IPCG

INTERNATIONAL POLYMER COLLOIDS GROUP

MAY 1994

VOLUME 25   NUMBER 1

NEWSLETTER

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CONTRIBUTIONS

FROM THE EDITOR'S DESK

MEMBERSHIP

Perhaps it was because I have been on sabbatical leave for several months but I found the contributions to this newsletter especially interesting. Members of IPCG are opening up many new areas and this is reflected in the following pages.

This volume contains the contributions to our Newsletter from Jung–Hyun Kim and from Haruma Kawaguchi. When you read what they have to say, you will understand why they were both elected to IPCG. Thank you both: We look forward with pleasure to your future participation in IPCG activities.

I was personally delighted to receive contributions this time from two of the most respected scientists in our business: Ron Ottewill and John Ugelstad. Thanks, guys!

UK POLYMER COLLOIDS FORUM
Peter Lovell has asked me to bring to your attention (piv) the formation of a UK Polymer Colloids Forum. This is an important development in the UK that merits strong support.

CONFERENCES
The 3rd International Symposium on Radical Copolymers in Dispersed Media held recently in Lyon proved to be a resounding success. A report is included on p(ii).

Advance notice of an International Conference on Multiphase Materials Prepared by Emulsion Polymerization is included on p(v), as is advance notice from Finn Hansen of the Associating Polymers Conference (pvi).

NEXT NEWSLETTER
Contributions for the next Newsletter should reach me at the University of Sydney by 31 October, 1994.

D H Napper
Editor

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

(submitted by C. Pichot)

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I-Report on the Third International Symposium: "Radical copolymers in Dispersed Media" by A. Guyot (LCPP-CNRS)

The 3rd International Symposium on Radical Copolymers in Dispersed Media has been held in Lyon (at the Ecole Normale Superieure) April 17 to 22, 1994 in the presence of 240 persons, i-e an attendance slightly higher than for the previous symposia. The attendance was well equilibrated with 100 from industry, 90 from university and 50 students. They come from 23 countries, chiefly from Europe with 110 from France, 28 from Germany, 20 from UK...
The scientific program included 30 invited lectures, 20 oral communications and 62 posters, divided in 6 topics:

1) Mechanisms and Modelling of Copolymerization processes in dispersed media

2) Chemical Engineering of Copolymerization in dispersed media

3) Characterization and Morphology Control

4) Film formation and properties

5) Special colloid synthesis and properties

6) New field of applications for colloid copolymers

The program began with an introductory lecture of Bob Fitch: " The Science of Polymer Colloids the State of the Art ", and was ended by the lecture given by Ton German: "Effect of Process Strategy on Microstructure and Properties of Emulsion Copolymers " in which he added a list topics for future research activities.

A special committee, chaired by Bob Gilbert, has been named to select 3 posters to be presented orally by young scientists the last day. The 3 awardees were:
1) I.Lacik, J.Selb and F.Candau " Copolymerization of acrylic acid and styrene in a aqueous micellar medium ".
2) K.Landfester, C.Boeffel and H.W.Spiess " Synthesis and Characterization of Core-Shell polymers with microscopic methods and solid state NMR ".
3) V.Favier, C.Canova, J.Y.Cavaille, H.Chanzy, A.Dufresne and C.Gauthier "Nanocomposite Materials from latex and cellulose whiskers ".

Most of invited lectures and a part of the oral communications will be published in a special issue of Macromolecular Symposia (The new name of the Symposium series connected with Die Makromolekulare Chemie).

In addition to that, two "Special Topic Issues " will be published in "Polymers for Advance Technologies ", a rather new Journal of Wiley (The publisher of Journal of Polymer Science). Thec two special topic issues will be named:
1) Improving material properties using Polymer Colloids
2) Surface functionnalization of latexes and applications

This symposium has well shown where the major interest of scientists of both university and industry has been put these recent years, as well as the emergence of new fields of interest. These topics were listed by C.Pichot in his concluding remarks as:

1) Synthesis of (co)polymer particles: kinetics, particle nucleation, quantitative predictions, reactive monomers and surfactants, new processes, chemical engineering .

 2) Characterization and properties of (co)polymer particles: molecular properties, surface and internal morphology, rheology, coalescence, film formation, mechanical and other properties of ultimate films (adhesion, permeability, etc...)

3) Application of copolymer colloids: blends, encapsulation, crosslinked particles, composites, conducting polymers, biology, catalysis, etc...)

Although the scientific program was non stop from monday morning at 10 to friday lunch time; 1.45 pm., the social events were not forgotten, including a cocktail at the city hall of Lyon, a dinner with the invited lecturers in the old Lyon, a 16th century built part of Lyon which has been visited by ladies during the afternoon, and a warm banquet in a restaurant connected with the "Museum of the Doll ", in the beautiful park of the "Domaine de Lacroix Laval" at a small distance of Lyon, animated by a jazz band from Lyon but with a good " New Orleans " style, and finally a tour in the Beaujolais Wineyards and the Dombes on saturday. During the banquet, a " Small ball award " was given to Françoise Candau (coinciding with her birthday), the " Big ball award " to Masayoshi Okubo, and the " Two colored ball award "to Mitch Winnik. These awards were decerned by Jean Claude Daniel, Ron Ottewill and Mohamed El-Aasser in the presence of the first awardee of 1984, John Vanderhoff.

We hope that a fourth symposium on the same "copolymer "topic will take place before the end the present " millenaire ".

II-Recent Publications:

"Reactive surfactants in emulsion polymerization" A. Guyot and K.Tauer - Advances in Polymer Sci.,111, 43 ,1994

" Heterophase Polymerizations: A physical and kinetic comparison and categorization " - D. Hunkeler, F. Candau, C. Pichot, A.E. Hamielec, T.Y Xie, J. Barton, V. Vaskova, J. Guillot, M.V . Dimonie, K.H . Reichert, Advances in Polymer Sci., 112, 117, 1994

"Adsorption of oligonucleotides onto negatively and positively charged latex particles- A. Elaissari, P. Cros, C. Pichot, V. Laurent, B. Mandrand
Colloids and Surfaces A: Physicochemical and Engineering Aspects, 83, 25, 1994

The UK Polymer Colloids Forum

About two years ago, UK industry expressed concern about the diminishing level of UK academic activity on synthetic aspects of polymer colloids, particularly emulsion polymerisation. In response to this concern, the UK Polymer Colloids Forum has been set up under MacroGroupUK, which is a joint group of the Royal Society of Chemistry and the Society of Chemical Industry. The aims of the Forum are "to progress knowledge in the science of polymer colloids by discussion, collaboration and education". The immediate priorities are to publicise the existence of the Forum, to arrange regular meetings and to seek increased support for academic work in the area of polymer colloids from funding bodies.

The committee of the Forum is balanced between academia and industry, and comprises:

Chairman: Dr. Peter Lovell (UMIST)

Secretary: Dr. Bob Pittilo (Polymer Engineering Group)

Treasurer: Professor Doug Hourston (Loughborough University)

Ordinary members:
  Professor Ron Ottewill (University of Bristol)
  Professor David Sherrington (University of Strathclyde)
  Dr. David Farmer (Vinamul)
  Dr. John Padget (Zeneca Resins)
  Dr. David Service (Courtaulds)

Co-opted members:
  Dr. James Goodwin (University of Bristol, representing the Colloid & Interface Science Group of the Royal Society of Chemistry)
  Dr. Paul Reynolds (University of Bristol, representing the Colloid & Surface Chemistry Group of the Society of Chemical Industry)

The inaugural meeting of the Forum was held on Wednesday 17 November 1993 at Badock Hall, Bristol University and was attended by 61 people of whom 45 were from industry. Invited papers were presented by Dr. Julian Waters (ICI Paints), Dr. Doug Hourston (then of Lancaster University), Professor David Sherrington (University of Strathclyde), Dr. Guru Satguru (Zeneca Resins), Dr. John Cawse (Ilford Ltd.) and Professor Ron Ottewill (University of Bristol).

The next meeting of the Forum will take place from 22-23 September 1994 at Keele University in the UK.

Anyone who would like to register with the Forum and receive information on future activities should write to me:

Peter Lovell
Chairman, UK Polymer Colloids Forum
Manchester Materials Science Centre, University of
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Announcement of an International Conference

Multi-Phase Materials
prepared by
Emulsion Polymerisation
Synthesis, Characterisation and Properties

4 - 7 April 1995, Lancaster University, England

Topics:

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

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Concerning Contribution to the International Polymer Colloid Group Newsletter, April 1994

Dear Don,

My contribution to the IPCG Newsletter has already been sent. However, I forgot one important thing, in June 1995 we are planning to arrange an international meeting in Associating Polymers in Norway, and it would be nice if this could be mentioned in the spring Newsletter. The program is not fixed yet, so this is only a preliminary announcement. The following may be written so far:

International Symposium on **Associating Polymers** - A symposium on the Structure, Relaxation and Dynamics in systems containing Associating Polymers.

Topics:
- Polymer structure and dynamics in solutions and gels
- Polyer/polymer interactions
- Polymer/surfactant interactions
- Polymer adsorption and interaction at surfaces

To be held at Alexandra Hotel, Loen, Norway, June 25 - 30, 1995.
Contact: Finn Knut Hansen, University of Oslo, Norway.

Sincerely yours
Finn Knut Hansen

CONFERENCES

CONFERENCE	LOCATION	DATE/CONTACT
1994		
208th ACS National Meeting	Washington	21–26 August
Polymer Surfaces & Interfaces (Discussion of Faraday Society)	Bristol	12–14 September (Ottewill)
UK Polymer Colloids Forum	Keele	22–23 September (Lovell)
1995		
20th Australian Polymer Symposium	Adelaide	5–8 February (Napper)
209th ACS National Meeting	Anaheim	2–7 April
Multiphase Materials Prepared by Emulsion POlymerization	Lancaster	4–7 April (Lovell)
International Symposium on Associating Polymers	Loen, Norway	25–30 June (Hansen)
210 ACS National Meeting	Chicago	20–25 August
Pacific Basin Congress	Honolulu	17–22 December

INTERNATIONAL POLYMER COLLOIDS GROUP NEWSLETTER

MOLECULAR WEIGHT DISTRIBUTIONS IN THE MINIEMULSION POLYMERIZATION OF STYRENE INITIATED BY OIL-SOLUBLE INITIATORS

Juan A. Alduncin and José M. Asua

The evolution of the molecular weight distributions in the batch miniemulsion polymerization of styrene initiated by different oil-soluble initiators (lauroyl peroxide, benzoyl peroxide and azobisisobutyronitrile) was investigated. Two series of polymerizations were carried out. In the first, miniemulsions contained only oil-soluble initiators to minimize monomer droplet degradation by molecular diffusion. In the second, the stability of the monomer droplets was reinforced with hexadecane. Also, a series of conventional emulsion polymerizations was carried out. The effect of both the type of initiator and the extent of the compartmentalization of initiator radicals between the polymer particles on the molecular weight distributions were analyzed by means of a mathematical model. A good agreement between experimental results and model predictions was achieved.

MINIMUM-TIME STRATEGY TO PRODUCE NONUNIFORM EMULSION COPOLYMERS. I.- THEORY

José C. de la Cal, Antonio Echevarría, Gregorio R. Meira and José M. Asua

A method for calculating the optimal monomer addition policy to produce emulsion copolymers with a given composition profile is presented. The approach allows the calculation of the time evolution of the monomer feed rates that ensure the formation of the desired copolymer composition profile in a minimum process time. The method was applied by simulation to obtain widely different copolymer composition profiles during the emulsion copolymerization of butyl acrylate and styrene. The results were compared with those obtained by means of the power feed method. In these calculations it was assumed that both the kinetic model and the values of the kinetic parameters are available. The implementation of this approach to real emulsion copolymerization systems in which only a limited kinetic information is available is presented in the second paper of this series.

MINIMUM-TIME STRATEGY TO PRODUCE NONUNIFORM EMULSION COPOLYMERS. II.- OPEN LOOP CONTROL

Antonio Echevarría, José C. de la Cal and José M. Asua

An iterative approach was developed to determine the optimal monomer addition policies in real emulsion copolymerization systems in which only a limited kinetic information is available. The approach was applied to obtain widely different copolymer composition profiles for the emulsion copolymerization of butyl acrylate and styrene. The approach involves a series of semicontinuous emulsion copolymerizations carried out in an open-loop control mode. Each reaction was used to get an estimation of the kinetics of the process that was used to calculate the monomer addition profiles for the next experiment. The method is model independent and converges rapidly.

MODELLING NUCLEATION AND PARTICLE GROWTH IN EMULSION COPOLYMERIZATION IN CONTINUOUS LOOP REACTORS

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

A mathematical model for emulsion copolymerization in continuous loop reactors is presented. The flow pattern of the loop reactor can be represented by a loop formed by two tubular reactors with axial dispersion. The mathematical model combines this flow model with the physico-chemical characteristics of the emulsion copolymerization. The outputs of the model are monomer conversion, copolymer composition, particle size distribution and latex viscosity. The model was checked during the redox initiated emulsion copolymerization of vinyl acetate and veova 10 carried out in a completely automated continuous loop reactor.

KINETICS OF LONG-CHAIN BRANCHING IN EMULSION POLYMERIZATION

Gurutze Arzamendi[1] and José M. Asua

1.- Universidad Pública de Navarra, Pamplona, Spain

A mathematical model for the kinetics of long-chain branching in emulsion polymerization systems was developed. The model takes into account the compartmentalization of the reaction system. Large errors were found when the effect of the compartmentalization of the free radicals was ignored. The model predicts that extremely high molecular weights can be reached when termination occurs by combination and the extent of the chain transfer to polymer reaction is significant. Extensive propagation to double terminal bonds can lead to gel formation irrespective of the type of bimolecular termination.

EFFECT OF THE MONOMER ADDITION POLICY ON THE MOLECULAR WEIGHTS OF EMULSION COPOLYMERS

Gurutze Arzamendi[1] , Jacqueline Forcada and José M. Asua

1.- Universidad Pública de Navarra, Pamplona, Spain

The effect of the monomer addition policy on the molecular weight of the copolymers obtained in the emulsion copolymerization of ethyl acrylate and methyl methacrylate was investigated. Batch process, semistarved optimal process and two starved processes with different feed times were considered. It was found that the monomer addition strategy has a marked effect on the molecular weight of the copolymer. The experimental results were analyzed using a mathematical model for long-chain branching in emulsion polymerization systems.

SURFACE AND ELECTROKINETIC CHARACTERIZATION OF FUNCTIONAL ALDEHYDE POLYMER COLLOIDS

D. Bastos, R. Santos, Jacqueline Forcada,
R. Hidalgo Alvárez[1] and F.J. de las Nieves[1]

1.- Departamento de Física Aplicada, Universidad Granada, Granada, Spain

Polymer colloids of aldehyde functionality were prepared by emulsifier-free emulsion copolymerization of styrene and acrolein with potassium persulfate as initiator. Two aldehyde latexes were prepared, one of them with methanol (10% w/w of the monomers) charged into the reactor. By conductimetric and potentiometric titration experiments, together with H-NMR and FTIR analysis was detected the presence of aldehyde groups with a surface concentration of approximately $1.2 \ 10^{-4}$ µeq/cm^2 for the two latexes synthesized. Also, sulfate groups were detected which gave rise to a surface charge density of around 2.9 mC/cm^2 for both latexes. The electrophoretic mobility (μ_e) of these functionalized latexes was studied versus the solution pH and in the presence of several electrolytes with different counter-ion valences. The μ_e values were constant in the pH range between 5 to 10, while exhibited a maximum against the electrolyte concentration. This maximum desappeared when the electrolyte was LaCl$_3$. The stability factor of these aldehyde latexes was measured at pH 6 and 9. The critical coagulation concentration (ccc) was very similar for both latexes at these pH. The average ccc was 367 mM which is too high considering the low surface charge density by the sulfate groups. The surface aldehyde groups seem to improve the colloidal stability of these latexes.

International Polymer Colloid Group Newsletter

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

Reporter: J. Barton

On the Kinetics of Free Radical Microemulsion Polymerization of Butyl Acrylate

Ignác Capek, Pavol Potisk, Viera Juraničová, Marta Klimová
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Summary

The o/w microemulsion polymerizations of butyl acrylate initiated by a water (ammonium peroxodisulfate, AP) - and/or oil (dibenzoyl peroxide, DBP) - soluble radical initiator at various monomer and initiator concentrations were investigated. The rate of polymerization shows initiation and termination intervals, but very short or no constant interval. The rate of polymerization is found to be proportional to the 1.4th and 1.8th power of the BA concentration for AP and DBP, and to the 0.46th and 0.24th power of the AP and DBP concentration, respectively.

Introduction

Generally, microemulsions are transparent or translucent "solution" which contain ordinarily immiscible liquids (water, oil, ..), coemulsifiers and/or emulsifiers. Microemulsions have attracted considerable interest and attention due to their great potential for application. In contrast to bulk or solution polymerization, high rates, high conversions, and high molecular weights can be achieved using microemulsion polymerization. The microemulsion polymerization differs from the homogeneous polymerization because oft the compartmentalization of radicals. The production of nano-polymer particles from oil-in-water microemulsions of monomers has not yet become routine. Very fine monomer microemulsions can be obtained for such systems, although their polymerization generally results in polymer latexes 20 - 80 nm. The particle size control in such systems remains an area of interest and opportunity [1].
Here we follow the effect of the initiator (type) and monomer concentration on the kinetics of the microemulsion polymerization of butyl acylate in the aqueous sodium dodecylsulfate medium.

