surfactant layers in the phases formed by the surfactant with water have also been measured using the osmotic swelling pressure method. The temperature dependence of these forces are fully consistent with the structure of the corresponding surfactant–water phase diagrams.

An abstract of recently published paper in Trans. Farad. Soc on amine oxide is enclosed. For monoglycerides the swelling pressure in the lamellar phase (area /molecule 0.32 nm^2) is considerably stronger than in the gel phase (area/molecule 0.22 nm^2). The same difference is observed for the interaction between monoglyceride layers deposited onto hydrophobed mica. Thus, the repulsive hydration force increases when the area per molecule increases. This may be due to changes in the hydrogen bonding between the monoglyceride head groups and between the head groups and water.

In addition, a project on polymeric surfactants has recently been finished. Three abstracts of papers are enclosed.

Submitted to Progr. in Polymer & Colloid Sci. (Sept -89).

Adsorption of Surfactants and Polymers on TiO_2-pigments

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Abstract:

The adsorption of nonylphenol deca (oxyethyleneglycol) monoether (NPE_{10}), sodium dodecyl sulphate (SDS), polyacrylic acid sodium salt (PAA) and ethyl hydroxyethyl cellulose (EHEC) on TiO_2-pigment coated with different mineral oxides is reported. The adsorption isotherms are compared with data obtained by electrophoretic mobility measurements. Despite the limitations inherent in the mobility measurements, we show that this technique can be used to gain adequate information on the adsorption.

Coating of the TiO_2-pigment with different mineral oxides has a strong influence on the adsorption. This can be understood from the different acid/base charac-teristics of the coatings, e.g. TiO_2 coated with Al_2O_3 or (Al_2O_3 + SiO_2) result in a basic and an acidic surface, respectively. SDS, PAA and EHEC adsorb on the basic pigment but not on the acidic one. NPE_{10} does not adsorb on either pigment, nor does it adsorb on pigment stabilized with pre-adsorbed PAA. The competitive adsorption of PAA and EHEC was studied by the consecutive addition of the polymers to the pigment dispersion. The total amount of adsorbed polymer was always larger with two polymers present compared to one single polymer. EHEC does not significantly influence the adsorption of PAA, irrespectively of whether it is adsorbed before or after the PAA. Contrary, 45% of the pre-adsorbed EHEC desorbs upon the addition of PAA. When EHEC is added to a pigment with pre-adsorbed PAA, the final amount of EHEC on the surface is lower than the amount adsorbed on the bare pigment.

COMPETITIVE ADSORPTION OF SURFACTANTS AND POLYMERS IN LATEX AND TITANIUM DIOXIDE SUSPENSIONS

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COMPETITIVE ADSORPTION OF SURFACTANTS AND POLYMERS IN LATEX AND TITANIUM DIOXIDE SUSPENSIONS, M. Huldén, and E. Sjöblom, Institute for Surface Chemistry, Box 5607, S-114 86 Stockholm, Sweden.

The competitive adsorption of nonylphenol deca(oxyethylene glycol) monoether (NP-E_{10}) and sodium dodecyl sulphate (SDS) on poly(butyl methacrylate) latex confirms the analogy between mixed adsorption and mixed micellization. The competitive adsorption can therefore be calculated from the critical micelle concentrations (cmc) of the two surfactants. Further, the influence of small amounts of organic solvent can be rationalized based on their effect on the cmc's of the surfactants.

Coating of TiO_2-pigment with different mineral oxides has a great influence on the adsorption. This can be understood in view of the different acid/base characteristics of the coatings, e.g. TiO_2 coated with Al_2O_3 and Al_2O_3 + SiO_2 result in a basic and an acidic pigment surface, respectively. The sodium salt of polyacrylic acid (PAA), ethyl hydroxyethyl cellulose (EHEC) and SDS do adsorb on this basic pigment but not on the acidic one. NP-E_{10} adsorbs on neither pigment.

The competitive adsorption of PAA and EHEC on Al_2O_3-coated TiO_2 depends on the order of addition of the polymers. Preadsorbed EHEC does not influence the adsorption of PAA compared to the adsorption on the naked pigment. About 20% of the preadsorbed EHEC desorbs when PAA is adsorbed. If the order of addition is reversed, EHEC adsorbs to the PAA covered pigment surface in a much lower degree than on naked pigment and very small amounts of the PAA desorbs. The results are of relevance for understanding the behavior of paint dispersions.

J. Chem. Soc., Faraday Trans. 1, 1989, 85(8), 1933–1943

Interaction between Amine Oxide Surfactant Layers Adsorbed on Mica

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A surface-force apparatus has been used to determine the interaction between two mica surfaces immersed in water solutions of a non-ionic surfactant dimethyldodecylamine oxide (DDAO). These interactions could be associated with three different adsorption states as the surfactant concentration was increased: hardly any adsorbed surfactant, a monolayer and a bilayer. The study has also been aimed at determining any temperature dependence in the interactions between bilayer-coated surfaces. In addition to the surface-force measurements, quantifications of the amount of adsorbed surfactant on mica sheets were made using X-ray photoelectron spectroscopy. The contact angles were also determined for the same mica samples. From these results we suggest an adsorption mechanism based on positively charged surfactant molecules adsorbing onto the negatively charged mica substrate. No temperature dependence is found of the forces between bilayer-coated surfaces and this is consistent with the absence of any temperature-induced phase separation of the DDAO–water system.

Synthesis and Characterization of Cationic Polymeric Surfactants of the Polymethacrylate Type

Nina Bruun, Bengt Kronberg, Eva Sjöblom and Per Stenius

Institute for Surface Chemistry, Stockholm, Sweden

ABSTRACT

Low molecular weight cationic polymeric surfactants were synthesized by free radical solution polymerization in ethanol/2-propanol. The polymers contain methylmethacrylate (MMA) as their main component, the strongly hydrophobic laurylmethacrylate (LMA) and as the hydrophilic monomer either 2-(N,N,N-trimethylamino)ethyl methacrylate chloride or 2-aminoethyl methacrylate hydrochloride. The molecular weight was adjusted by the chain transfer agent CBr_4 to be <10 000. The polymerizations were effected to a conversion of about 10%. The reason for this is the significantly higher reactivity of the cationic monomers compared to that of MMA and LMA. The polymers were separated from their monomers by Gel Permeation Chromatography (GPC) and the polymer composition was determined by ^{1}H NMR, ^{13}C NMR and elemental analysis. The ratio MMA/LMA in the polymers are about the same as in the feed, which is expected considering the similar reactivity ratios of the two monomers. The polymers contain a significantly higher concentration of the cationic monomer than the feed, but the amount is considerably lower than predicted from the reactivity ratios. In the two following papers in this series the ability of the terpolymers to reduce the surface tension between water/air and to adsorb at the negatively charged muscovite mica will be reported.