Experimental Part

The batch polymerizations were run at 60 ^{o}C. In all runs the recipe comprises 100 g water, 20 g SDS and 0.025 g NaHCO$_3$. Amounts of AP, DBP, and BA varied as shown later. Concentrations of monomer, initiator and particles and polymerization rates as well are related to the aqueous phase. The polymerization technique and the measurements of particle size and number were the same as described earlier [2,3].

Results and Discussion

It was found that the conversion curves take on a shape more similar to that for the solution polymerization. Besides, he polymerization proceeds quantitatively in systems with larger concentration of BA than 0.78 mol.dm^{-3}. In the systems with [BA] $\leq$ 0.78 mol.dm^{-3} the limiting conversion appears. Variations of the limiting conversion with the weight ratio monomer/water ([AP = 0.001 mol.dm^{-3}) can be expressed as

$$100\% \ (0.1) > 92\% \ (0.064) > 84\% \ (0.026)$$

The final conversion was found to be independent of the AP concentration in the range from 0.00005 to 0.01 mol.dm^{-3}. In all DBP systems, however, the limiting conversion appeared at 70 - 80% ([BA] varied from 0.3 to 0.78 mol.dm^{-3} and [DBP] from 0.00006 to 0.001 mol.dm^{-3}).

The polymerization rate versus conversion relationship reveals two distinct intervals (1 and 3 according to the micellar model [4]), as the example serves the following run ([AP] = 0.001 mol.dm^{-3}, [BA] = 0.78 mol.dm^{-3}):

3.2 (5% conversion) < 4.8 (10%) < 5.6 (15%) < 6.0 (20%) < 6.4 (30%) > 6.0 (40%) > 5.2 (50%) > 4.4 (60%) > 1.6 (80%)

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

Interval 1 is much longer than in the emulsion system the most likely due to much higher concentration of emulsifier required in microemulsion polymerization. It ends when all free monomer or monomer-swollen micelles are depleted. Here, however, the monomer - swollen micelles act as emulsifier and monomer reservoirs and therefore interval 1 ends when the free monomer - swollen micelles disappear.

The maximum rate of polymerization is observed at 20 - 30% conversion. The decrease of the rate beyond ca. 30% conversion is due to the depletion of free monomer phase.

The rate of polymerization (R_p) was found to increase with increasing the monomer and initiator concentration, as well. For example, in the run with [AP] = 0.001 mol.dm^{-3}, the R_p varies with [BA] as follows

0.35 . 10^{-3} mol.dm^{-3}.s^{-1} (0.2 mol.dm^{-3}) < 0.56 (0.3) < 0.8 (0.4) < 1.14 (0.5) < 1.2 (0.6) < 2.5 (0.78).

The reaction order x from $R_p \propto [BA]^x$ was found to be 1.4 and 1.8 for AP and DBP, respectively. These results can be discussed in terms of solution polymerization and/or the polymerization under the monomer starved conditions.

The reaction order y from $R_p \propto [I]^y$ was found to be 0.46 and 0.26 for AP and DBP, respectively. The reaction order 0.46 favors the solution polymerization. The small y for DBP probably results from the strong cage effect and/or the primary radical termination.

The size of polymer particles was found to increase with increasing [BA], i.e., for the run ([AP] = 0.001 mol.dm^{-3}) D varies:

24 nm (0.2 mol.dm^{-3}) < 32 (0.3) < 40 (0.4) < 41 (0.5) < 46 (0.6) < 48 (0.78).

On the contrary, the number of particles decreases with increasing the monomer concentration. For these limit [BA] values, the N decreased from 2.6 x 10^{18} to 1.6 x 10^{18} per dm^3.

The particle size was found to decrease and the number of particles increase with increasing [AP]. However, the oposite trend is found with DBP. Here, the D varied with [DBP] as follows

54 nm (0.001 mol.dm^{-3}) = 54 (0.0005) > 53 (0.0001) > 50 (0.00001)

The addition of a small amount of acrylonitrile (AN) (the high water-soluble monomer) was found to decrease the rate of polymerization and the particle size as well. The decrease of the rate was very strong and was more pronounced at low [AN]. Beyond [AN] = 1.0 mol.dm^{-3} the polymerization rate increases only slightly. For example, in the presence of [AN] = 0.47 mol.dm^{-3} the rate of polymerization decreased ca. 5 times and the particle size 1.4 times (the volume of monomer phase is kept constant). At very high [AN] (> 2.0 mol.dm^{-3}) the latex becomes instable.

Conclusion

Polymerizations of transparent o/w microemulsions of SDS/water/BA initiated by AP and DBP produce stable and bluish-translucent microlatexes. These latexes contain spherical poly-butylacrylate particles with diameter ranging from 40 to 60 nm.

A common feature of these microemulsion polymerizations is the relatively long rise to a maximum rate and the two - intervals process. Monomer - swollen micelles are considered to act as monomer and emulsifier reservoirs. The polymerization initiated by AP is faster than that initiated by DBP.

The radicals are proposed to be generated : 1) by the decomposition of initiator (a water-soluble and the fraction of the oil-soluble initiator) in the aqueous phase and 2) and by the decomposition of initiator in the monomer-swollen micelles or particles.

Literature

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RHEOLOGICAL INTERACTION BETWEEN ASSOCIATIVE EMULSION POLYMERS AND SURFACTANTS

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The need to improve the performance of formulated aqueous systems that contain associative polymers and to clarify their mechanisms of interaction with surfactants have prompted studies on the interactions between associative polymers and surfactants. Recent studies have examined the interaction of anionic, cationic, zwitterionic, or nonionic surfactants with a variety of associative polymer types, such as hydrophobically modified poly(ethylene oxide), cellulose, copolymers of acrylamid, and copolymers of acrylic or methacrylic acid. Hydrophobically modified polyelectrolytes combine polyelectrolyte behavior with associative character in interactions with surfactants (especially charged surfactants). This report examines the influence of the structure and solubility characteristics of nonionic surfactants, and the composition of associative emulsion copolymers based on methacrylic acid, on solution rheology.

Although the rheological consequences of these interactions are system dependent, some phenomena such as "co-thickening", where the viscosity of a associative polymer solution increases when surfactants are added, have been seen in general across the many types of associative polymers. Often the rheological properties increase to a maximum as surfactant concentration increases, and subsequently decrease as surfactant concentration increases, indicating that the addition of surfactant changes the functionality and the strength of the associative network junction when surfactant is added.[1] Annable et al.[2], suggested that the addition of surfactant produces an entropically driven change from intramolecular associations (i.e., self-loops), that do not contribute to modulus, to intermolecular associations that do contribute to modulus. This is consistent with the "flower" or "rosette" model advocated by Yekta and Winnik[3]. Since self-loops force the functionality of the association cluster to be small due to geometric packing constraints, the conversion from intra- to inter- molecular associations increases the functionality of the associative junction. All of these effects increase viscosity, shear modulus, and relaxation time constant as surfactant concentration increases. Once all of the intramolecular associations have been converted to intermolecular associations, additional surfactant
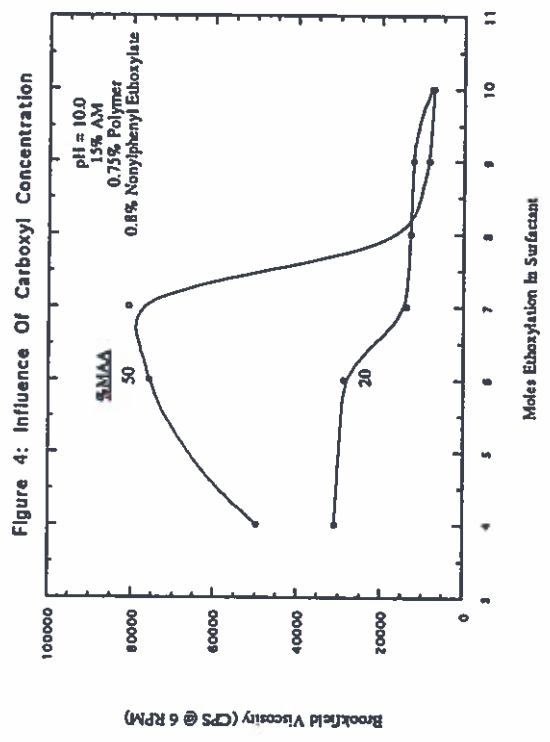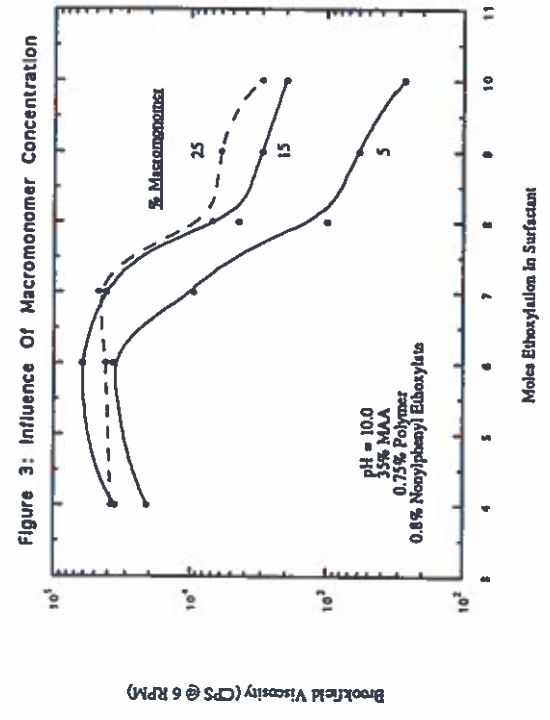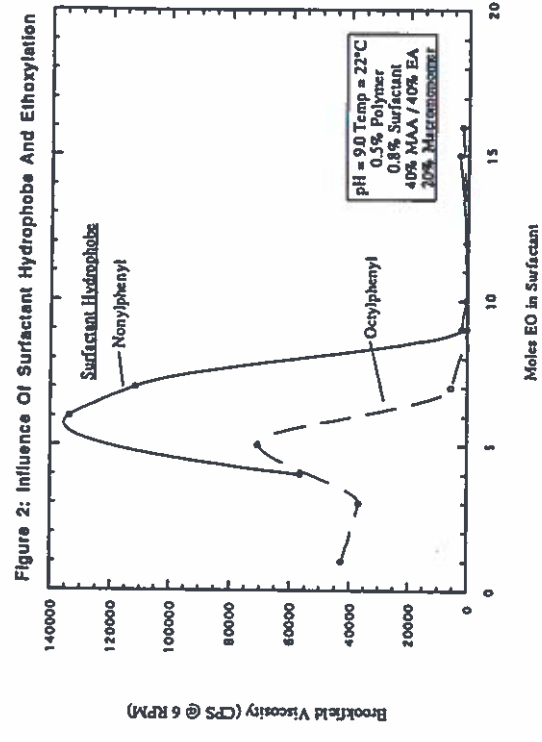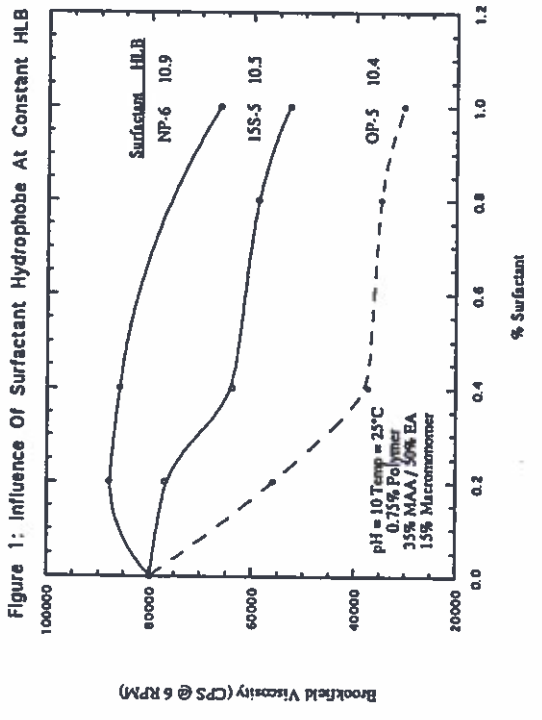
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[3] Yekta, A., Duhamel, J. ,Brochard, P., Adwidjaja, H., Winnik, M.A.,*Macromolecules* **26** (1993),p. 1829

dilutes the number of associative polymer hydrophobes in a junction to reduce rheological properties.

The extent of co-thickening depends on the structures of the surfactants and associative polymer, and their stoichiometry. Figure 1 shows the influence of surfactant concentration on the viscosity of one polymer solution containing three different surfactants that have 5-6 moles of ethoxylation (and are therefore of nearly the same HLB), but vary in hydrophobe structure: octylphenyl, nonylphenyl, and linear secondary alcohol of 12-15 carbon units. Surfactants that have marginal solubility in water, such as NP-6, often produce synergistic co-thickening, whereas surfactants with larger water solubility, such as 15-S-5, generally lower solution viscosity. Nonetheless, that the response depends on hydrophobe structure shows that the interaction between associative polymers and surfactants depends on more than just the HLB of the surfactant. With either nonylphenyl or octylphenyl based surfactants, solution viscosity reaches a maximum at 5 - 6 moles of ethoxylation in the surfactant, and diminishes rapidly as the moles of ethoxylation increases further (Figure 2). The surfactant hydrophobe strongly influences the magnitude of the viscosity at the viscosity maximum. Therefore, a 'systems approach' maximizes the economic and performance benefit when using associative polymers, as contrasted to an 'additive' approach, where the components of the formulation are selected individually without regard to the presence of other ingredients. With regard to the structure of the polymer, the amount of associative character (i.e., "macromonomer") in the polymer influences the magnitude of co-thickening with surfactants, but does not strongly influence the moles of ethoxylation that maximizes solution viscosity (Figure 3). When the surfactant has low moles of ethoxylation, the magnitude of the viscosity increases as the carboxyl concentration in the polymer increases (Figure 4). This increased interaction could be due to adsorption of the surfactant onto the backbone of the polymer through the ethoxylated portion of the surfactant to increase the apparent associative functionality of the polymer.

Figure 1: Influence Of Surfactant Hydrophobe At Constant HLB

Figure 2: Influence Of Surfactant Hydrophobe And Ethoxylation

Figure 3: Influence Of Macromonomer Concentration

Figure 4: Influence Of Carboxyl Concentration

POLYMER COLLOID GROUP NEWSLETTER

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

Françoise CANDAU

COPOLYMERIZATION OF ACRYLAMIDE AND A POLYMERIZABLE SURFACTANT: SYNTHESIS AND ASSOCIATIVE PROPERTIES

(with **D. RENOUX** and **J. SELB**)

Introduction.

Hydrophobically associating polymers consist of a water-soluble polymer containing a small amount of hydrophobic groups [1]. We report here some results of an investigation into the synthesis, characterization and solution properties of a new class of associating polymers. These were synthesized by free-radical copolymerization of a water-soluble monomer (Acrylamide : AM) with a cationic micelle-forming polymerizable surfactant (Hexadecyldimethylvinylbenzylammonium chloride : N16).
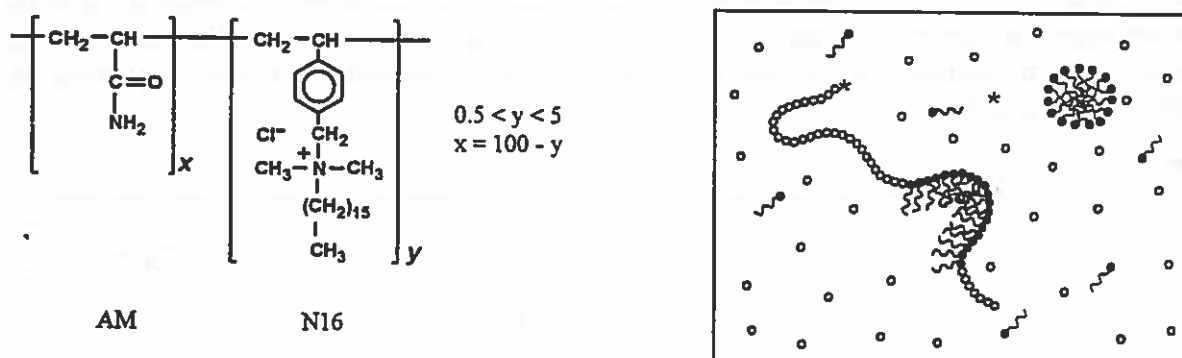

$$0.5 < y < 5$$
$$x = 100 - y$$

AM   N16

Fig. 1: Schematic representation of the copolymerization media
o Acrylamide   ↘ N16   * Initiator

Synthesis and characterization of the copolymers.

The reaction mixture that contains acrylamide and the polymerizable surfactant in its micellar state (*figure 1*), is actually a microheterogeneous system : micelles behave like microdomains with a very high local N16 concentration and therefore a copolymer with a blocky structure is expected [2]. The copolymer molecular weights are in the range 1.5 to 3×10^6 g/mol.

Kinetics of the copolymerization.

The studies have shown that the conversion does not progress significantly above ~3 hours of reaction time, and the final degree of conversion is lower than for polyacrylamide ; the higher the N16 concentration, the stronger the effect (final weight conversion of ~85, 80 and 75% for 3, 4 and 5 mol.% respectively). As shown in the next section, this behavior is related to an incomplete consumption of the polymerizable surfactant.

Copolymer composition.

Figure 2 shows the variation of the polymer composition as a function of conversion for two different initial N16 concentrations. Examination of the data leads to the following comments:

- the composition of the final compounds does not correspond to the initial monomer composition. This reveals that the incorporation of the polymerizable surfactant is far from being complete (~50-60%). This can be explained by the fact that some surfactant monomers are adsorbed onto the previously formed hydrophobic sequences [3] (formation of mixed micelles of polymerized and non-polymerized surfactant species). This trapping effect of the polymerizable surfactant molecules hinders their further consumption during the polymerization reaction.

- an important drift in copolymer composition is observed (*figure 3*) and the hydrophobe content exceeds the feed composition at the early stages of the reaction. It can be inferred that the drift in copolymer composition is mainly related to the dynamics of the micellar system : the polymerizing micelles are fed surfactant molecules coming from unnucleated micelles [4], leading to a faster incorporation of N16 at the beginning of the copolymerization.

Solution properties : Polymer concentration effect.

Figure 3 shows the effect of polymer concentration on the solution viscosities for a copolymer sample and a homopolyacrylamide. The improved thickening properties for the copolymer can be ascribed to two complementary effects : coil expansion due to charge-charge repulsions and intermolecular hydrophobic associations. These data were supported by fluorescence experiments (*figure 3*) using pyrene as a fluorescent probe that reveals the formation of an increased number of hydrophobic microdomains in the solution.

Conclusion.

The radical copolymerization of acrylamide in aqueous solution with a micelle-forming polymerizable surfactant yields copolymers with a somewhat blocky structure as a consequence of the microheterogeneous nature of the reaction media. Such copolymers are effective thickeners in aqueous solution with a rheological behavior controlled by the competition between electrostatic repulsions and hydrophobic attractions.
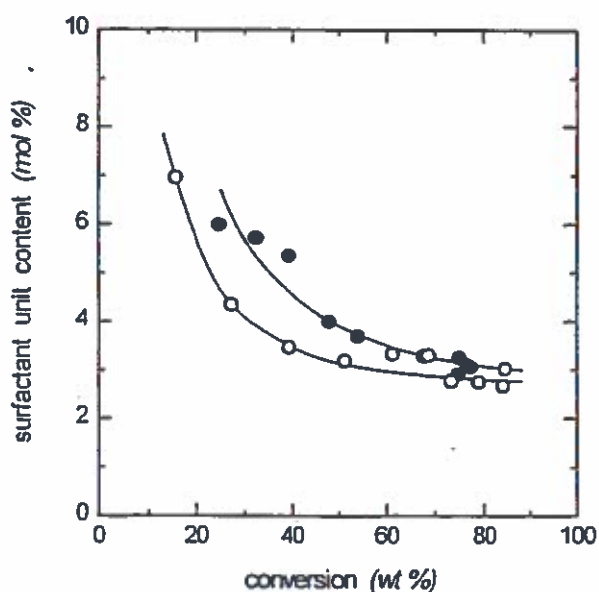

Fig. 2: Variation of the copolymer composition as a function of conversion for two different N16 contents (mol.% of the monomer feed)
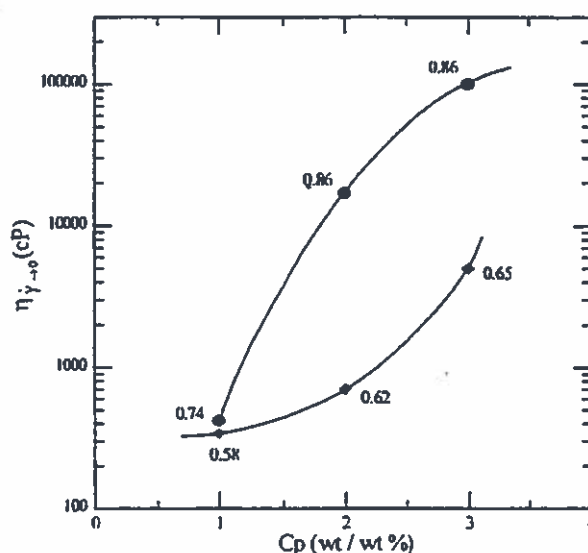O 4 mol.%
● 5 mol.%

Fig. 3: Zero shear viscosity as a function of polymer concentration in pure water
Data point labels are I_3/I_1 pyrene fluorescence ratio
◆ Polyacrylamide
● Copolymer (N16 = 3 mol.%)

References :

1 : Glass, J.E., Ed. *Polymers in Aqueous Media : Performance Through Association*; Advances in Chemistry Series 223, American Chemical Society : Washington, D.C., 1989
2 : Hill, A.; Candau, F.; Selb, J. *Macromolecules* **26**, 4521 (1993)
3 : Biggs, S.; Selb, J.; Candau, F. *Langmuir* **8**, 838 (1992)
4 : Cochin, D.; Candau, F.; Zana, R. *Macromolecules* **26**, 5755 (1993)

RECENT PUBLICATIONS

J.M. Corpart, F. Candau, <u>Colloid Polym. Sci.</u> **271**, 1055 (1993)
"Formulation and polymerization of microemulsions containing a mixture of cationic and anionic monomers"

J.M. Corpart, J. Selb, F. Candau, <u>Polymer</u> **34**, 3873 (1993)
"Characterization of high charge density polyampholytic copolymers prepared by microemulsion polymerization"

D. Cochin, F. Candau, R. Zana, <u>Macromolecules</u> **26**, 5755 (1993)
"Photopolymerization of micelle-forming monomers. I. Characterization of the systems before and after polymerization"

D. Cochin, R. Zana, F. Candau, <u>Macromolecules</u> **26**, 5765 (1993)
"Photopolymerization of micelle-forming monomers. II. Kinetic study and mechanism"

A. Hill, F. Candau, J. Selb, <u>Macromolecules</u> **26**, 4521 (1993)
"Properties of hydrophobically associating polyacrylamides : influence of the method of synthesis"

M. Skouri, J.P. Munch, S.J. Candau, S. Neyret, F. Candau, <u>Macromolecules</u> **27**, 69 (1994)
"Conformation of neutral polyampholyte chains in salt solution: a light scattering study"

Contribution to the International Polymer Colloids Group Newsletter

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The titles of our current research projects are given in the **Contents** of our *Graduate Research Progress Reports*, No. 41, January, 1994, which can be found at the end of this report. Summaries of progress in several research areas are presented here.

1. Suprastructured Latex Thermoplastics - A ^{13}C NMR Characterization Study
Veera Nelliappan

For several decades, efforts have been made to improve the fracture resistance of brittle thermoplastics like poly(methyl methacrylate) (PMMA) via rubber toughening. Toughening of these brittle polymers can be achieved by incorporating particles which consist of radially alternating rubbery and glassy layers into the brittle matrix. The properties and the size of the different core/shell layer interphases as well as the particle/matrix interphase have a profound influence on the overall properties of the polymer composite. Recent research efforts have been devoted to the characterization and understanding of the effect of the interphase on the overall properties of the composite polymer. However, the small relative volume of the interphase results in it being obscured by the bulk phase.

Schaefer et al. [Schaefer, J., Stejskal, E.O., and Buchdahl, R., *Macromolecules*, **10**, 384 (1977)] obtained high resolution NMR spectra of solid polymers. Solid-state ^{13}C NMR has been used to characterize the interphase in polymer blends. Recently, solid-state ^{13}C NMR has been used to characterize the interphase of core/shell particles [Tembou Nzudie, D., Delmotte, L., and Reiss, G., *Makromol. Chem., Rapid Commun.* **12**, 251 (1991)] through measurement of spin-lattice relaxation times ([H]$T_1\rho$).

The interphase region of core/shell latexes consisting of a core made of poly(divinylbenzene) (PDVB) and a shell of poly(butyl acrylate) (PBA) is being investigated. The PDVB core latex particles were synthesized by miniemulsion polymerization and the stage II BA was added semicontinuously. Core/shell latexes consisting of different PDVB/PBA ratios were synthesized. Measurements of the spin-lattice relaxation times of the methyl group in the PBA of these core/shell latexes were made using a General Electric (GN-300) spectrometer operating at a field strength of 300 MHz. The (H)$T_1\rho$ values are listed in Table 1.

A model has been proposed for compatible blend systems having a relaxation time which changes with the composition [McBreity, V.J., Douglass, D.C., Kwei, T.K., and Frisch, H.L., *Macromolecules*, **11**, 1265 (1978)]. We have applied this model to the core/shell system to calculate

the percentage of interfacial PBA:

$$M_1 = \frac{[(1/T_1\rho(H))_m - (1/T_1\rho(H))_2]}{[(1/T_1\rho(H))_1 - (1/T_1\rho(H))_2]}$$

where,

M_1 is the mole fraction of phase 1

$T_1\rho(H)_m$ is the experimentally determined $T_1\rho(H)$ value of the core/shell latex,

$T_1\rho(H)_1$ is the extrapolated value of the relaxation time (2.4 ms),

$T_1\rho(H)_2$ is the relaxation time of the PBA homopolymer.

TABLE 1: PROTON $T_1\rho$ VALUES FOR THE CORE/SHELL LATEX PARTICLES AND THEIR CORRESPONDING HOMOPOLYMERS.

PDVB/PBA Weight Ratio	(H)$T_1\rho$ (ms)
1/0	4.2 [§]
1/0.1	5.1
1/0.25	5.9
1/0.5	8.0
1/1	13.2
0/1	23.5

[§] The (H)$T_1\rho$ of the secondary aromatic carbon was recorded for PDVB and the (H)$T_1\rho$ of the methyl group in PBA was measured for all other samples.

The variation of interfacial PBA/PDVB is plotted in Figure 1 as a function of the PBA content in the core/shell latexes. We can see that the maximum amount of interphase is formed when the PBA content in the core/shell latexes is 25 % by weight. This corresponds to a particle radius of 93.2 nm; using the radius of the seed particle (86.5 nm) one is able to estimate the thickness of the interphase region as ~ 7 nm.

2. Telechelic Polybutadiene as Crosslinking Agent in Latex Films
Jiangtian Xu

Telechelic polymers have low molecular weights and are terminated with functional groups capable of further reaction such as chain extension and crosslinking. An initial investigation in our lab showed that telechelic polybutadiene (PBD) can crosslink with
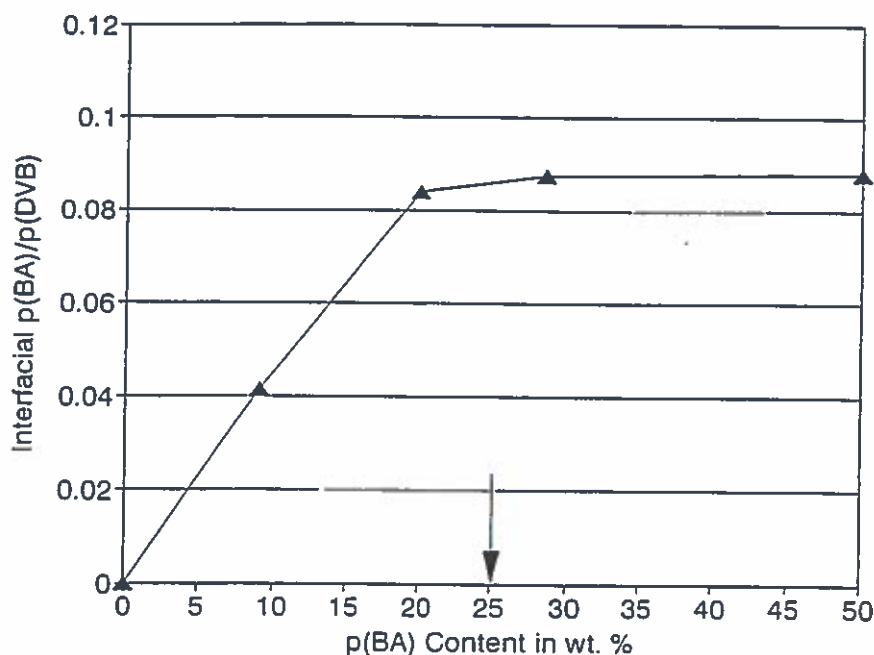
Figure 1: *Plot of the interfacial PBA/PDVB vs. the PBA content in the core/shell latex.*

functionalized polymer latexes during film formation.

Amino-terminated PBD was obtained by polymerizing butadiene with 2,2'-azobis(2-amidino propane) dihydrochloride (V50) as initiator in an ethanol/water medium at 60°C for 48 hours, and modifying the end-groups with lithium aluminum hydride in tetrahydrofuran. ^{13}C NMR was utilized to characterize the structure of the PBD before and after the end-group modification. The number average molecular weight of the PBD determined by GPC and VPO was 2800. The amine functionality determined by acid-base titration was 1.7. Carboxyl-terminated PBD was synthesized with 4,4'azobis(cyanovaleric acid) (ACVA) initiator. The telechelic PBD was miniemulsified to form an artificial (post-emulsified) latex having a 3% solids content and was then mixed with the functionalized copolymer latex as described below.

The functionalized copolymer latex was obtained by emulsion copolymerization of styrene/*n*-butyl acrylate/dimethyl *m*-isopropenylbenzyl isocyanate (TMI). The molar ratio of styrene/n-BA/TMI was 49/49/2 and the solids content was 30%. The TMI functional monomer was added to the system using either batch or shot-growth techniques, so that the NCO functional groups were distributed either in the core region or in the shell region of the particles.

A room temperature curable latex film was obtained from a 1/1 weight ratio mixture of the copolymer latex with the PBD artificial latex. When the content of the PBD was increased, the swellability of the film in toluene decreased as shown in Figure 3, indicating that the crosslink density of the film increased with the increased concentration of the telechelic PBD, which acted as a crosslinking agent in the film. The crosslinking reaction was studied by FTIR observation of the NCO group: the ratio of the NCO group absorbance to the aromatic absorbance (mainly from

the styrene units), $A_{NCO}/A_{aromatic}$, is proportional to the concentration of the NCO groups in the film. The higher the crosslinking density, the more NCO is consumed, and the lower the value of $A_{NCO}/A_{aromatic}$. It was observed that when amine-terminated PBD was used as the crosslinking agent, and the copolymer latex used was prepared by batch polymerization, 37% of the NCO groups in the film were consumed by the crosslinking agent over a period of 24 hours at room temperature; when the copolymer latex was that prepared by shot-growth polymerization, 42% of the NCO groups were consumed. Under the same conditions, the carboxyl terminated PBD did not act as a crosslinking agent, i.e., no NCO groups were consumed by the PBD.
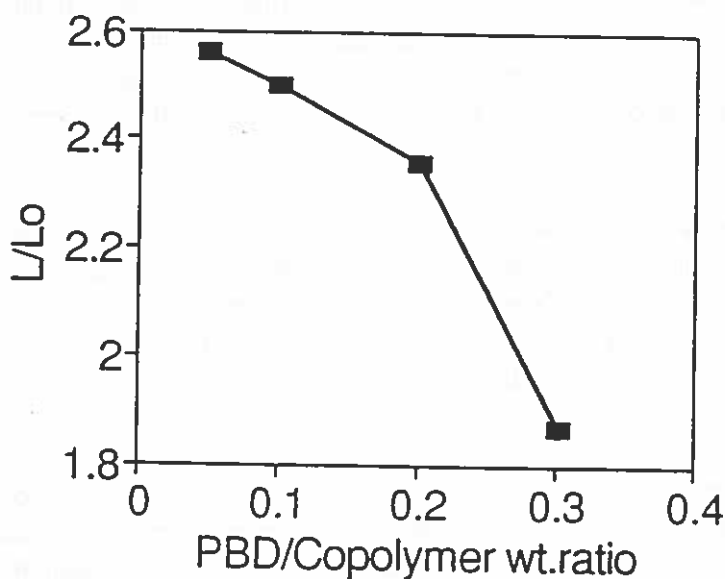

Figure 2: *Swelling ratio (L/Lo) of the St/BA/TMI - PBD latex films as a function of the PBD latex/copolymer latex ratio; L = length of swollen sample, Lo = length of unswollen sample. The films were cured at room temperature for 24 hours prior to swelling with toluene (24 hrs, room temperature).*

3. The Use of Styrene - Maleic Anhydride Copolymers (SMA Resins) in Emulsion Polymerization
Denis Tembou Nzudie

Three kinds of SMA resins (SMA1000, 2000, and 3000 with 1/1, 2/1, and 3/1 styrene/maleic anhydride molar ratios, respectively) were used as the sole surfactant or in combination with conventional surfactants, in batch and semicontinuous emulsion copolymerizations of methyl methacrylate (MMA) and butyl acrylate (BuA). Parameters, such as the type of SMA, its concentration when used alone or in a surfactant mixture , and its mode of addition were found to have an influence on the course of the polymerization and the latex characteristics.

All three SMA's were found to have a lower stabilization efficiency when used as the sole surfactant in batch emulsion polymerizations and to interact with the conventional surfactants (anionic

and nonionic nonyl phenol poly(ethylene oxide)) over a wide range of SMA/conventional surfactant ratios leading in many cases to the formation of coagulum and an increase in the particle size in either batch or semicontinuous polymerizations. It was demonstrated, by using SMA as the sole surfactant in batch emulsion polymerizations, that SMA2000 and 3000 acted as better stabilizers, and induced smaller particle sizes than SMA1000. However, by using the SMA's in combination with the conventional surfactants, a better stabilization of the resulting latex particles was found in the presence of SMA1000.