Surface Tension of Aqueous Cationic Polymeric Surfactant Solutions Determined by the Pendant Drop Method

Nina Bruun, Bengt Kronberg, Eva Sjöblom and Per Stenius
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ABSTRACT

The surface activity of aqueous solutions of four different surface active terpolymers was measured with the pendant drop method. The terpolymers are composed of methylmethacrylate, laurylmethacrylate, and 2-(N,N,N-trimethylamino)ethyl methacrylate or alternatively 2-aminoethyl methacrylate hydrochloride. All four polymers reduce the surface tension to about 45-50 mN/m in the polymer concentration range 0.1-1 w%. The results indicate that a reversibel association of the polymers into water soluble aggregates occur at ~1 w%. In sodium chloride solution (10^{-2} M) the aggregation concentration is reduced to 0.14 w%.

Analysis of the surface tension curves indicate that it is the flexibility of the backbone, and not the amount of ionic groups in the terpolymer, that determines the ability of the polymer to cover the surface.

Adsorption of Cationic Polymeric Surfactants on Muscovite Mica

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ABSTRACT

The adsorption of low molecular weight cationic polymeric surfactants on muscovite mica from water/2-propanol mixtures was investigated. The polymers contain methylmethacrylate (MMA) as their main component, the strongly hydrophobic monomer laurylmethacrylate (LMA) and either 2-(N, N, N-trimethylamino)ethylmethacrylate chloride or 2-aminoethyl methacrylate hydrochloride (1) as the hydrophilic monomer. The structure of the adsorbed layers was investigated by ESCA and their wetting properties were characterized by water contact angle measurements.

The polymers adsorb in multilayers with the first layer oriented with the cationic groups towards the negatively charged mica basal plane. The water-soluble polymers appear to form bilayers on the surface, with hydrophilic properties (contact angles < 15^{0}) that become more hydrophobic as the outer layer is removed by rinsing(advancing contact angle $60-70^{0}$, strong contact angle hysteresis). The solution properties of the polymers have a strong influence on the adsorption and the ionic binding is not strong enough to prevent some ion exchange and rearrangement when the layers are immersed in electrolyte solution.

Contribution to the Polymer Colloids Group Newsletter
Fall 1989

Polymer Research Laboratory
University of New Hampshire

Donald C. Sundberg

1. Morphology Control in Polymeric Microparticles

In the past couple of years we have been using the artificial latex approach (dissolution of two or more incompatible polymers in a mutual solvent, emulsification in water/surfactant, evaporation of solvent from emulsion particles accompanied by phase separation with the particles) to study the interfacial tension(s) contribution to the control of particle morphology. Recently we have run parallel experiments in which the solvent used in the artificial latex approach is replaced by the monomer of the second polymer, followed by conversion of the monomer to the second, phase incompatible polymer. The system we have principally been studying is that of PMMA/PSty. Our approach has been to dissolve PSty in MMA/B_zO_2, produce an emulsion and carry out the polymerization reaction in the 60-90°C range. We have also looked at the inverse arrangement in which PMMA is dissolved in Sty/B_zO_2, followed by emulsification and polymerization. The results of these studies, although not complete, have shown that the particle morphologies obtained via polymerization are of the same characteristic forms (i.e. core/shell, hemisphere, etc) as those obtained by the solvent evaporation process. In particular it was found that with a high interfacial tension (polymer/water interface) yielding surfactant, such as a pectin, the resulting equilibrium morphology is core/shell, with PSty as the core. When the surfactant is switched to sodium lauryl sulfate, the equilibrium morphology of the same polymer system switches to that of hemispheres. Some of the comparative results were presented at the 1989 Gordon Conference on Polymer Colloids in mosquito laden New Hampshire.

The earliest portions of our work on morphology has now been published [Journal of Microencapsulation, 6, 327 (1989)]. A second paper, detailing the computational approach to predicting equilibrium morphology, has been accepted for publication in the Journal of Applied Polymer Science and should appear in print next spring. Members of the IPCG are welcome to write to me for a reprint or a preprint.

a reprint or a preprint.

2. Antifouling Marine Coatings

Our laboratory is now part of a group of universities participating in a U.S. Navy Research Office supported program to develop marine paints which produce sustained release of non-polluting, biofilm inhibiting organic compounds. Present antifouling paints employ heavy metals to accomplish their objectives. One approach which is being carried out in our laboratory is that of microencapsulating candidate inhibitors, followed by dispersion in the paint formulation. Release rates of the inhibitors from such films are studied in an apparatus which provides a continuous flow of sea water over the paint film under defined hydrodynamic conditions.

3. Grafting Copolymerization

We have just recently begun a new research program in the area of graft copolymerization. This is a cooperative program with Gary Poehlein at Georgia Tech and is supported by a consortium of industrial firms. We will be studying grafting onto a variety of polymer backbones via solution, bulk and emulsion polymerization. The emphasis of this research is to be on graft site initiation, grafting efficiency, molecular weight control, and the influence of grafting upon morphology of bulk phase blends and composite latex particles.

FROM THE POLYMER GROUP AT SINTEF,
UNIVERSITY OF TRONDHEIM

BY

JOHN UGELSTAD

Our work at SINTEF is still to a very large extent concentrated around monosized polymer particles. The main part of this is confidential research supported by industry.

Our work may be divided into two categories.

1. Porous particles for chromatography.

Besides our work with separation of biological compounds in aqueous systems we have recently started a cooperation with Chalmers Technical University in Sweden on the evaluation of porous particles for size exclusion chromatography in organic solvents. We intend to do a thorough investigation of the effect of particle size, pore volume and pore size distribution on the separation efficiency. Our special aim is of course to study the effect of monodispersity.