In the semicontinuous polymerizations, the use of the bicarbonate was found to induce a substantial induction period or a drop in the monomer conversion; its elimination led to higher conversions. Semicontinuous emulsion polymerizations using no buffer showed that at lower concentrations of SMA in the surfactant mixture, there was no major effect on the monomer conversion and the particle size compared to the conventional surfactants. A decrease in the monomer conversion occurred at higher concentrations of SMA.

It was demonstrated that a considerable amount of SMA can be incorporated into the SMA/conventional surfactant mixtures without inducing coagulum or a significant increase in latex particle size. Higher concentrations of SMA led to a substantial amount of coagulum and an increase in the particle size. A second stage addition of SMA during the polymerization was found to be the best way to incorporate greater amounts of SMA in the latex without inducing coagulum, and maintaining the particle size close to that of the conventional latex.

SMA1000 was found to be the most suitable of the three SMA samples to use together with the conventional surfactants in these polymerizations for a number of reasons including: 1) its lower interaction with the conventional surfactants; 2) its ability to form a stable, coagulum free latex even at higher concentrations; and 3) its ready incorporation into the latex and its insignificant effects on the particle size.

By using conductometric titrations on the cleaned latexes, no grafted SMA could be detected on the particle surfaces of those prepared via semicontinuous polymerization.

4. Preparation of Uniform Micron-Size Polystyrene Particles with Narrow Molecular Weight Distribution by Anionic Dispersion Polymerization
Muhammad A. Awan

Uniform size latex particles (e.g., polystyrene and poly(methyl methacrylate)) with diameters in the micron size range are readily prepared by free radical dispersion polymerization in alcohol. These are typically made at a relatively low solids content and the polymers prepared in this way have relatively low and broad molecular weight distributions. Functionalization of the chain-ends, moreover, can not be carried out in a controlled manner. In order to overcome these shortcomings, we have combined the elements of dispersion and anionic polymerization to prepare narrow and controlled size polystyrene particles having narrow and controlled molecular weights.

Anionic dispersion polymerizations of styrene were carried out under an ultra high purity nitrogen atmosphere using polystyrene-*block*-polybutadiene copolymers as stabilizer. A diblock copolymer containing 25% polystyrene (M_w = 140,000 g/mole, M_w/M_n = 1.05) as the anchoring moiety (Stereon S-730A, Firestone) was found to be the most suitable steric stabilizer for polystyrene particles in a hexane medium. Through a systematic study, the initiator (*sec*-butyl lithium), stabilizer, and monomer (styrene) concentrations, along with the temperature were found to be effective experimental parameters for controlling the particle size and distribution. Particle sizes were prepared varying in size from 0.5 to 6.5 μm with molecular weights ranging from 20,000 to 66,500 g/mole having polydispersities between 1.03 - 1.14. As found in free radical dispersion polymerization, the particle size increased with decreasing stabilizer concentration but increasing initiator concentration (up to 5.12 mM after which the size was not affected). The aggregative nucleation mechanism used to describe the formation of particles in the former system would also appear to explain these results. The molecular weights were little affected by changes in the stabilizer level while they decreased with increasing initiator, as expected. They also remained narrow under the given experimental conditions.

The preceeding studies were performed at a final solids content of about 20%. However, it is highly desirable for commercial application to prepare polymer dispersions with higher solids contents and low viscosities. It is also important to be able to control independently the particle size and molecular weight. The living character of anionic dispersion polymerization offers the possibility of achieving these goals and overcoming the drawbacks of free radical dispersion polymerization such as the nucleation of new particles when trying to grow the particles to larger sizes and higher solids. High solids content dispersions (> 40%) were prepared by monomer multi-addition. In these experiments, a controlled second, third, and fourth addition of monomer was made. Polystyrene particles were increased in size from 4.16 to 5.16 μm in diameter without any change in the resulting particle size distribution. The particle size increase and the size distribution resulting from each new monomer addition confirmed that no new nucleation had occurred. This finding was also confirmed by the resulting increase in the molecular weights while their distributions remained narrow, indicating that all the monomer was consumed only by the existing growing anions and that no new chains were initiated. These controlled and narrow size dispersions, therefore, should provide an opportunity for a better understanding of the mechanism of nucleation in dispersion polymerization.

5. Grafting Reactions of Vinyl Acetate onto Poly[(Vinyl Alcohol)-co-(Vinyl Acetate)]
   Thomas J. Markley and Robert K. Pinschmidt, Jr. (*Co-Advisor*)

The present research has examined the ability of vinyl acetate (VAc) to preferentially graft onto the methine carbon of poly(vinyl alcohol) (PVOH) over poly(vinyl acetate) (PVAc) to highly branched PVOH.

The grafting polymerizations were run in a methanol medium in the presence of poly[(vinyl alcohol)-co-(vinyl acetate)]. Low concentrations of vinyl acetate were added continuously during each reaction in order to favor branching, and the overall conversion of the reaction was determined titrimetrically and gravimetrically.

The effects of varying the concentration of monomer and initiator on the molecular weight of the graft copolymer was studied. The results showed that decreasing the monomer or initiator concentration decreased the molecular weight of the graft copolymer formed. Also, the influence that initiators have on the extent of grafting onto the copolymer was studied. It was determined that of the initiators studied, ammonium persulfate led to copolymers with the largest increase in molecular weight.

After polymerization, the samples were hydrolyzed and reacetylated in order to determine where grafting occurs along the poly[(vinyl alcohol)-co-(vinyl acetate)] chain. The change in molecular weight of the original poly[(vinyl alcohol)-co-(vinyl acetate)] due to the grafting reactions was determined by gel permeation chromatography (GPC) for each polymer (copolymer, fully hydrolyzed or reacetylated) form. ^{13}C NMR was also used to determine the number of grafts that occurred on the main chain methine carbon of the fully hydrolyzed form. The results showed that grafting occurred on the acetate groups of the PVAc units rather than the methine carbon of the PVOH or PVAc units.

Recent Publications

"Dispersion Polymerization of Methyl Methacrylate: Mechanism of Particle Formation", Shen, S., Sudol, E.D., El-Aasser, M.S., *J. Polym. Sci.: Part A: Polym. Chem.*, 32, 1087 (1994).

"Characterization of Miniemulsion Droplet Size and Stability Using Capillary Hydrodynamic Fractionation", Miller, C.M., Venkatesan, J., Silebi, C.A., Sudol, E.D., and El-Aasser, M.S., *J. Colloid and Interf. Sci.*, 162, 11 (1994).

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"Core-Shell Morphology as a Model for the Study of Gas Permeation in Composite Systems", Correa, C.R. and Klein, A., *Polym. for Advanced Tech.*, 4, 525 (1993).

"Characterization of Film Formation from Direct Mini-Emulsified Polystyrene Latex Particles via SANS", Kim, K.D., Sperling, L.H., and Klein, A., *Macromol.*, 26(17), 4624 (1993).

"Calorimetric Monitoring of Emulsion Copolymerization Reactions", Urretabizkaia, A., Sudol, E.D., El-Aasser, M.S., and Asua, J.M., *J. Polym. Sci: Part A: Polym. Chem.*, 31, 2907 (1993).

EMULSION POLYMERS INSTITUTE
Lehigh University

Graduate Research Progress Reports
No. 41   January 1994

CONTENTS

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Abstracts:

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"Aggregation Studies of Superparamagnetic Latex Particles"

Aqueous suspensions of superparamagnetic particles behave analogously to electrorheological (ER) fluids. In the presence of an applied magnetic field, the particles acquire a dipole moment aligned with the external field and experience an attractive dipolar interaction, causing them to aggregate tip-to-tip. The particles thus form linear chains parallel to the field, which may then coalesce laterally into columns. For sufficiently large particle volume fraction and applied field strength, the crosslinking between chains is extensive enough that the suspension effectively solidifies. This capacity for a dramatic rheological change on a very short timescale is at the heart of the interest in and potential applications of ER fluids. Using our model system of superparamagnetic latex particles with a narrow size distribution, we elucidate the transitions in suspension structure accompanying these rheological changes. We study the structural evolution as a function of applied field strength and particle volume fraction in order to determine the characteristic scaling of this aggregation behavior.

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"Influence of Structure on Diffusion in Screened Coulombic Suspensions"

Aqueous dispersions of monodisperse, highly-charged, polystyrene colloids are ideal for the study of the influence of interparticle structure on dynamics. The well characterized screened Coulombic interaction in these systems is easily controlled via solution ionic strength and particle volume fraction, yielding a rich variety of interparticle structures;
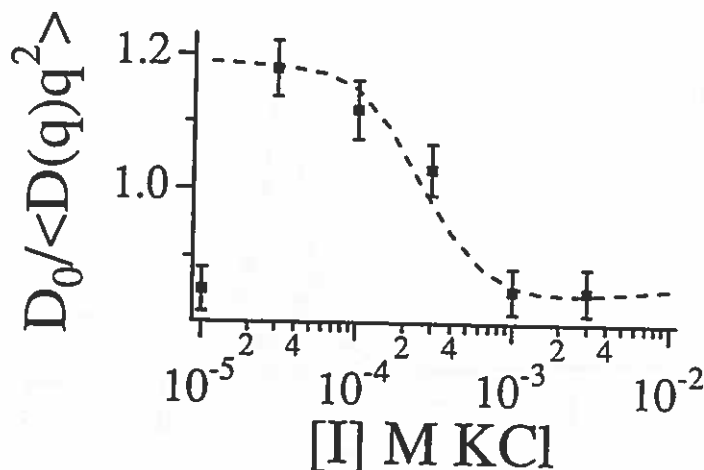
Figure 1: Plot of the inverse q-averaged diffusion coefficient normalized on the free particle value versus ionic strength for a suspension of 55 nm particles at a volume fraction $\phi = 0.04$. Points are experimental results, and lines show theoretical predictions.

these range from liquid-like structures to long-ranged ordered particle arrays with both face-centered and body-centered cubic lattices. Statistical mechanics predicts that the q-dependent diffusion coefficient, $D(q)$, in these strongly interacting systems is modified by the static structure factor, $S(q)$, and hydrodynamic response function, $H(q)$. In dilute suspensions, we can neglect the hydrodynamic contributions ($H(q) = 1$), and directly probe the changes in suspension dynamics arising solely from interparticle structure. Until recently, experimental studies of this type have been circumscribed by the strong scattering exhibited by these systems. However, the development of high-speed correlators and theoretical treatments for multiply scattered light have given us a new experimental probe called *diffusing wave spectroscopy* (DWS) to interrogate these systems.

In our work, we probe the relaxation dynamics in these turbid systems with DWS as we vary the interparticle structure by holding the suspension volume fraction constant and varying the solvent ionic strength. DWS models the transport of the photons in the sample as a diffusive process and allows us to interpret the autocorrelation function of the scattered laser light to obtain an averaged, q^2-weighted, diffusion coefficient, $\langle D(q)q^2 \rangle$. The averaging arising from the multiple scattering is over the finite q range from 0 to $2\pi n\sigma/\lambda$, where σ is the particle diameter, λ is the wavelength of light, and n is the index of refraction of the solvent. It is important to note that the q^2 contribution to the averaging preferentially weights features near the upper q limit. By modeling the screened Coulombic interaction with the hard-core Yukawa potential, we interpret the measured dynamics with theoretical predictions of $S(q)$ obtained from statistical mechanics.

In Figure 1, we plot the inverse of the q-averaged diffusion coefficient normalized on
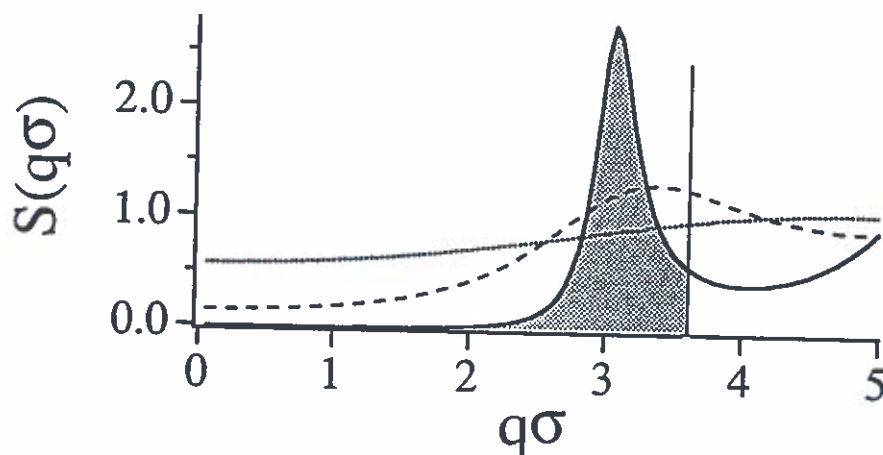
Figure 2: Plots of $S(q)$ versus q normalized on the particle diameter σ for three ionic strengths: 3×10^{-3} M KCl (dotted), 3×10^{-4} M KCl (dashed), and 3×10^{-5} M KCl (solid). The vertical line indicates the upper limit of the q averaging and the shading highlights the structure for the lowest ionic strength.

the free particle diffusion coefficient, D_0, versus ionic strength for a suspension of 55 nm particles at a volume fraction of $\phi = 0.04$. The points indicate experimental results, and the lines show calculations based on predictions of $S(q)$. Values of $D_0/\langle D(q)q^2\rangle$ greater than one represent slowed diffusion, while values less than one indicate enhanced diffusion. We see excellent agreement between theory and experiment.

We can better understand the influence of structure on diffusion by plotting the structure factor, $S(q)$, used in our calculations for several values of the ionic strength. In Figure 2 we show the structure factor plotted versus $q\sigma$ for three ionic strengths: 3×10^{-3} M KCl (dotted), 3×10^{-4} M KCl (dashed), and 3×10^{-5} M KCl (solid). The vertical line indicates the upper limit of the q averaging and the shading highlights the structure for the lowest ionic strength sample. We can see that the slowing down with decreasing ionic strength arises directly from the increasing strength of the first peak in $S(q)$ located near the upper q-averaging limit.

Finally, we see in Figure 1 that the experimental point for the 1×10^{-5} M KCl sample shows an abrupt increase in the diffusion which is not predicted by our theory. Visual inspection of this sample shows that it has formed a colloidal crystal and thus should not be expected to exhibit behavior similar to that of disordered suspensions. We are currently working on developing a better understanding of the enhanced dynamics occurring in ordered suspensions.

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

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In emulsion copolymerization monomer partitioning and composition drift are now well understood. For good control of product properties (*e.g.* the molecular weight distribution) also a good understanding of the kinetics of emulsion copolymerization can be very important.

Recently extensive models for the rate-determining kinetic mechanisms in emulsion polymerizations have been developed for and applied to the homopolymerizations of styrene[1,2], methyl methacrylate[1,3] and butyl methacrylate[4]. These models are mainly concerned with descriptions of radical entry[5,6] and exit[1,2], the kinetic processes that are typical for compartmentalized systems such as emulsion polymerizations. Some researchers have also paid attention to copolymerizations such as styrene-methyl methacrylate[7,8].

However, most industrial recipes involve also more water-soluble monomers. As it is now well-established that the aqueous phase plays a dominant role in the kinetics[6], the question rises whether the same kinetic mechanisms are dominant if more water-soluble monomers are used.