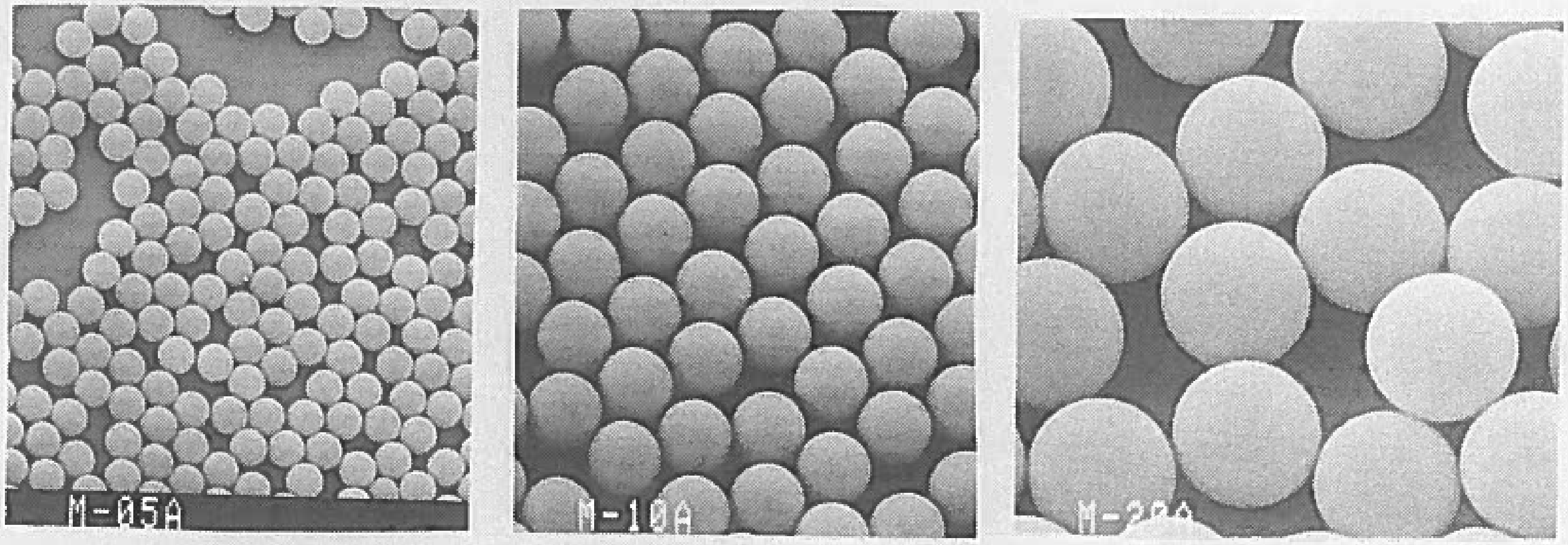
We have already submitted our first paper in a series we plan to publish. This paper deals with the effect of particle size keeping the pore volume and pore size distribution constant.

In the included figures we show a picture of macroporous particles of similar type but of three different sizes - 5 µm, 10 µm and 20 µm - , and moreover a graph of their pore size distributions. As will be seen the three sizes are extremely monodisperse and their pore size distributions are almost similar. Experimental results in chromatography show that the separation efficiency (measured as HETP) increases considerably as the particle size decreases. With monodisperse particles relatively low and acceptable backpressures are achieved as compared to polydisperse separation medias.

2. Magnetic monodisperse particles.

Our magnetic particles have become quite a success both in clinical use and in research within biology and medicine. We have been busy with scaling up problems in these quite sensitive systems, but have also been able to do some research on special types of particles. One of our new particle types, just recently made available, is a relatively small particle with a rough surface suitable both for immunoassays and for coupling to DNA. In the latter case we bind streptavidin to the particle surface and couple with a biotinized DNA. A SEM picture of these particles is shown below.

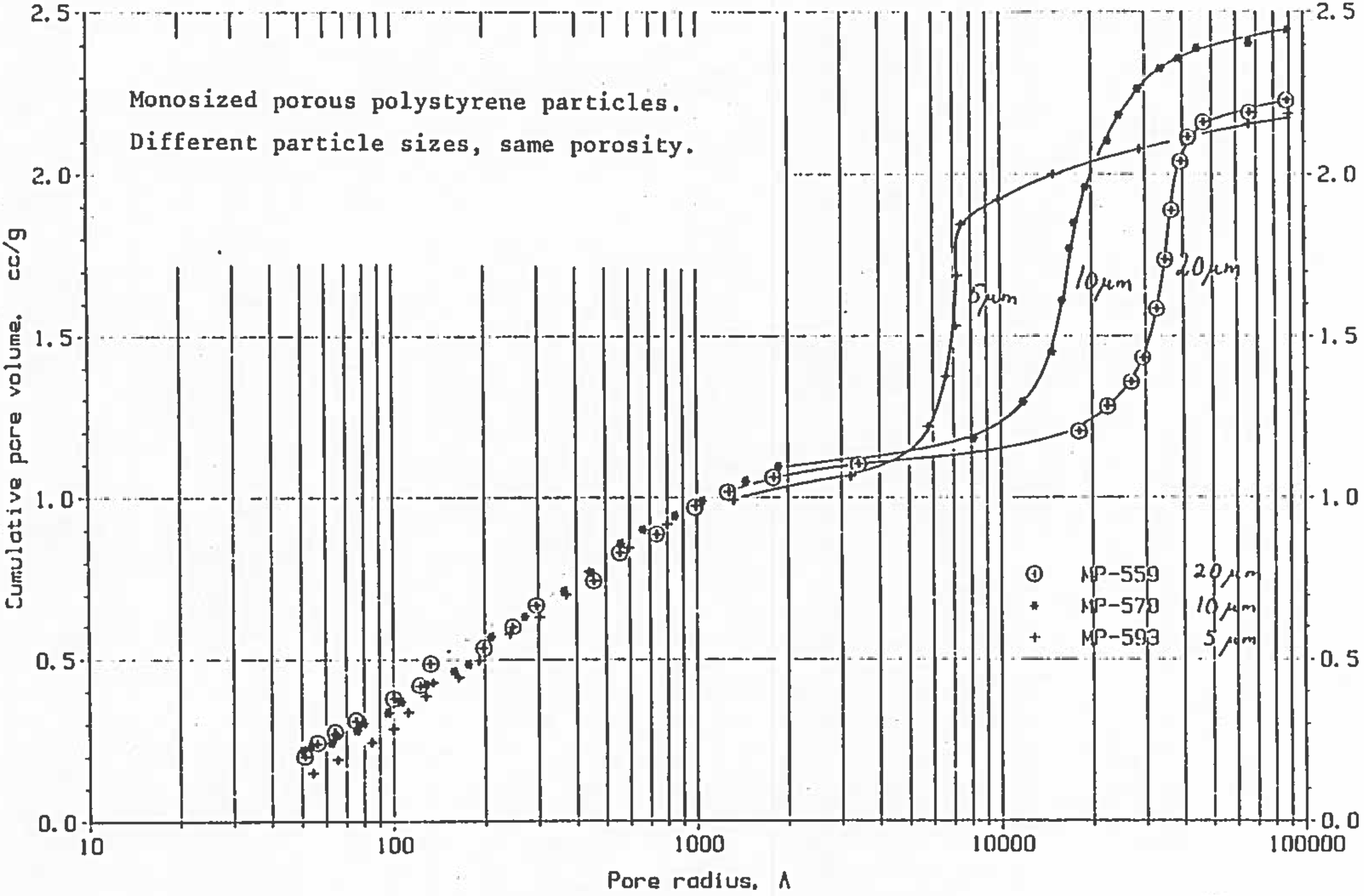
For sake of interest I include a copy of a short presentation in Nature on the use of our beads in connection with DNA, a system with great potentials.
I should also mention that up to now there have been published 300 scientific papers on the use of our magnetic particles, and the areas of applications are steadily increasing.