Therefore a kinetic study of the seeded emulsion copolymerization of styrene (S) and methyl acrylate (MA) was carried out so as to elucidate the mechanisms of radical entry into latex particles, radical exit from the latex particles, and the fate of radical species in the aqueous phase. S is a relatively water-insoluble monomer while MA is relatively water-soluble. The seeds comprised a range of poly(S-co-MA) latices with varying particle sizes and a poly(S) latex. Conditions were such that the system followed zero-one kinetics (Smith-Ewart cases 1 and 2) which means that no latex particles contain more than one growing radical. Data were obtained for the steady-state rate of polymerization with persulfate as initiator, and for the non-steady-state relaxation kinetics in γ-radiolysis initiation experiments. The latter kinetics are dominated by radical loss mechanisms such as radical desorption and termination. The data are consistent with the following

mechanisms. Radical exit occurs via the same transfer-diffusion mechanism as found in a number of other systems (transfer of the radical activity to monomer(s) and subsequent desorption into the aqueous phase), with the desorbing radical being mostly an MA monomeric radical except for low overall fractions of MA. These desorbed monomeric radicals always re-enter the particles and either terminate or propagate therein. Initiation by persulfate is inefficient, with 50-90 % of the persulfate-derived radicals undergoing termination in the aqueous-phase (see Figure 1).
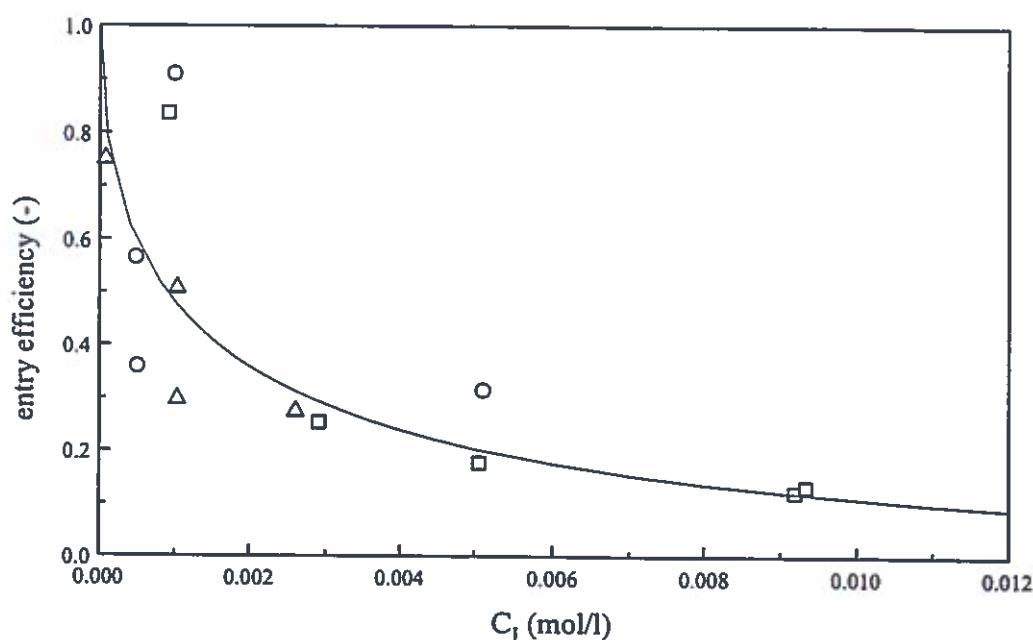
Entry efficiencies calculated for three series of persulfate-initiated runs with different seed latex particles sizes: swollen radius: (□) 55 nm; (O) 39 nm; (▵) 28 nm. The line is calculated with $z = 17$, $k_{t,aq} = 3 \cdot 10^9$ l/mol·s, $\bar{k}_{p,aq}$ $= 740$ l/mol·s, $[M]_{aq} = 0.1$ M, using the Maxwell-Morrison approximation[5].

For low fractions of MA this is in accord with the mechanism for entry which states that the rate-determining events are aqueous-phase propagation and termination. When some critical degree of polymerization is reached the oligomeric radical enters a particle irreversibly and instantaneously. At high fractions of S in the S-MA system, although MA polymerizes quickly (high k_p), the occasional addition of S in the aqueous phase slows the propagation rate down considerably. Thereby it also decreases the probability of the attainment of a sufficiently high degree of polymerization for surface activity (perhaps $z = 10$-20 monomer units with the relatively water-soluble MA). At lower fractions of S the initiator efficiency is also low, but the low concentration of S cannot account for this. It is

possible that there is some barrier against entry of relatively long MA-oligomers, which is consistent with the fact that it is difficult to grow a monodisperse seed with relatively water-soluble monomers, and the ease with which secondary particle formation occurs in such systems as the entry barrier may favour new particle formation above entry.

A critical parameter in the exit mechanism is the rate of transfer to monomer, as this determines the rate of production of S and MA monomeric radicals, which are kinetically important. It appeared to be possible by obtaining the slope of the logarithm of the number molecular weight distribution to calculate a value for the rate constant of transfer from a radical with a S-ultimate unit to MA monomer, by assuming that the concentration of radicals with an MA-unit as the ultimate unit is negligible, the MA radical being very reactive. The average transfer rate coefficient should then be a linear function of the composition, at least at high fractions of S in the feed. It is possible to check this assumption by measuring the average transfer rate coefficient as a function of the fraction of S. These measurements are currently being undertaken.

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

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

The measurement and meaning of rate coefficients in free-radical polymerizations

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Abstract: New experimental data and theory are reported for obtaining three types of rate parameters controlling kinetics and molecular weight distributions in free-radical polymerizations. (1) (a) Propagation rate coefficients (k_p) for butyl acrylate are found using pulsed-laser polymerization, with the novel variant of carrying out the procedure at very low temperatures (-10 to -40 °C); this obviates some problems hitherto found with the technique. (b) A means of calculating k_p from first principles from transition state theory is given, using accurate quantum mechanical computation of the transition state properties. These calculations give quantitative accord with experiment for ethylene, and reveal that the magnitude of the frequency factor for propagation is dominated by three hindered rotors in the transition state. Since these rotations are influenced by the penultimate unit, this suggests that significant penultimate unit effects are likely in copolymerizations. The effect of these rotations also explains the observed effect of deuteration on k_p. (2) A new technique for measuring the transfer rate coefficient (k_{tr}) is presented: initiation by pulsed laser, whence k_{tr} can be obtained from the high molecular weight slope of a plot of ln(number molecular weight distribution) against molecular weight. The method, which can be employed even when extensive termination is taking place, is tested with transfer from MMA to triethylamine. (3) The rate coefficient for termination can be successfully modelled from a knowledge of the diffusion coefficients for oligomeric species as functions of the degree of polymerization and the polymer fraction. New PFG NMR diffusion data for a series of model compounds in polystyrene/benzene give results for this dependence which are in accord with a semiempirical scaling law suggested previously [Piton MC, Gilbert RG, Chapman BE, Kuchel PW (1993) *Macromolecules* 26: 4472], suggesting that this scaling should be a useful basis for predicting termination rate coefficients.

Molecular Weight Distributions in Free-Radical Polymerizations. Understanding the Effects of chain-length-dependent Termination.

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ABSTRACT: Many properties (e.g., film formation) of a polymer depend on the full molecular weight distribution (MWD) as well as on the averages of this distribution. Moreover the MWD contains the complete kinetic history of a polymerization system and hence an experimental MWD can yield considerable mechanistic information. Complete equations are developed which enable the MWD to be calculated for a wide range of straight-chain free-radical polymerizations. These equations also give insight into the qualitative form of the MWD, thus providing a method for extracting kinetic and mechanistic information from experimental MWDs. Methods are also described

which enable numerical solutions to be obtained for the resulting non-linear integrodifferential equations. The scheme takes into account initiation, transfer, propagation and termination, allowing all of these to be dependent upon the degrees of polymerization of the chains involved. The model is applicable to bulk and solution polymerizations, and to compartmentalized systems (conventional, micro- and mini-emulsion polymerizations); in the latter case, phase-transfer events (radical entry into and exit from latex particles, and the aqueous-phase kinetics of the various radical species) are specifically included. The dependence of the termination rate coefficient upon the lengths of both participating chains is especially important in systems where termination is kinetically significant. Approximate analytical solutions are also developed for a number of cases of interest. These show that the instantaneous number MWD at high molecular weights is a single exponential—even when termination occurs to a significant extent—which is a direct consequence of the chain-length-dependence of termination rate coefficients, i.e. most termination events involve at least one very short chain. When the concentration of radicals in the system is low, the "decay constant" of the exponential part of the MWD is given by the ratio of transfer to propagation rate coefficients. In addition, the cumulative MWD frequently has the same behavior as the instantaneous MWD. This has the important implication that considerable mechanistic information can be obtained from size exclusion chromatography data by plotting ln(number MWD) against molecular weight. Such plots can reveal, for example, the termination mechanism that controls the MWD, values of transfer constants, and nucleation mechanisms in emulsion polymerization. Illustrative calculations are carried out for a number of systems. These verify the conclusions from the approximate analytic solutions, and show also that the MWD in bulk or solution polymerizations at low conversions and high initiator concentrations is sensitive to the mode of termination (combination or disproportionation).

Conditions for secondary particle formation in emulsion polymerization systems

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Abstract: A simple treatment is deduced for determining conditions for secondary particle formation in emulsion polymerization systems. A new radical formed from initiator in the aqueous phase will undergo some degree of polymerization with aqueous-phase monomer, but must have three possible eventual fates: aqueous-phase termination, entry into a pre-existing particle, or creating a new particle. There will be extensive (new) particle formation if the overall entry rate is significantly less than that of creation of new particles. The criterion for new particle formation is to find conditions where these two rates are equal; because particle formation tends to stop or start relatively abruptly, this criterion therefore defines regimes where particle formation can be avoided. This requires models for both entry and particle formation. The model for entry is that of Maxwell *et al.* [*Macromolecules*, 24, 1629 (1991)] which states that entry occurs if and only if the aqueous-phase radical has achieved a critical degree of polymerization z. Particle formation models are given for both below and above the cmc; the former is homogeneous/coagulative nucleation (largely HUFT theory) which (if coagulation is ignored) gives an upper bound for the formation of precursor particles; these are of a degree of polymerization $j_{crit} > z$; above the cmc, simple micellar entry gives an upper bound to the putative rate of particle formation. The resulting equations are readily solved, and require only a knowledge of the aqueous-phase propagation and termination rate coefficients (the latter is very high: *ca.* 10^9 dm^3 mol^{-1} s^{-1} for termination between the very small radicals, as discussed later), z and j_{crit}. Easily applied means are given for estimating all these quantities. The

treatment is found to give good accord with experimentally observed conditions for the onset of secondary nucleation

* The following publications have appeared since the previous Newsletter from various members of the SUPC (with their publication details):

Measurement of propagation rate coefficients using pulsed-laser polymerization and matrix-assisted laser desorption/ionization mass spectrometry. P.O. Danis, D.E. Karr, D.G. Westmoreland, M.C. Piton, D.I. Christie, P.A. Clay, S.H. Kable and R.G. Gilbert. Macromolecules, 26, 6684-5 (1993).

Free-radical exit in emulsion polymerization: II. Model discrimination via experiment. B.R. Morrison, B.S. Casey, I. Lacík, G.L. Leslie, D.F. Sangster, R.G. Gilbert and D.H. Napper. J. Polym. Sci. A: Polym. Chem., 32, 631-49 (1994).

Free-radical exit in emulsion polymerization: I. Theoretical model. B.S. Casey, B.R. Morrison, I.A. Maxwell, R.G. Gilbert and D.H. Napper. J. Polym. Sci. A: Polym. Chem., 32, 605-30 (1994).

Contribution to the International Polymer Colloid Group Newsletter
April 1994

from

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Work here in the Polymer and Colloid Science group at the University of Oslo is now expanding and is following several routes. The main activity is in associating polymers, where we have a very fine collection of people with different abilities, which have increased our understanding of these complex systems considerably. The main work on POE-based polymers (HEURs) was summarised at the Lyon meeting. This work is continued on more complex multi-component systems and on other polymer types, in addition to the adsorption work.

Other activities are concentrated on particle surface analysis by ESCA and other techniques, surface tension measurements by our Automatic Drop Shape Analysis instrument and around a newly installed Langmuir surface balance. All these activities are presently centred around the adsorption and stabilization of proteins at surfaces, both on polymer particle surfaces and on the air/water interface. Some result from the air/water interface have been reported earlier; more results will be presented at the Colloid Symposium at Stanford.

NMR diffusion measurements on different types of cellulose derivatives has been carried out for some time now, and several papers will be submitted shortly. An abstract of the first paper is printed below.

Interactions of Ionic Surfactants with a Nonionic Cellulose Ether in Fluid Solutions and in the Gel State Studied by Pulsed Field Gradient NMR

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Abstract: Surfactant and polymer NMR self-diffusion measurements were carried out at different temperatures on gelling and non-gelling aqueous systems of ethyl(hydroxyethyl) cellulose (EHEC) in the presence of sodium dodecyl sulfate (SDS) or with cetyltrimethylammonium bromide (CTAB). The surfactant self-diffusion experiments revealed strong surfactant-EHEC interactions. By using a two-site model it was demonstrated that the degree of surfactant binding to EHEC, at a given total surfactant concentration, is higher in the presence of CTAB than with SDS. In both cases, the level of binding is independent of temperature, even when the gel transition region is approached. The results for a more polar EHEC

sample show that in the presence of SDS (a non-gelling system in the considered temperature range) a significant increase of the binding parameter is observed at elevated temperatures, whereas no change of the parameter is found in solutions containing CTAB. In the analysis of the interaction situation, the interplay between surfactant induced associations and enhanced polymer-polymer interactions are considered. A picture emerges, where strong polymer-polymer interactions evolve at higher temperatures due to gradually deteriorated thermodynamic conditions. The polymer self-diffusion results suggest that the decay of the spin echo attenuation can initially be described by a stretched exponential ("fast" diffusion) followed by a single exponential ("slow" diffusion). The observations indicate that the interactions are stronger in the EHEC/SDS system as compared with the corresponding EHEC/CTAB system.

INTERNATIONAL POLYMER COLLOIDS GROUP NEWSLETTER

Contribution from <u>Martin V. Smalley</u>*, Physical Chemistry Laboratory, Oxford University, Oxford, England, <u>Hideki Matsuoka and Hiroshi Yoshida</u>*, Department of Polymer Chemistry, Kyoto University, Kyoto, <u>Toshiki Konishi and Norio Ise</u>, Fukui Research Laboratory, Rengo Co., Ltd. Kanazu-cho, Sakai-gun, Fukui, and <u>Kensaku Ito</u>, Department of Chemical and Biochemical Engineering, Toyama University, Toyama, Japan

Reporter: Norio Ise

I. Determination of the Size of the Localized Ordered Structure in Polyelectrolyte Solutions and Latex Dispersions

We have observed a clear upturn at small angles in the small-angle neutron scattering profile of polystyrenesulfonate in heavy water [1]. The upturn itself was not at all novel: It was reported and ascribed to the presence of impurities in the solution. This view was recently retracted, however [2]. Our interpretation of this upturn has been and is that it is due to the existence of long-range structural inhomogeneities in apparently homogeneous solutions or dispersions. By using the Guinier method, we estimated, though very approximately, the size of the ordered structure (cluster) for NaPSS-D_2O solutions. The radius of gyration, R_G, was for example 516 A at [NaPSS] = 0.02 g/ml, containing about 1000 macroions in one cluster. Further study was carried out at various salt concentrations [3]. It was found that R_G and the number of macroions in one cluster increased with increasing polymer concentration while R_G stayed practically constant with NaCl concentration from 0 to 0.5 M [3]. The experimental data were also analyzed in terms of the Debye-Bueche method. The possibility of the presence of void structures (which were observed by microscopy for latex dispersions [4]) was also considered.

Because of a large density fluctuation in latex dispersions, an ultra-small-angle X-ray scattering (USAXS) apparatus had to be used to detect the upturn. Polymethylmethacrylate-based latex (MC-8) (diameter d: 2900 A, charge density ρ_e: 1.9 $\mu C/cm^2$) was investigated at 1.3 % in water by USAXS apparatus I [5] on the 0th, 6th and 12th days after 6-week purification by ion-exchange resin [6]. In all cases, a distinct upturn was observed. Fig. 1 shows the data on the 6th and 12th days. The R_G values of the cluster computed from the Guinier plot was 2.2 μm on the 0th day, and increased to 2.6 μm on the 12th day. The cluster grew. The relative positions of the first and second peaks were found to be $3^{1/2} : 4^{1/2}$, indicating that the lattice system was fcc. The interparticle spacing in the ordered structure, $2D_{exp}$, was then found to be about 1 μm when the USAXS measurement was initiated, which was very close to the average interparticle spacing calculated from concentration, $2D_0$. $2D_{exp}$ decreased to 0.79 μm on the 9th day. This implies that what we call the two-state structure grew even in the interior part of the dispersion. From $2D_{exp}$ and R_G, one

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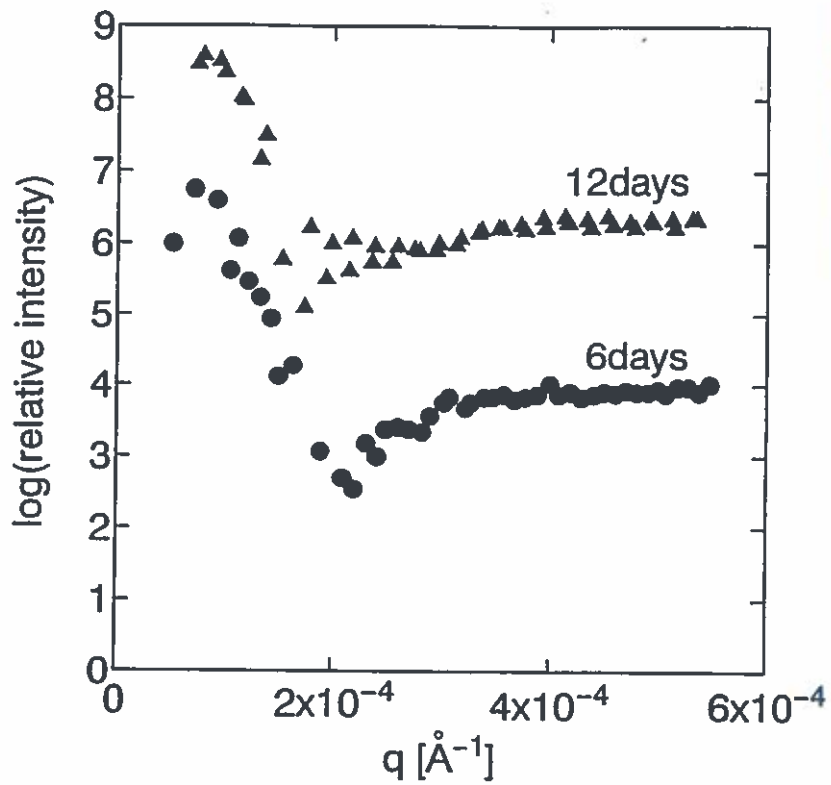
Fig. 1. The upturn of the USAXS curves of a 1.3 % water latex dispersion. Latex: MC-8 (polymethylmethacrylate-based latex, diameter, d : 2900 A, charge density, ρ_e : 1.9 $\mu C/cm^2$).
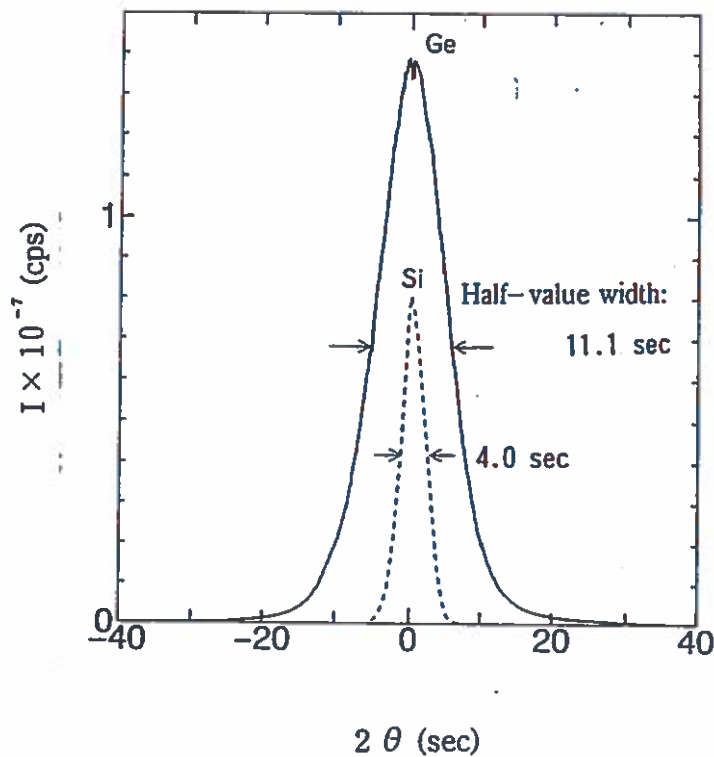
Fig. 2. Rocking curves of USAXS apparatus II with Ge and Si crystals. X-ray generator: Rigaku Rotaflex RU-300 (60 KV - 300mA). wavelength: 1.540562 A.

spherical cluster was concluded to contain on the average about 300 particles at 1.3 % on the 12th day. Further study is in progress.

II. Construction of USAXS Apparatus II and Preliminary Applications

An improved version of the USAXS apparatus was constructed in Fukui with Si and Ge crystals using Bonse-Hart principle [7]. Its rocking curve is shown in Fig. 2. At a fixed source power and with Si crystal, apparatus II has an intensity five time higher than and a small-angle resolution (half-value width : 4 seconds of arc) as good as apparatus I previously reported [5].

Apparatus II was applied for a silica particle dispersion. Its USAXS profile is demonstrated in Fig. 3. The measurement was done as follows: Silica dispersion was dialyzed against ultra-pure water for 16 days, introduced into a glass capillary of a diameter of 2 mm together with Bio-Rad ion-exchange resin particles, and kept to stand for 84 days. The radius of the particles and its standard deviation were 570 A and 8 %, respectively, which were determined by fitting observed USAXS profile under salt-containing conditions to a theoretical prediction for an isolated sphere. We note that the multiple scattering peaks were observed only at every multiple angles of 60 degrees when the capillary tube was rotated around its axis. The present observation indicates that a very large, and not highly distorted crystal is formed. As for the size, we mention that it was too large to determine by the Hosemann plot; all we can say at the moment is that it is larger than 1 μm. Further systematic study is in progress.

Fig. 3. The USAXS profile of a 3.76 % water dispersion of silica particles. Silica particles: KE-P10W of Nippon Shokubai Co., Ltd., Osaka (d: 0.10 μm, ρ_e: 9.70 μC/cm^2). USAXS apparatus II with Ge crystal.

III. Paradox of the Repulsion-Only Assumption.
Photothermal Compression of Colloidal Crystal

Colloidal phenomena have traditionally been interpreted in terms of the purely repulsive DLVO (or Yukawa) potential [8]. However, recent experimental techniq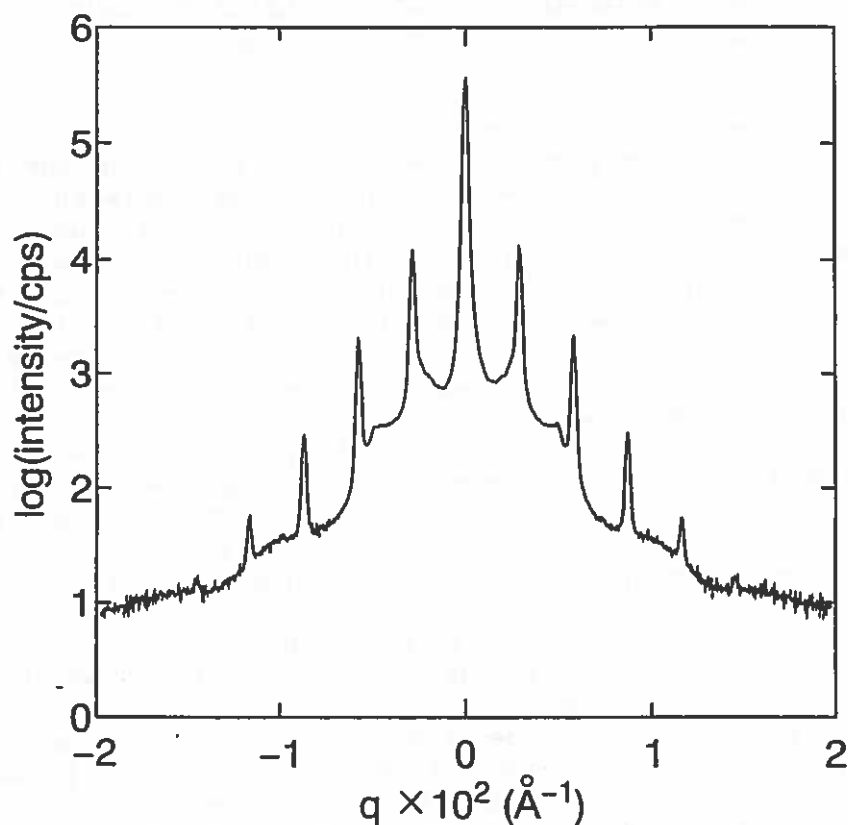ues are providing results which cannot be explained by the repulsion-only assumption without ad hoc assumption. Furthermore, recent analyses show that experimental observation of the structure factor and elastic modulus of colloidal crystals, which has been claimed to be explicable in terms of the repulsion-only assumption, can be likewise satisfactorily reproduced by the long-range attraction-repulsion assumption [9,10], namely the Sogami potential [1]. This means that the DLVO potential cannot be claimed to be the exclusively correct one.

We found that photothermal compression of colloidal crystals, which was claimed to be explicable in terms of the DLVO theory by Asher et al. [12], can be explained by the Sogami theory [13]. It is worth noting that the charge number of latex particles obtained by the so-called renormalization procedure on the basis of the DLVO theory was unrealistically large, while the charge number obtained from the Sogami theory was very close to that directly found by transference experiments [14].

The frequent claim, that the repulsion-only assumption is exclusively correct, is not warranted, since the counterinterpretation has not been disproved.

IV. Positive Adsorption of Negative Latex Particles
near Negatively Charged Glass Surface

The long-range attraction mentioned above is due to counterion-mediated attraction between particles according to our interpretation. Then a similar attraction can be expected between ionic plate and similarly charged particles, provided that there is enough space between the plate and particles for counterions. If this attraction is strong enough, adsorption of latex particles may be observed in the region near the plate. From this point of view, previous experiments were looked over again. In our previous study of crystal growth [15, 16], the radial distribution function of particles, $g(r)$, in dispersion was directly determined by measuring particle-particle distances using an image data analyzer. The number of nearest-neighbor particles, n, was then determined from $g(r)$ by using the standard method in liquid theory. The interesting point is that n increased with time (See Fig. 10 in Ref. 15). Since the micrographs were taken in the region near the glass-dispersion interface using AXIOMAT IAC, the increase in n implies that particles were accumulated to the glass surface and its vicinity. In other words, positive adsorption of negative latices took place to glass, which is believed to be negatively charged. This is inconceivable, if only repulsion is present between the glass surface and the latices: Such an adsorption is understood if there exists an attractive interaction between the glass surface and latices.

By a laser scanning microscope (LSM), a similar adsorption is seen to have occurred in a much larger range of distance from glass surface [17]. Fig. 4 shows particle distribution taken by LSM on three horizontal planes under density-matching condition. Obviously, the number of particles becomes smaller with increasing distances from glass surface from 1.2 to 25.7 μm.

This adsorption is being investigated in a more systematic way [18].

4

Though the details are to be referred to elsewhere, one point is worth mentioning here. Addition of neutral salt to dispersion hinders the positive adsorption, suggesting that the attraction is not due to hydrophobic interaction but is of electrostatic origin.

Quite independently Thomas et al. [19] studied the structure of the surface of a cationic surfactant solution above cmc by neutron specular reflection. It was disclosed that the surface consisted of the usual monolayer of surfactant, an aqueous layer containing no surfactants, and a further layer of surfactant micelles at about double the bulk concentration. Though different materials were used in this experiment and ours, a basically similar positive adsorption of ionic entities near similarly charged plane has been observed.
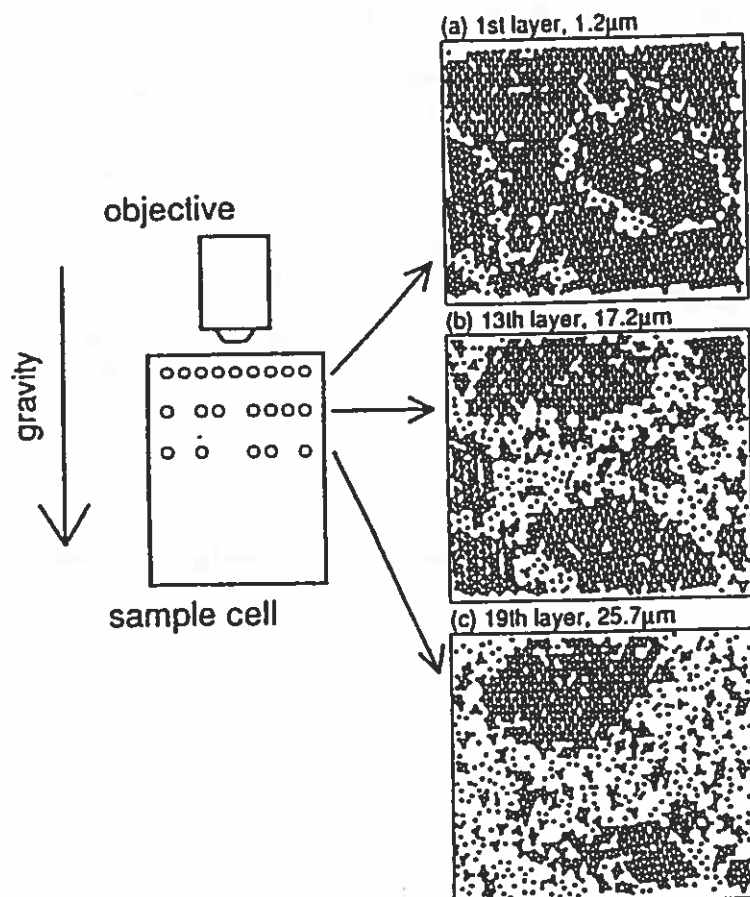
Fig. 4. Computer-assisted micrographs showing particle centers on three planes at various distances from the top of a latex D_2O - H_2O dispersion under density-matching condition. Microscope: laser scanning microscope LSM of Carl Zeiss, Oberkochen, Germany. Latex: N300 (d: 0.3 μm, ρ_e: 1.3 $\mu C/cm^2$). [latex]: 0.7 %. The photographs were taken 6 hrs after crystallization started.

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Contribution to the International Polymer Colloids Group Newsletter

Functions of Temperature-Sensitive Hydrogel Microspheres

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Our recent studies on thermosensitive hydrogel microspheres are summarized.

1. Introduction

Polymers of acrylamide derivatives and some other amphiphilic monomers have the lower critical solution temperatures (LCST) at which volume phase transition takes place[1]. Submicron particles composed of such temperature-sensitive hydrogel are expected to exhibit very sharp and quick transition or response to the change of environmental conditions. Monodisperse, temperature-sensitive hydrogel particles and core-shell particles having temperature-sensitive hydrogel shell were prepared by heterogeneous polymerizations.

They exhibit thermo-sensitive water up-take/release, hydrophilicity change, expansion/contraction, softening/hardening, increase/decrease in polarity, etc. These changes can be detected or observed by measuring particle size, electrophoretic mobility of particles, affinity with bio-compounds, permeability of shell layer, dispersion stability, etc. In this paper, such colloidal phenomena are presented, suggesting some possible applications.

2 Preparation of Particles and Particle Size

Pelton developed a new technique to prepare monodisperse, crosslinked poly-N-isopropylacrylamide (PNIPAM) particles by precipitation polymerization which was carried out at a temperature above the LCST of PNIPAM (32°C) [2].

Monodisperse core-shell particles having poly(acryloylpyrrolidine) (PAPr, LCST 50°C) shell and polystyrene (PSt) core were prepared by soap-free emulsion copolymerization of APr and St[3,4]. The same technique was applicable for the preparation of core-shell particles having poly(oligo-oxyethylene methacrylate)(OEM) shell[5]. The LCST of poly-OEM ranged from room temperature to close to boiling point. Core-shell particles with PNIPAM shell were prepared by

two-shot soap-free emulsion copolymerization in which additional NIPAM was charged in the later stage of polymerization[6]. The core-shell structure was confirmed by electron microscopy and hydrodynamic size measurement as a function of temperature. Two-dimentional ordering of particles with constant interparticle distance also proved the formation of core-shell structure, in which the interparticle distance almost coincided with twice the thickness of hydrated layer of the particles[2, 7]. Such two-dimentional ordering can be prepared only when the particles were settled at a temperature below LCST as expected.

3 Electrophoretic mobility

Electrophoretic mobility of the particles with and without PNIPAM shells was measured at different temperatures and ionic strength. The PSt core – PNIPAM shell particles had appreciable electrophoretic mobility above the LCST of PNIPAM but negligible mobility below the LCST while the particles having no PNIPAM shell had almost constant electrophoretic mobility in the temperature range examined. The remarkable temperature dependence of electrophoretic mobility of core-shell particles was attributed to the dilution/concentration of the charges or polymer chains in the PNIPAM shell.

Ohshima and Kondo proposed an equation for the electrophoretic mobility of soft particles, based on the idea that the hydrated layer of particles allows water pass through itself and the slipping plane exists inside it[8]. Their equation includes two parameters, λ and N. The parameter λ is the one proportional to the friction exerted on the liquid flow in the hydrogel layer and, therefore, $1/\lambda$ indicates the softness of hydrogel layer. N represents the density of charges possessed by the polymer in the hydrogel layer. The λ and N were determined for our particles and the results are shown in Fig. 1. As shown in it, N of core-shell particles was zero around room temperature but gradually increased with temperature. This means that the electric species in the hydrogel shell are diluted extensively at room temperature but gradually concentrated with temperature. Therefore, core-shell particles behave as nonionic particles at room temperature but as anionic one at higher temperatures. $1/\lambda$ -temperature curve supported this interpretation.

4 Dispersion stability

Concentration of hydrated shell of core-shell particles above the LCST affects two factors deciding dispersion stability, electrostatic force and steric force. The

latter governs the dispersion stability below the LCST but loses its contribution to the stability above it. The electrostatic force gives quite opposite temperature effects on the dispersion stability as expected from the facts described in the previous section. In addition, the electro-repulsive force is a function of the electrolyte concentration or ionic strength.

The stability of 10 % dispersion of PSt core – PAPr shell particles was measured at different temperatures and ionic strength. A curve was drawn in ' ionic strength vs. temperature ' matrix, indicating the boundary between stable and flucculated conditions.

Copolymers of APr and acryloylpiperidine (APp, polymer's LCST 5°C) have their characteristic LCSTs and, therefore, we could make up a series of PSt core – (APr/APp copolymer) shell particles having different stability curves by copolymerizing St with APr and APp at different monomer ratio. PSt core – poly-OEM shell particles also gave the similar stability curves whose position in the matrix depended on the length of oxyethylene chain[5].

Such thermosensitive and reversible coagulum formation was also observed in PNIPAM dispersion and Kondo et al. utilized this feature for the separation of particles from the supernatant in bioseparation[10].

5 Permeation control

PNIPAM shell of core-shell particles can be regarded as a membrane whose permeability is controlled by temperature. Mass transfer between the particle core and the surrounding medium through the shell was examined by use of the particles, in whose core ubiquinone was included, in the medium which contained ferricyanide or ascorbic acid, oxidizing or reducing reagent for ubiquinone, respectively[11]. The amount of remaining reagents in the medium was measured as a function of incubation time at different temperatures. The results are shown in Fig.2. The permeability is proportional to the product of diffusibility and solubility, both of which for PNIPAM are affected uniquely by temperature. Diffusibility is a function of viscosity or polymer concentration in hydrated layer and expected to decrease discontinuously above the LCST of PNIPAM. The solubility of solutes such as ferricyanide and ascorbic acid in hydrogel shell would change with the hydrophilicity of shell which also decreased with temperature.