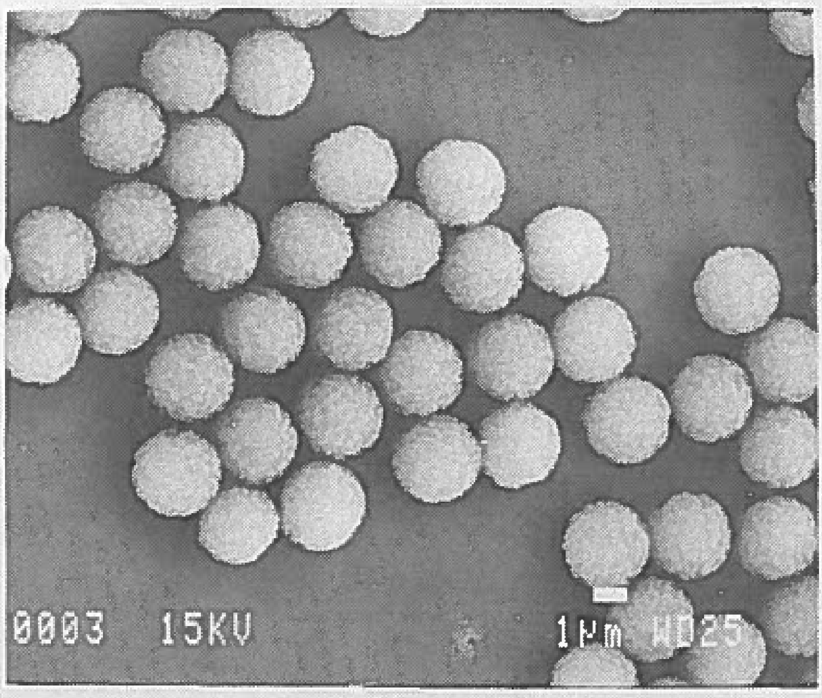


5 µm 10 µm 20 µm

Monosized macroporous PS/DVB particles for Size Exclusion Chromatography in organic solvents.

PORE SIZE DISTRIBUTION
Sample: MP-559 MP-570 MP-593





MAGNETIC DIAGNOSTIC PARTICLES

Magnetic separation of DNA

M. Uhlen

Originally developed for immunoassays, magnetic beads in combination with streptavidin-biotin technology have demonstrated their power for separating DNA and RNA.

Solid-phase methods have proven to be very useful for the separation, synthesis and diagnostic detection of biomolecules. The solid-phase approach produces reproducible reactions with high yields, and allows solutions to be changed rapidly. Routine methods suitable for automation can be designed relatively easily using a solid phase, because of the ease with which it can be separated from the reaction solution.

The solid phase may consist of the walls of test tubes or microtitre wells, or polymer particles (such as agarose or silica) packed in columns. Magnetic particles can also be used as a solid support for the separation of non-clarified cell suspensions or lysates without the need for centrifugation or filtration. If the magnetic beads are non-porous, adsorption and desorption of biomolecules occur at the surface, providing reaction kinetics similar to those found in free solution.

Attractive separations

Early magnetic particles, made by the polymerization of acrylamide and agarose with paramagnetic materials[1], were heterogeneous in size and magnetite content. Hydrophilic beads have now been developed that are identical in size, density and amount of magnetized material[2]. Such beads sediment homogeneously in magnetic fields, and separations using them can often be accomplished within a few seconds. The chemical structure of the particle surface may be varied[3], providing a flexible system for the immobilization of biomolecules.

Immunomagnetic separations, using immobilized monoclonal and polyclonal antibodies, have been described where the magnetic beads are directed to targets such as cells, organelles or macromolecules. The speed of magnetic separation is thus combined with the specificity of antibodies. Immunological applications based on this concept have been developed for tissue typing and cancer therapy, as well as for the selection of monoclonal antibody-producing cells and the separation of subcellular components[4].

Biotin-streptavidin

Magnetic separation can also be used as a tool in molecular biology, by coupling specific DNA fragments to the beads and using them as probes or templates. The fragments can be bound to the beads through a reactive amino or thiol group on a synthesized oligonucleotide, using the procedures developed for the immobilization of antibodies. But a more versatile system uses magnetic particles covalently bound to streptavidin, for the directed immobilization of both double-stranded and single-stranded biotinylated DNA. The remarkable stability and strength (K_d = 10^{-15}) of the non-covalent biotin–streptavidin interaction allows DNA manipulation reactions, such as strand melting, elution and hybridization (using alkali, temperature or formamide), to be performed without interfering with the binding of the DNA to the beads[5].

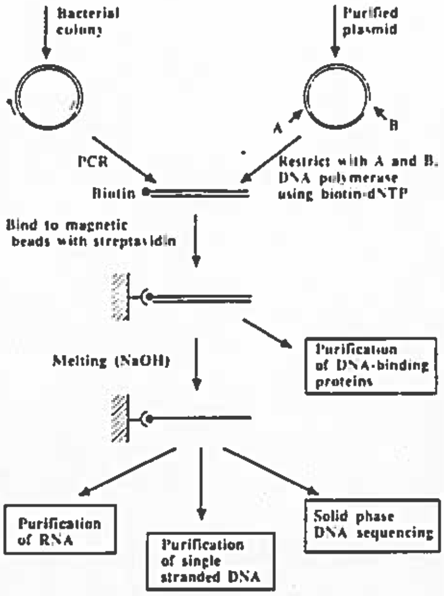


FIG. 1 Possible applications for DNA–containing magnetic beads in molecular biology.