The results in Fig. 2 reveals that the permeability of ferricyanide and ascorbic acid was affected by the thermal properties of PNIPAM and decreased gradually with increasing temperatute even below the LCST and was shut off above the

LCST.

6 Adsorption control

Protein adsorption on PNIPAM particles was examined extensively[6,12]. Typically hydrophobic particles, PSt particles, adsorbed a large amount of globulin regardless of temperature. On the contrary, PNIPAM particles adsorbed different amounts of globulin at 25°C and 40°C. At 40°C, above the LCST of PNIPAM, the surface of PNIPAM particle is hydrophobic, although not so hydrophobic as PSt, and adsorbed an appreciable amount of globulin while the surface at 25°C is hydrophilic and adsorbed little despite of an increase in the surface area. The change in the hydrophilicity of PNIPAM particles with temperature was confirmed by fluorescence study[13]. Proteins once adsorbed on PNIPAM particles at 40°C were desorbed more or less from the particles when the particles were cooled to 25°C. More than 60 % of myoglobin adsorbed at 40°C was desorbed at 25°C. Lysozyme and ribonuclease A were desorbed not so much on cooling. Among the proteins examined, human serum albumin exhibited the highest desorption efficiency. In general, hydrohobic and flexible proteins seem to be susceptible to desorption when cooled. It was found that the enzyme activity was retained in such adsorption/desorption process for peroxidase. Thus, PNIPAM particles seem to be a feasible material for protein collection or separation.

7 Cell activation

Interactions between PNIPAM particles and blood cells, especially granulocytes were evaluated by measuring oxygen consumption and chemiluminescence by granulocytes in contact with PNIPAM particles and observation of the granulocytes coexisting with PNIPAM particles[14]. PNIPAM particles at 37 ℃ stimulated granulocytes in dispersion. This was also the case when PNIPAM was deposited on a plate. On the contrary, PNIPAM particles at 25 ℃ little stimulated the cells. The temperature-dependent stimulation would be attributed to the change of hydrophilicity of particles above and below the LCST of PNIPAM. In the system of deposited particles at 37 ℃, surface unevenness is likely to contribute to the stimulation as well as hydrophobicity and hardness of the surface.

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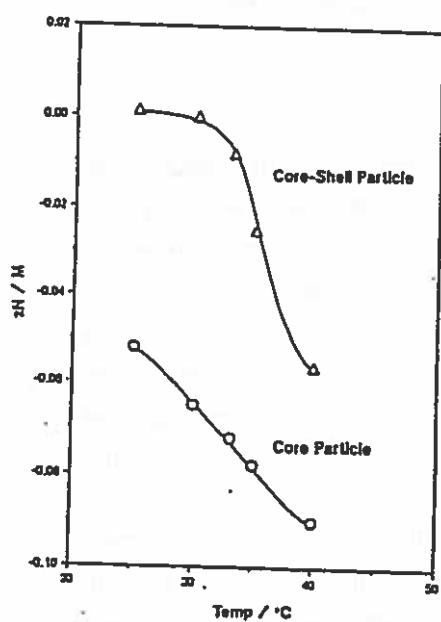
Fig. 1 N of two kinds of particles
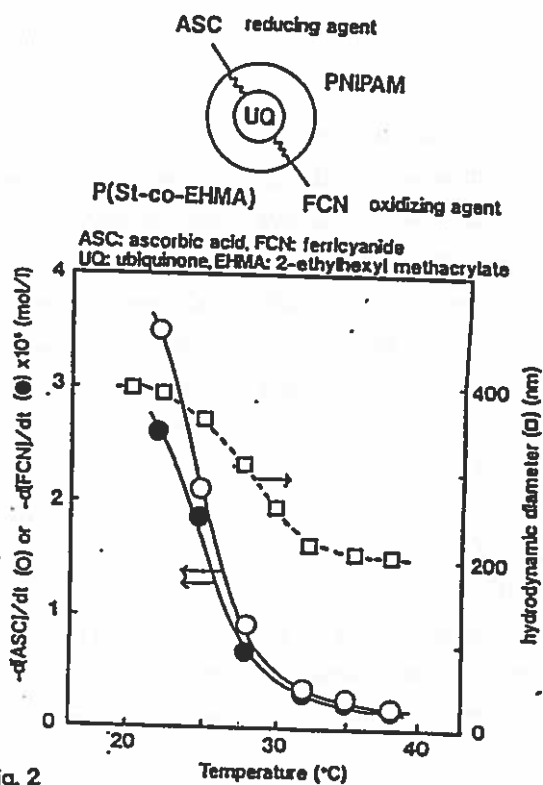
Fig. 2

PERMEABILITY OF REAGENTS IN PNIPAM LAYER

CONTRIBUTION TO
THE INTERNATIONAL POLYMER COLLOIDS GROUP NEWSLETTER

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

Reported by Jung-Hyun Kim

This letter is my first contribution to the IPCG. Our research group contains 11 graduate students. Reserch interests are following ; (1) Functional microspheres for biochemical engineering application, (2) Modeling and controlling particle morphology of composite latex, (3) Agglomeration mechanism of rubber latex, (4) Conducting polymer latex, (5) Reaction kinetics of emulsion / suspension polymerization, (6) Emuslion polymerization under high pressure. Recently we have carried out three interesting experiments. Some of the results were summarized in the following contributions.

Also I will participate in the ACS Colloid Meeting at the Stanford University this summer with "Adsorption of BSA on highly carboxylated microspheres - effects of surface charge density".

Reaction Characteristics of Resin-Fortified Emulsion Polymers

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

Alkali-soluble resins containing a polymerizable group could be copolymerized with the monomers to form the polymer particles. In this manner these reactive alkali-soluble resins are prevented from subsequent migration. Alkali-soluble resin is used as stabilizer/comonomer in the emulsion polymerization of methyl methacylate and butyl acrylate with ammonium persulfate as the water-soluble initiator. Upon initiation, the monomers polymerized in the resin solution, which results in grafting and the formation of stable emulsion without the presence of any added surfactants.

The grafting reaction of monomers onto alkali-soluble resin was observed by FT-IR analysis using serum replacement technique. With increasing alkali-soluble resin concentration, the rate of polymerization was decreased and particle size was increased. The chain transfer to alkali-soluble resin was the main factor for explaining the decreased rate of polymerization. The final particle size is smaller (ca. 80 nm) than that of conventional latex.

Preparation of Cationic Emulsion Copolymers by "Two Stage Shot Growth Technique"

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

The work present here shows the technique to produce monodisperse , highly charged cationic emulsion copolymer model colloids. Experimental results indicate that conventional batch and seed batch process was unsuccessful to incorporate high concentration of cationic comonomer with monodispersity. But "Two Stage Shot Growth Process" was successful to incorporate high concentration of cationic comonomer as much as 13 wt % based on styrene monomer without secondary particle generation. Comonomer injection stage and ratio slightly influence on final particle size distribution. Adventages of this process are that (1) high concentrations of comonomer can be polymerized without undue wastage or loss of monodispersity, (2) controlling independently the particle size and surface charge density is possible. The key factor of this process is the capture of oligoradicals before they become large enough to nucleate independently.

Analysis of Two Stage Shot-Growth Emulsion Polymerization System Using Particle Nucleation Mechanism

(E. S. Park, J. H. Kim)

Emulsion copolymerizations were unsuccessful at high concentration of the functional comonomer in that broad and sometimes bimodal size distribution, and generation of large amount of water soluble homopolymer. To overcome these problems, a two stage shot-growth technique was developed by Kim and co-workers. It was possible to control both surface charge density and particle size simultaneously.

However under certain reaction conditions, undesirable secondary particles were still formed. Influential varialbes to this phenomenon are second monomer injection time, the amount of second stage monomer and the ratio of second stage functional monomer to non-polar monomer. Emulsion copolymerization and coagulative particle nucleation theory is combined to analyse these phenomena. Calculations were made on the whole polymeriaztion period and compared with the experimental data.

It was possible to predict secondary particle generation by the reaction condition in St/Nass soap-free system and the result shows good agreement with experimental data. But it was hard to fit this model to St/Acrylic acid system containing emulsifier. It seems that particle nucleation is also influenced by the charateristics of functional monomer and the emulsifier. Secondary particles was seldom found in the latter system and study on this matter is in progress.

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Studies of Water-Borne Pressure-Sensitive Adhesives

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

Research student: Roger D. Viney

A brief report of the effects of structured particle morphologies (comprising a glassy core polymer and a rubbery shell polymer) upon the properties of acrylic, water-borne pressure-sensitive adhesives, PSA's, prepared by emulsion polymerisation is given.

The PSA's were prepared as 50% solids latexes under a swept nitrogen atmosphere at 75 °C by semi-continuous emulsion polymerisations involving three sequential stages. The first stage was common to each preparation and involved the formation of crosslinked poly(methyl methacrylate), PMMA, seed particles of 110 ± 2 nm diameter, employing 1 mol% allyl methacrylate, ALMA, as the crosslinking agent. The first growth stage involved completion of the crosslinked PMMA core and the second, formation of a shell of rubbery poly[(n-butyl acrylate)-*co*-(acrylic acid)], PBA-AA. The instantaneous conversions during the growth stages were high (>90%), showing that the reactions operated under essentially monomer-starved conditions. The values of z-average particles diameter, d_z, measured by photon correlation spectroscopy correspond closely with values predicted for sequential growth of the seed particles, indicating that the particles grew in accordance with expectation. The range of PSA's with different particle morphologies prepared by changing the relative proportions of the two growth stages are defined in Table 1.

The glass transition temperature, T_g, of each PSA material was determined by differential scanning calorimetry, DSC, and by dynamic mechanical analysis, DMA. For each of the PSA's the T_g of the PBA-AA phase was found to be -48 ± 2 °C by DSC and -25 ± 2 °C by DMA. The difference between the values of T_g from the two techniques is usual and results both from procedural differences and differences in the method of location of T_g. The values of T_g may be compared with those predicted from theory, namely: -49 °C (linear equation [1,2]) and -51 °C (Fox equation [1,3]). Thus the T_g values measured by DSC are in close agreement with the theoretical predictions. The glass transition of the crosslinked PMMA phase of the particles could only be detected by DSC, and then only for PSA's for which the volume fraction of crosslinked PMMA in the particles was ≥ 0.35. The values of T_g obtained were 121 ± 1 °C and are higher than the T_g of PMMA homopolymer (105 °C [1]) due to the crosslinks introduced by copolymerisation with ALMA. The fact that the glass transition temperatures of the two phases forming the latex particles are independent of the relative proportions of the phases shows that the phases are discrete.

Contribution to IPCG Newsletter
Peter A. Lovell, Manchester Materials Science Centre, University of Manchester & UMIST, UK

Table 1. Summary of the range of pressure-sensitive adhesives prepared

Pressure-sensitive adhesive	z-average particle diameter, d_z / nm [a]		Volume fraction of crosslinked PMMA core, V_c
	after complete growth of the crosslinked PMMA core	of the final latex	
PSA1	112	301	0.052
PSA2	161	303	0.150
PSA3	180	295	0.227
PSA4	207	292	0.356
PSA5	220	297	0.406
PSA6	237	300	0.493
PSA7	252	298	0.605

[a] Measured by photon correlation spectroscopy

The PSA latexes (adjusted to pH 5.5 with aq. NH$_3$) were coated onto 36 mm Melinex film using a No.7 K-bar and dried at 105 °C for 4 min to give dry coating weights of ~50 g m^{-2}. The coatings were used to determine peel adhesion and shear resistance as described below. Adhesive bonds were formed by applying a section of the coated Melinex to the appropriate substrate with light finger pressure and then rolling a standard 2 kg roller across the bonded area five times. All adhesive testing was performed at 23 °C and 50% relative humidity. Peel adhesion was measured after 24 h contact time as the force required to peel a 25 mm wide strip of the coated Melinex from a steel plate at an angle of 180° using a cross-head displacement rate of 200 mm min^{-1} on an Instron. Shear resistance was measured as the time taken to complete failure of an overlap bond (contact area of 20 × 20 mm^2) between the coated Melinex and a glass plate (held at an angle of 2° to the vertical) under a shear force applied by suspending a 1.5 kg weight from the Melinex after 10 min contact time.

The results from adhesive testing are presented in Figure 1 and show that increasing the volume fraction, V_c, of crosslinked PMMA in the particles has significant effects upon the adhesive properties. As V_c increases from 0 – 0.15 there is a steady decrease in both peel adhesion and shear resistance. However, in the range $0.15 < V_c < 0.22$ there is a significant decrease in peel adhesion, but no corresponding effect on shear resistance. As V_c increases further from 0.22 – 0.50 there is a steady decrease in peel adhesion and a very substantial increase in shear resistance. Finally, PSA7 with $V_c = 0.605$ has no measurable adhesive properties, most probably due to system being close to the maximum packing fraction of 0.64 for spheres dispersed in a continuous matrix, leaving insufficient rubbery polymer to form a bond.

Contribution to IPCG Newsletter
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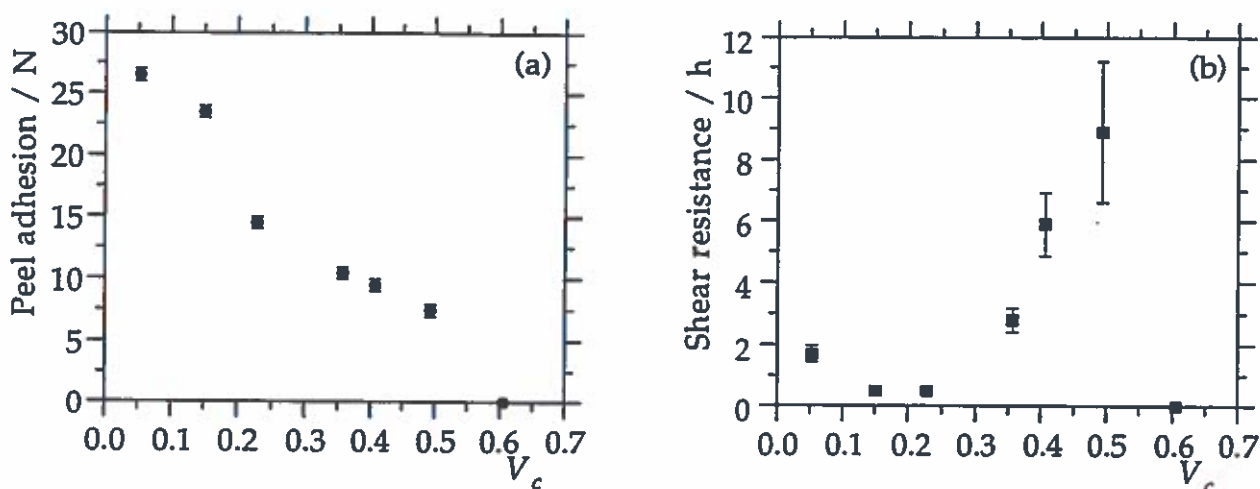
Figure 1. The effects of the volume fraction, V_c, of crosslinked PMMA in the particles upon adhesive properties: (a) peel adhesion and (b) shear resistance. Where error bars are not shown, the size of the data points represent the magnitude of the errors in the respective measurements. The data for $V_c = 0$ are for a latex prepared as described for PSA's 1–7 except that poly(n-butyl acrylate) was formed in the seed stage.

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Publications related to Polymer Colloids (October 1993 - April 1994)

1. "Rubber-toughened Acrylic Polymers", A.C. Archer, Z.J. Lee, P.A. Lovell, J. McDonald, B. Rochanapon, A.J. Ryan, M.N. Sherratt, R.J. Young, Z.A.M. Yusof, *Polym. Mat. Sci. Eng.*, 70, 153, 155, 157 (1994)

2. "Deformation Micromechanics and Mechanical Properties of Rubber-toughened Acrylic Polymers", A.C. Archer, P.A. Lovell, J. McDonald, A.J. Ryan, M.N. Sherratt and R.J. Young, *Proc. 9th Conf. Deformation, Yield & Fracture of Polymers*, papers 3 & 104, Institute of Materials, London, 1994

CONTRIBUTION TO THE INTERNATIONAL POLYMER COLLOIDS GROUP NEWSLETTER

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Martien Cohen Stuart and Hans Lyklema

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I. KINETICS OF LATEX COAGULATION IN TURBULENT FLOW

The kinetics of rapid coagulation of polystyrene latex particles was studied under conditions of turbulent flow in order to verify the theoretical predictions for this process. Turbulent flow was generated in a controlled fashion by simply tumbling the samples in small cylindrical containers. In this way, the effective shear is probably not distributed very homogeneously but this does not seem to affect the results very much. The samples were analysed both in terms of total particle number concentration and in terms of cluster size distributions by means of a Single Particle Opticle Sizer (SPOS) and the data were compared to predictions based on the theory of Saffman and Turner. It was found that the *initial* orthokinetic collision rate, i.e. the initial rate corrected for the rate of Brownian collisions, followed not only the predicted proportionality to the initial particle concentration but also, and very precisely, the $r^{2.46}$ dependence on the latex particle radius r that was predicted by Van de Ven and Mason for collisions slowed down by hydrodynamic interaction.