The DNA-bead complex is also resistant to high concentrations of urea and salt. Several alternative strategies exist for the selective introduction of biotin into one of the strands of the DNA. The most straightforward approach is to synthesize an oligonucleotide containing a chemically introduced biotin molecule[6], and then directly immobilizing the oligonucleotide onto the streptavidin-coated bead. An even more flexible approach (Fig. 1) is to perform endonuclease restriction of a purified plasmid, followed by a fill-in reaction with DNA polymerase using one or several biotinylated nucleotides[5]. Alternatively, a polymerase chain reaction (PCR)[7] can be performed using thermostable DNA polymerases such as *Taq* or *Tth* and a biotinylated oligonucleotide[6]. The latter two procedures can immobilize cloned fragments in sizes ranging from a few nucleotides to several kilobases. The techniques also yield immobilized double-stranded DNA, which may be converted into single-stranded DNA through an appropriate melting procedure[5,6].

Molecular applications

The use of magnetic beads in combination with the biotin–streptavidin system has allowed the direct solid-phase sequencing of both genomic and plasmid DNA[8]. The system allows the *in vitro* amplification and sequencing reactions to be performed under optimal conditions because the buffers and enzymes can be changed easily. A protocol has been described for the direct sequencing of plasmid DNA starting from a single bacterial colony, without the need for previous template purification[8].

The rapid magnetic system can also be substituted for conventional affinity chromatography for the purification of DNA-binding proteins. Three cycles of adsorption and desorption to magnetic beads containing a specific double-stranded recognition sequence has yielded a nearly homogeneous nuclear factor (IIIC) in less than one hour from a yeast crude extract[9].

Beads containing single-stranded DNA can be used for the separation and isolation of RNA and single-stranded DNA. Using monosized beads with coupled oligo(dT)$_{25}$, mRNA has been purified with a high yield from a crude extract of a mouse hybridoma cell line within two minutes[10]. The low number of RNA handling steps and the short time required to perform the technique reduce the risk of physical and enzymatic degradation of the RNA. It is also possible to isolate specific RNA molecules using cloned or synthesized DNA fragments as probes. Obviously, the RNA molecules recovered on the magnetic beads can subsequently be used for solid-phase cDNA synthesis.

The magnetic particles can also be used to recover specific single-stranded DNA fragments from a complex mixture of fragments[11]. New cloning strategies can be envisioned where DNA fragments obtained from plasmid, lambda, cosmid or genomic DNA could be specifically recovered by the magnetic beads and subsequently amplified using PCR. In this way, chromosome walking and other operations could be achieved without the need for subcloning.

Finally, the magnetic solid-phase technology can be used for separation steps during the analysis of specific DNA or RNA sequences. Such an assay has been described which uses a DNA probe-based hybridization reaction for the detection of HIV-1-specific RNA in infected cells[12]. Specific hybridization complexes can be purified using a magnetic approach called target cycling/background reduction, in which hybrids are captured from solution with a complementary sequence attached to magnetic particles. We have recently used magnetic beads in an assay for the detection of immobilized amplified nucleic acids, in which samples amplified using a two-step PCR are directly captured using the biotin–streptavidin system. The amount of immobilized amplified fragment can then be detected using an isotope or colourimetric procedure. The assay is rapid and might — in some applications — eliminate the need for electrophoresis, restriction mapping or hybridization assays in the analysis of PCR-amplified materials. ☐

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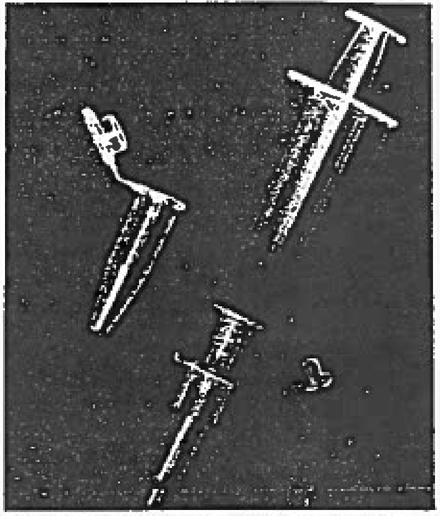
Separation systems

This week features a range of products to help with difficult separations, from isoelectric focusing to the concentration of shear-sensitive cells.

Mobitec says its **immobilized enzymes** in compact, reusable reaction columns are ideal for enzymatic reactions involving small substrate volumes (*Reader Service No. 101*). The immobilized enzymes available include specific and nonspecific proteases, DNase I, RNases, lipases, esterases, oxidases, alkaline phosphatase and β-galactosidase. The enzymes are covalently bound to agarose using "elastic" linkers, which Mobitec says achieves high enzyme density without reducing enzyme activity. Up to 100 μl of substrate can be applied to the column: larger volumes can be treated by attaching a standard syringe. The enzyme-treated substrate is then spun out of the column while the enzyme is retained. Mobitec says enzymes are more stable in an immobilized form than in solution, and can be stored at 4 °C between use.



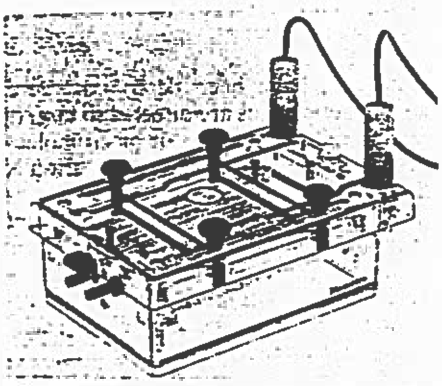
Immobilized enzymes in ready-to-use reaction columns from Mobitec.

Free copies of Bio-Rad's 1989 Chemical Division **catalogue** are now available (*Reader Service No. 102*). The 200-page colour catalogue features new products for chromatography, HPLC, electrophoresis, immunochemistry, molecular biology, and liquid handling. New ideas for chromatography include chromatography gels and resins that are free of endo- and exonucleases, ion exchange membranes as an alternative to column chromatography, prepacked Econo-Pac 10 columns for MAb and IgG purification, and fraction collectors for use in coldroom operations. The section on HPLC offers a new line of isocratic and gradient HRLC systems, columns for hydrophobic interaction chromatography, and a programmable refrigerated autosampler. New items for electrophoresis include a high-performance capillary electrophoresis system, which Bio-Rad says combines the high resolution of electrophoresis with the rapid on-line detection of HPLC, and a semi-dry electrophoretic blotting cell. The CHEF-DR megabase DNA pulsed field electrophoresis system is new in the molecular biology section.

For achieving high filtration rates without clogging, Bio-Recovery, Inc. recommends its X-FLO **tangential flow cell harvesting** system (*Reader Service No. 103*). The membrane-based system has an open-channel design, which the company says can concentrate 20 litres to 200 millilitres with flux rates of 200–400 LMH. The system can continue to function even at solid levels of 40 per cent dry weight, says Bio-Recovery. When operations are scaled up for processing 500- and 5,000-litre batches, Bio-Recovery says results are accurate to ± 5 and 10 per cent, respectively. X-FLO systems are available in sanitary, autoclavable and solvent-resistant designs.

Electrophoresis essentials

Mini-Focus is the name of the new gel apparatus from Biometra for flat bed isoelectric focusing using either polyacrylamide or agarose gels (*Reader Service No. 104*). The electrodes — made of synthetic carbon — are placed in direct contact with the gel surface, eliminating the need for extra buffers and wicks. Biometra says this arrangement produces a uniform electric field and results in sharp bands and high reproducibility. The £645 (UK) gel apparatus comes complete with condensation shield, height-adjustable cooling device and electrodes. The gel chamber can accommodate either analytical or preparative gels on gel bond foils that



Mini-Focus — new electrophoresis hardware for isoelectric focusing from Biometra.

The following are abstracts of recent papers that have been submitted or accepted for publication in Langmuir.

POLYMER COLLOID MORPHOLOGY STUDIED BY FREEZE-FRACTURE ELECTRON MICROSCOPY

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ABSTRACT

The technique of freeze-fracture electron microscopy has been applied to study the morphology of PMMA and PS polymer colloid particles. Both aqueous emulsion polymerized and non-aqueous dispersion polymerized particles have been examined. We distinguish essentially two types of fracture pattern, one is composed of irregularly organized globules; the other has a well developed structure with radiant lines directed from the center to the surface of the particles. The fracture pattern does not seem to be simply a material property of the polymer. Neither is the polymerization medium the determining factor. We believe that the fracture pattern is characteristic of polymer particle growth mechanism.

FLUORESCENCE STUDIES OF THE INTERACTION OF SODIUM DODECYLSULFATE WITH HYDROPHOBICALLY MODIFIED POLY(ETHYLENE OXIDE)

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ABSTRACT

A poly(ethylene oxide) [PEO, M = 8000] (1) containing pyrene [Py] groups at both ends attached via ether linkages has been prepared, and the fluorescence properties of its aqueous solutions examined. These solutions show a weak excimer emission which is at first strongly enhanced and then suppressed by adding increasing amounts of sodium dodecylsulfate [SDS] to the solutions. From the sharp onset of enhanced excimer emission and a correspondingly sharp change in the vibrational structure of the localy excited Py emission, we infer the formation of mixed micelles with an apparent CMC of 8×10^{-4} M. SDS-polymer interaction occurs at concentrations well below that of SDS with either Py itself or PEO itself, indicating that in the hydrophobically modified polymer 1, the chain and end groups act cooperatively to promote interaction with the surfactant. At low SDS concentrations the chains tend to cyclize to put both Py groups in the same micelle.

FLUORESCENCE PROBE TECHNIQUES TO STUDY MICELLE FORMATION IN WATER-SOLUBLE BLOCK COPOLYMERS

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ABSTRACT

Micelle formation in water by poly(ethylene oxide)–polystyrene and PEO–PS–PEO triblock copolymers was studied by the fluorescence probe technique using pyrene as the fluorescent dye. Solutions containg 6 x 10^{-7} M pyrene and varying block copolymer concentrations were prepared, and four separate features of the pyrene fluorescence were examined. In the excitation spectrum the (0,0) band shifts from 333.5 nm for pyrene in water to 339.5 nm for polymer–bound pyrene. At the cmc, sharp increases were observed in the total fluorescence intensity and mean fluorescence decay time. From the decay time measurements and fluorescence vibrational fine structure (I_1/I_3), the location of the pyrene within the polystyrene phase of the micelle can be determined. For polymer samples of mean degree of polymerization PEO(240)–PS(37) and PEO(102)–PS(41)–PEO(102) we find cmc values in the range of 4 x 10^{-7} M (6 x 10^{-3} g/L).

On the Peculiarities of Alkylmethacrylates Emulsion-free Polymerization in the Presence of PA Initiators and the Properties of the Latexes Formed

Eliseeva V.I., Aslamazova T.R.

A comparative study has been performed of the peculiarities characterizing the emulsion-free polymerization (EFP) of (meth)-acrylic monomers - methylmethacrylate (MMA), butylacrylate (BA), initiated by potassium persulphate (PPS) and PA-aniogenic azoinitiator with SO_4^- as well $_I$ end- groups (SAAI) (CMC = $13.0\cdot10^{-4}$ mol/l at = 37.2 dyn/cm),γas of the properties of the formed latex systems and films. In view of the bifunctionality of both these initiators (stabilizing and initiating action), EFP experiments were performed with the equalization of both their molar concentrations (C_I) and the concentration of radicals formed upon their decomposition

The kinetics of MMA EFP was studied in the presence of equimolar concentrations of both the initiators with SAAI C_I below CMC. The obtained kinetic dependences are shown in Fig.1. The initial polymerization rate with SAAI initiation is seen to be higher than with PPC. Based on the calculated values of the decomposition rate constants of initiators one can assume the observed difference in the polymerization rates (2.2-fold) in the presence of PPS and SAAI to be associated not only with a difference in the initiation rate (1.5-fold) but also with a difference in the nucleation mechanism and the initiators stabilizing ability.

Fig.2 shows the results of gel-chromatographic investigation of the MWD in PMMA isolated from the latexes synthesized with PPS and SAAI at different phase ratios (PR) and, correspondingly, at different initiator concentrations in the aqueous phase. From the location of peaks on the chromatograms, for both the concentrations of the initiator and the monomer,the molecular weight is seen to be higher and the MWD to be narrower for the polymer synthesized in the presence of SAAI. This may indicate high contributions made by the micellar mechanism of particle formation in the polymerization with the initiator - emulsifier, and with PPS initiation - in the polymerization in aqueous phase. This conception is supported by the fact that with an increase in initiator and monomer concentrations, when PPS is used, one observes a decrease in MW and its wider distribution, whereas in the case of SAAI the

MW value and the nature of its distribution remain practically unchanged.

The presence of a low-molecular fraction of polymers in both cases indicates the formation of certain quantities of oligomeric products as a result of the termination of radicals in the aqueous phase*). At the chosen PA initiator concentration (below CMC) mixed micelles can be formed out of its molecules and PA oligomers, which can explain the nucleation mechanism assumed by us for the case of PA initiator.

Fig.3 shows the electron photographs of PMMA latexes obtained in the presence of PPS and SAAI. In the second case particles of a smaller size are seen to be formed. The mean diameter values of the particles of these latexes, determined by the light-scattering technique, are shown in Table 1. The difference in diameters can be associated with a different size of stable nuclei of the particles formed, in one case - from micelles and in the other - from the associates of PA oligomers. The surface tension of latexes with the above concentrations of initiators has rather high values, but different from the σ value of water, which indicates the presence of a certain amount of SAS in solution when EFP is performed with both the initiators present.

Table 1

Physico-chemical properties of PMMA latexes synthesized[*] in the presence of PPS and SAAI in equimolar concentrations

	Initiator	$C_I \cdot 10^4$ mol/lH_2O	PR, vol.pts	σ, dyn/cm	$\bar{d}$, nm	pH
1	PPS	3.29	1:9	69.4	364	3.53
2	PPS	6.58	2:8	65.6	502	2.94
3	SAAI	3.29	1:9	68.3	134	3.85
4	SAAI	6.58	2:8	63.7	149	3.25

[*] EFP was performed in inert atmosphere at 80°C and the stirrer rotation frequency 520 min^{-1}.

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*) The absence of such a fraction in PMMA synthesized at PR = 1:9 and C_I = 90 mg/l H_2O in the case of PPS (Fig.2, curve 1) can be explained by the formation of low concentrations of oligomeric SAS that seem to be chromatographically untraceable.

To ascertain the practical advantages of the compared methods of obtaining latexes, film-forming MMA-BA (1:1) copolymers with PR 2:8 were synthesized and their properties investigated (Table 2). As in the case of PMMA latex (Table 1), when the copolymer latex is obtained in the presence of SAAI, particles of a smaller size are seen to be formed. As the SAAI concentration rises the particle size decreases with decreasing σ and increasing stability, which is characteristic of EP in the presence of an emulsifier. The surface tension differs but slightly for both types of initiation, but in all cases it is somewhat lower for PPS, possibly because of a greater molar content of the stabilizing groups (SO_4^-). This probably explains the rise in the aggregative stability (decrease of coagulum content) in these latexes. Worthy of notice is a higher conductance of the latexes obtained in the presence of PPS, rising with the increasing concentration. This is evidently associated with the formation of low-molecular electrolytes during its decomposition.

Table 2

Physico-chemical properties of PMMA-BA latexes synthesized* in the presence of PPS and SAAI with equalized decomposition rate (V_d)

	Initiator	$C_I \cdot 10^4$, mol/l	$V_d \cdot 10^9$, mol/l·s	Dry residue %	Coagulum %	σ, dyn/cm	$\bar{d}$, nm	pH	$\chi \cdot 10^3$, $\int$	Sedimentation (% of transparent phase) after 2 months
1	SAAI	8.0	0.82	17.2	4	68.9	183	3.66	0.32	none
2	PPS	11.8	0.82	17.4	1	64.0	239	2.75	0.76	67
3	SAAI	16.0	1.64	16.3	5	64.3	183	3.12	0.15	none
4	PPS	23.6	1.64	17.6	3	62.4	228	2.45	1.37	67
5	SAAI	32.0	3.28	16.8	1	61.7	140	3.72	0.17	none
6	PPS	57.2	3.28	18.1	0.8	59.9	227	2.46	1.04	67
7	SAAI	40.0	4.0	17.5	-	62.1	157	3.29	0.55	none
8	PPS	59.0	4.10	16.7	0.5	59.4	239	2.52	2.23	77

* EFP was performed in inert atmosphere at 80°C with the stirrer rotation frequency 200 min^{-1}

A characteristic difference between the compared latexes is their sedimentation stability, decreased in the case of PPS, which may be associated with the size of the particles, as well as with the degree of hydration of their surfaces.

Fig.4 shows the water absorption kinetic curves for films of the latexes listed in Table 2. At a low concentration of both the initiators, when the concentrations of electrolytes are close to each other, water absorption is seen practically not to differ and not to exceed a few percent. However, with increasing PPS C_I, accompanied by a considerable increase in the latex conductance, water absorption rises substantially, rapidly reaching its equilibrium value; this is not observed for the films of latexes that were synthesized with SAAI, the water absorption of which gradually rises, staying lower than in the previous case. The difference in the water resistance of films is obviously associated with the content of low-molecular electrolytes in them. A higher water resistance of the films obtained with SAAI should also be facilitated by a higher MW of the polymer (Fig.2).

Analyzing the obtained EFP data with both the the initiators one can form an opinion on the mechanism of the process and the properties of the formed latexes and polymers. Comparison of MMA polymerization kinetics with the gel chromatogrammes indicates a substantially greater contribution of polymerization in the aqueous phase when persulphate is used, as compared with micelle-forming PA azoinitiator, and a lower-molecular polymer with a wider MWD being obtained. In the former case the polymer-monomer particles are formed from the associates of PA oligomers, in the latter - from PA initiator micelles or mixed micelles (p.2). This difference manifests itself in the particle size. An increase in the concentration of both the initiators raises the stability of latexes, but in the case of PPS this is accompanied not only by a decrease in MW but also by an increase in the content of low-molecular electrolytes in the latter, which tells on the water resistance of films. A great advantage of PA initiator is the sedimentation stability of resulting latexes, which may be associated with a higher effectiveness of the hydrate layers of particle surfaces.

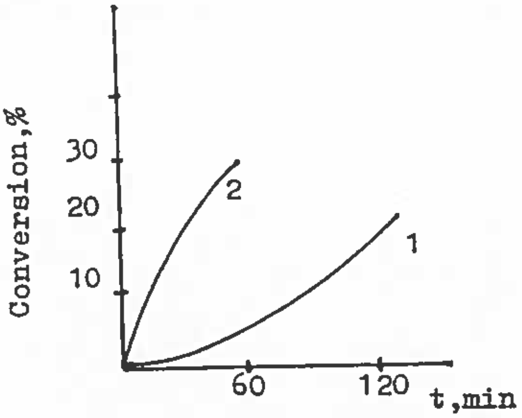

Fig.1.Kinetic curves of MMA polymerization in the presence of C_I=6.58·10^{-4} mol/l
1 - PPS, 2 - SAAI

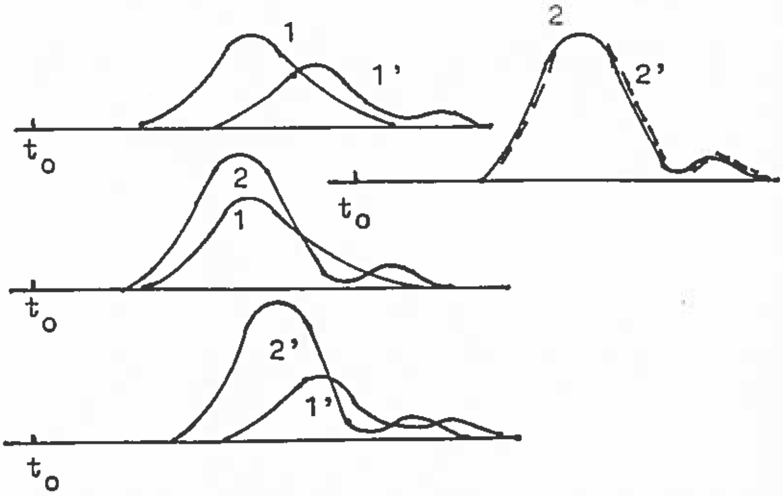

Fig.2.Gel-chromatographic curves of the MWD of PMMA obtained by MMA polymerization:
1 - PR 1:9, C_{PPS} 3.29·10^{-4} mol/l
1' - 2:8 6.58·10^{-4}
2 - PR 1:9 C_{SAAI} 3.29·10^{-4} mol/l
2' - 2:8 6.58·10^{-4}

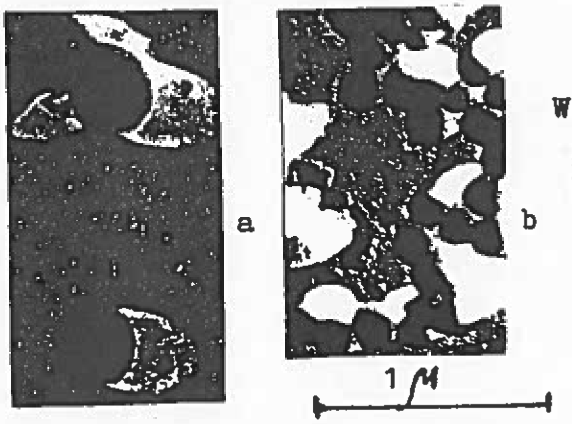

Fig.3.Electron photographs of the paricles of PMMA latexes obtained in the presence of equimolar concentrations of initiators
a) PPS, b) SAAI

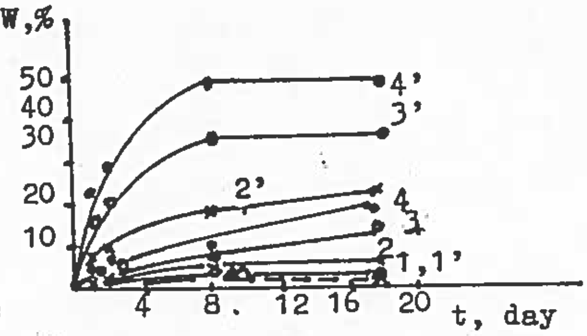

Fig.4.Water absorption kinetic curves of PMMA-BA latex films (Table 2) synthesized in the presence of PPS and SAAI with equalized 10^{9}mol/l·s decomposition rates:
1,1' - 0.82; 2,2' - 1.64; 3,3' - - 3.28; 4,4' - 4.10. Curves 1-4: SAAI; curves 1' - 4' - : PPS

On the Hydrophilic Component of the Free-emulsifier Concentrated Latexes Stability

V.I.Yeliseeva, T.R.Aslamazova

The hydrophilic component of acrylate latex stability was controlled by 1) copolymerization of butylacrylate (BA) with increasing amount of methylmetacrylate (MMA) (from 20 to 80 mass.%) and by 2) copolymerization of the BA-MMA mixture with the increasing amount of metacrylic acid (MAA) up to 2 mass.% (pH of latexes was 2÷2,2). Latexes were obtained in concentrated systems (50 vol.%) in the absence of an emulsifier at low concentrations of initiator (the initiator being ammonium persulfate) at 80°C. The polymer hydrophilicity was evaluated by measuring of the wetting angle of the films obtained from latexes on the boundary with water (after keeping them in water for 24 hours). The stability of latexes was evaluated by the mass of coagulume formed in the process of polymerization. It is shown that in both cases the stability of latexes increases with an increase of the surface hydrophilicity (a decrease of the wetting angle of the films). However, in the first case it increases constantly with increase of the MMA concentration; in the second case the dependence of the stability on the MAA concentration in copolymer has the maximum at 1 mass.%. Conductometric titration has shown in this case the constant increase of the surface carboxyl groups concentration with an increase of the MAA content in the copolymer composition. The discrepancy observed herein is likely to be due to the structural factor.

POLYMER ASSOCIATION STRUCTURES: Microemulsions and Liquid Crystals

ACS Symposium Series No. 384 Ed. Magda A. El-Nokaly (American Chemical Society , Washington DC 1989) pp xii + 362 ISBN 0-8412-1561-8 Hardcover $95-95.

Until the early decades of this century, polymer science was considered to be a subset of colloid science (polymers being regarded as physically associated micelle-like species).Once Staudinger had established the existence of covalently linked macromolecules, however, the two disciplines diverged rapidly so that their contact is now limited.Yet in many important industrial systems (e.g., paints), the two disciplines are intimately intertwined.One of the stated aims of this book is to 'attempt a rapprochement' between colloid and polymer science in the area of polymer association structures,such as microemulsions and liquid crystals.Although the book will undoubtedly expose colloid and polymer scientists to areas of the other discipline unknown to them, the book is only partially successful in its stated aim for for reasons of omission elaborated below.

The 21 chapters included in this compilation span 6 different areas:W/O, O/W and middle phase microemulsions of monomers and their polymerization, as well as liquid crystals and polymer-polymer and polymer-surfactant associations. The real strength and usefullness of the book stems from the excellent overviews that many of the articles provide of work performed in their authors' laboratories.The many distinguished contributors include F.Candeau, Frigberg, Fellers, R.D.Gilbert, Vanderhoff and El-Aasser, Ise, Riess and Tadros. A major weakness of the book derives from the absence (with the notable exception of Finklemann's chapter) of prefatory reviews of each section that unifies its contents, as well as establishing its links with the other 5 sections. This frustrates the editor's well intentioned attempt to persuade colloid and polymer scientists to touch hands. Notwithstanding these criticisms , the book will make a welcome addition to academic and industrial libraries alike, both for its unique flavour and its wealth of information.

Don Napper (University of Sydney)