These results imply that hydrodynamic interaction plays an important role in reducing the capture efficiency of colliding particles, and also that it is possible to have good control over the collision rate, despite the simplicitry of the experimental technique. This is result was exploited in the study on polymer bridging effects in flocculation reported below.

II. DYNAMIC ASPECTS OF BRIDGING FLOCCULATION

When colloidal particles floculate under the action of a polymer that forms bridges, the rate and efficiency of flocculation may well depend on the configuration of the adsorbed polymer. This configuration, however, is itself changing over time, so that the outcome is not easily to predict. We have conducted a kinetic study of bridging floculation under conditions of high salt concentration (rapid coagulation) and in such

a way as to control the hydrodynamic conditions, which were those of turbulent flow (see above). By comparing the data with those of the equivalent polymer-free experiment it is possible to extract the effect of the adsorbing polymer on the flocculation kinetics.

It was found that adsorbing homopolymer was able to substantially enhance the initial flocculation rate. In some cases the enhancement factor could be as large as 60 or more. After a short period, however, the flocculation stopped abruptly. By varying the concentration of the polymer and subsequent analysis of the data we ascertained that the flocculation stops as soon as the particles become saturated with polymer so that a steric repulsion builds up.

Our data show that the enhancement effect on the initial rate is entirely due to the increase of the effective collision radius of the particles when polymer gets attached. We infer from this the effective thickness of the layer of attached polymer and find that it corresponds well to the radius of free polymer coils in solution. When the polymer concentration is lowered, the flocculation rate returns gradually to its value for the bare particles, which suggests that the thickness of the adsorbed layers also decreases. As the polymer flux towards the particle surface also drops when the concentration is lowered this seems to imply that the reduction in thickness is due to the fact that the polymer has more time to unfold.

With poly(ethylene oxide) (PEO) as the flocculant, enhancement factors are sometimes exceptionally large. Further work revealed that the initial flocculation rate with PEO also depends upon whether or not the PEO solution has been filtered prior to the flocculation experiment. Recent reports in the literature describe the occurence of large, reversible clusters that form in PEO solutions. The size of these cluster is about 100 nm, which corresponds well to the enhancement factors that we find with unfiltered PEO solutions. It seems likely that bridging by PEO is mainly caused by adsorbing aggregates.

CONTRIBUTION FROM THE POLYMER COLLOIDS GROUP
UNIVERSITY OF SYDNEY

REPORTER: DH NAPPER

Experimental Observation of Coil-to-Globule Type Transitions at Interfaces

PENG WEI ZHU AND DONALD H. NAPPER[1]

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Coil-to-globule type transitions have been measured by dynamic light scattering for poly(N-isopropylacrylamide) chains attached to the surfaces of polystyrene latex particles dispersed in water. Both sterically and electrosterically stabilized latices were studied. The transitions were induced merely by changing the temperature. That observed on heating the electrosterically stabilized system appeared to conform with theoretical predictions in that the transition was continuous and spanned a broad (20°C) temperature range compared with that for free chains (1–2°C); furthermore, most of the reduction in chain dimensions occurred under worse than θ-solvency conditions under which the latices remained stable due to residual electrostatic stabilization. In sharp contrast, the latices that were solely sterically stabilized appeared to display a coil-to-globule type transition under solvency conditions that were better than a θ-solvent. The apparently paradoxical results that involved the simultaneous observation of steric stabilization and a coil-to-globule transition have been interpreted in terms of the theory of n-cluster formation proposed by de Gennes and co-workers. The addition of the anionic surfactant sodium dodecyl sulfate at concentrations below its CMC had little effect on the coil-to-globule type transitions, whereas the addition of the cationic surfactant dodecyl trimethyl ammonium bromide below its CMC had a profound effect. For the sterically stabilized latex, the cationic surfactant eliminated the occurrence of the transition; for the electrosterically stabilized latex, its presence seemingly converted the latex into a purely sterically stabilized one so that the coil-to-globule type transition now took place under better than θ-solvency conditions and flocculation occurred upon passage into the worse than θ-solvent domain. These effects can again be rationalized on the basis of the promotion or inhibition of n-cluster formation. © 1994 Academic Press, Inc.

INTRODUCTION

Coil-to-globule transitions of individual linear polymers have attracted considerable attention, both experimental (1–8) and theoretical (9–11), in recent times. In their random coil form, macromolecules adopt somewhat expanded average conformations that maximize their entropy but occupy only a small percentage of the spatial domains that they invade. By way of contrast, chains in their globular form are

essentially space filling as a result of the minimization of their enthalpy. Globules thus occupy only a small percentage of their corresponding random coil volume (12). The concept of globular conformations was first proposed in 1929 in a different context by Langmuir (13) for hydrocarbon chain molecules *in vacuo*, an idea that was subsequently extended by Stockmeyer to encompass polymer molecules (14). Ptitsyn *et al.* (15) argued on theoretical grounds that the coil-to-globule transformation of individual polymer chains in free solution should be a first-order transition (i.e., the first derivatives of the Gibbs free energy with respect to either temperature or pressure should be discontinuous). Collapse would thus be accompanied by a jumpwise change in the polymer dimensions. On the other hand, des Cloizeaux and Jannink (16) have recently summarized the now widely held viewpoint that the coil-to-globule transition cannot be first-order for flexible polymers; they pointed out that the connectivity of the polymer chains imparts a large, if finite, number of degrees of freedom (proportional to the number of backbone bonds) to the polymer so that their conformational statistics must necessarily change in a continuous manner. Such continuity is a characteristic of a second-order rather than a first-order transition. At most, collapse, without ever being discontinuous, could approach a first-order transition and appear to be quite abrupt if the flexible chains are of sufficiently high molecular weight (17, 18). There now exist experimental data for polystyrene that support this consensus viewpoint of continuity (17).

For polymer chains end grafted onto interfaces, the nature of the analogous coil-to-globule transition is expected theoretically to depend upon a number of factors, including the chain grafting density and the curvature of the interface. However, if it can be generally stated that where there are interchain interactions in a layer, they render the collapse transition weaker than for an isolated chain. If the grafting density is sufficiently high, lateral repulsions should cause the conformations of the chains to be significantly extended normal to the surface so that the chains constitute polymer brushes (19, 20). For brushes on spherical or cylindrical surfaces, the transition is expected to retain its second-order character, although it is broadened relative to that of an isolated polymer (21, 22). According to Zhulina *et al.* (21), the possibility of a jumpwise change is extinguished. For

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ENTANGLEMENT KNOTTING IN GLOBULE-TO-COIL TRANSITIONS OF POLY (N-ISOPROPYACRYLAMIDE) AT INTERFACES

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ABSTRACT

An unexpected size hysteresis effect was observed in the globule–to–coil transition of poly (N–isopropylacrylamide) attached to surfaces of latex particles. The magnitude of the effect was found to be critically dependent upon the period for which the polymer was incubated in the globular form and the temperature of incubation. Hysteresis was attributed to the physical formation of knots when the globular chains were rapidly swollen during their transformation into coils. These knots were associated with topological entanglements that were formed in the globular state and which had insufficient time to disentangle in the rapid globule–to–coil transition. A simple theory was developed that permitted the rate coefficients for the formation of entanglements that led to knotting to be evaluated, along with the activation energy for the process.

Studies of aggregation kinetics of polystyrene lattices sterically stabilized by poly(N-isopropylacrylamide)

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The aggregation of polystyrene lattices sterically stabilized by poly(N-isopropylacrylamide) has been studied using dynamic light scattering. The time dependence of the aggregate growth could be monitored under appropriate experimental conditions. The measured fractal dimension was found to increase with an increase in the aggregation rate and the salt concentration, as well as the temperature. These unexpected observations do not conform to the predictions of the current models for aggregation of electrostatically stabilized particles. It was also inferred that the restructuring process was different from that reported in the literature. The hydrophobic interaction (or hydration), which is controlled by the salt concentration and temperature, is believed to play a crucial role in the present system in the aggregation process and in the nature of the aggregate structures formed. The results indicate that the fractal dimension increases with an increase in the hydrophobic interaction, i.e., with a decrease in the interparticle interaction energy. This is in good agreement with the predictions of the computer simulations of Shih, Aksay, and Kikuchi [Phys. Rev. A **36**, 5015 (1987)].

PACS number(s): 81.10.Dn

Contribution to the IPCG Newsletter   April, 1994

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Main activity of our group is on (1)colloidal crystals(morphology, crystal growth, etc.), and (2)deionized polyelectrolyte solution. Following papers will be presented at the 43rd annual meeting of the Society of Polymer Science, Japan held in Nagoya, end of May, 1994.

(1)**Dynamic Light Scattering of Colloidal Crystals. I.**, by T.Okubo, K.Kiriyama, H.Yamaoka and N.Nemoto.

(2)**Growth of Colloidal Single Crystals under Pseudo Microgravity. I. Direct Observation in an Direct-Current Electric Field,**   by T.Okubo and N.Nemoto.

(3)**Colloidal Single Crystals of Cationic Spheres,**   by T.Okubo, H.Fujita, K.Kiriyama and H.Yamaoka.

(4)**Close-up Observation of Giant Colloidal Single Crystals in a Plane Cell,** by T.Okubo

(5)**Colloidal Crystals as Studied by a Diffusion Equilibrium Technique,** by T.Okubo

(6)**Two-dimensional Colloidal Crystals. I. Surface Tension Measurements,** by T.Okubo

Publications(1993-)

(1)**"Large Single Crystals of Colloidal Silica Spheres Appearing in Deionized and Diluted Suspension"**, T.Okubo, *Colloid & Polymer Sci.*, **271**, 190-196 (1993).

======*Giant colloidal single crystals are excitingly beautiful!!!*======

Close-up color photographs are taken for crystallites(single crystals surrounded by the grain boundaries) in the colloidal suspensions of monodisperse silica spheres(diameter; 110 nm + 4.5 nm) Very large crystallites(3 to 4 mm) are observed with the naked eye(for the first time) for the completely deionized and diluted suspensions. Deionization is carefully made with the mixed beds of ion-exchange resins more than 2 weeks old. Size of the crystallites increases sharply as the concentration of spheres decreases, and becomes small at the concentrations slightly higher than the critical concentration of melting toward liquid-like structure. Shape of the crystallites, i.e., mixture of triangle, cubic, pentagonal, hexagonal, cone-like,etc., is recognized in the photographs.

(2)"Polymer Colloidal Crystals", T.Okubo, *Prog.Polymer Sci.*,18,481-517(1993).
======*So fantastic characters of colloidal crystals are caused by the electro-static interparticle repulsion and expanded electrical double layers!!!======*

Reviews on the colloidal crystals including, (a)introduction, (b)preparation, purification and characterization of colloidal dispersions, (c)Structure of colloidal crystals, (d)morphology of colloidal single crystals and crystal growth, (e)phase equilibria and interparticle interaction, (f)influence of an external field on colloidal crystals, (g)dynamic properties of structured particles, (h)elastic properties of colloidal crystals, (i)viscometric properties of colloidal crystals, (j)miscellaneous, and (k)concluding remarks.

(3)"Elasticity of the Crystal-like, Amorphous Solid-like, and Liquid-like Structures in Deionized Suspensions of Colloidal Silica Spheres", T.Okubo, *Colloid Polymer Sci.*,271,873-883(1993).

======*Rigidity of colloidal suspension is determined mainly by the number density of sphere per unit suspension volume and also by the sphere distribution. Intersphere interaction is negligible!!!======*

Elastic moduli(G) of deionized suspensions of colloidal silica spheres(diameter=45-192 nm; standard deviations of sphere size divided by thye mean diameter=0.05-0.21; surface charge densities=0.33-0.94 $\mu C/cm^2$; volume fraction of sphere(ϕ)=0.019 - 0.21) have been determined by the reflection spectrum measurements in a sedimentation equilibrium and the rotatory viscometry. The G-values are 56-460 Pa (ϕ=0.019-0.051), 330-890 Pa (0.06-0.09), and 100 Pa(0.025) for the crystal-like, amorphous solid-like, and liquid-like structures, respectively. The G-values seem to be in the order amorphous solid-like > crystal-like > liquid-like at the same sphere concentration. The suspension structures and their elastic moduli are highly influenced by the sizes and their monodispersities of the spheres. These results support that the electrostatic intersphere repulsion and the long Debye-screening length around the spheres are important for the appearance of the suspension structures.

(4)"Another Look at the Melting Temperature of Colloidal Crystals in the Completely Deionized Suspension", T.Okubo, *Colloid Polymer Sci.*,271, in press.

======*Colloidal crystals melt away to the "liquid" structure when suspension temperature is raised, since colloidal crystals are really crystals!!!======*

Melting temperature(T_m) of colloidal crystals of monodispersed polystyrene and silica spheres has been measured for the completely deionized suspensions as a function of sphere concentration. More than 3 weeks are needed before achievement of the completelydeionized state. T_m increases substantially are the deionization process of the suspension proceeds. The most reliable values of T_m observed for the completely deionized suspension are successfully analyzed again with the theory of Williams et al. The new T_m values are compared also with the theory of Robbins et al., which treats the repulsive Yukawa potential between colloidal spheres.

(5)"Phase Diagram of Ionic Colloidal Crystals", T.Okubo, ACS Symposium Ser.548, "Macro-ion Characterization. From Dilute Solutions to Complex Fluids"K.S.Schmitz(ed), 364-380,ACS, Washington,DC(1994).

======*Reviews on the melting and/or crystallization of giant colloidal single crystals!!!   Interparticle repulsion is exclusively important!!!======*

Very large single crystals(3 to 8 mm) are observed with the naked eye in the highly deionized colloidal suspensions of monodisperse polystyrene and silica spheres. Deionization is carefully made with the mixed beds of ion-exchange resins more than three weeks. Two kinds of single crystals,i.e., block-like crystals from homogeneous nucleation in the bulk phase far from the cell wall and the pillar like ones from the heterogeneous nucleation along the cell wall are observed. Size of the single crystals increases sharply as the concentration of spheres decreases, and is largest at the concentration slightly higher than the critical concentration of melting(ϕ_c). ϕ_c and the melting temperature(T_m) have been measured again for the completely deionized suspensions. New fc values are very small compared with the previous data, whereas T_m values are high. Important role of the long Debye-screening length around spheres and the intersphere repulsion is strongly supported.

(6)"Sedimentation Velocity of Colloidal Spheres in Deionized Suspension", T.Okubo, *J.Phys.Chem.*,98,1472-1474(1994).

======*Electrical double layers play an important role on the suspension properties of colloidal particles including sedimentation!!!* ======

Sedimentation velocities(S) of silica spheres(diameter 311 and 507 nm) and heavy polystyrene spheres(diameter 937 nm) are measured in the completely deionized suspensions and in the presence of sodium chloride. S decreases slightly and then starts to increase as the ionic concentration of the suspension decreases. The first decrease is explained with the retarded Brownian movement of colloidal spheres coated with the electrical double layers. Increase of S in the completely deionized suspension is much more significant for the small spheres. One of the most plausible reasons for the increase is the strengthened gravitational forces on the colloidal particles coated with the expanded double layers. The other factor will be the reduced surface charges on the colloidal spheres in the deionized suspension. The experimental results show clearly that the expanded electrical double layers play an important role on the translational self-diffusion of colloidal spheres especially in the exhaustively deionized suspension.

(7)"Giant Colloidal Single Crystals of Polystyrene and Silica Spheres in Deionized Suspension", T.Okubo, *Langmuir*, in press.

======*Giant crystals appear only in a very diluted suspension, 0.0002 in volume fraction, where number of nuclei comes very few!!!*======

Shape and size of colloidal single crystals of polystyrene and silica spheres ranging 81 and 212 nm in diameter(d) are studied mainly with the close-up color photographs in the diluted and exhaustively deionized suspensions with ion-exchange resins. Two kinds of single crystals, (1)block-like crystals grown up from the homogeneous nucleation mechanism in the bulk phase far from the cell wall and (2)pillar-like ones from the heterogeneous nucleation along the cell wall are observed clearly. Size of the colloidal single crystals is very large(3 to 8 mm) at the sphere concentration slightly higher than the critical concentration of melting(ϕ_c). ϕ_c-values are around 0.0002 in volume fraction irrespective of sphere diameter ranging 90 and 210 nm, and much high for the spheres smaller than 90 nm,e.g., 0.0036 and 0.0014 for colloidal silica(CS-61, d=81 nm) and polystyrene spheres(D1C25, 85 nm), respectively. Crystal size decreases very sharply as sphere concentration increases, since number of nuclei increases substantially with sphere concentration.

SMALL ANGLE NEUTRON SCATTERING STUDIES ON ASSOCIATION POLYMERS

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INTRODUCTION

The polymers examined had the basic structure,

RO-[DI - PEG]y - DI - OR

with DI = phenyl di-isocyanate, PEG = polyethylene glycol (Carbowax 8000) with a nominal molecular weight of 8200. For the material without hydrophobes R = H giving hydrophilic end groups. In the case of the hydrophobed samples R = $C_{16}D_{33}$-, giving a so-called "association polymer". The value of y was ca.6 giving an estimated molecular weight for the samples of 50,200. Samples of both types have been examined by small angle neutron scattering.

Aqueous solutions of association polymers at relatively low concentrations, e.g. 2% w/v, form rigid gels under static conditions and exhibit complex rheological behaviour under shear (1,2).

EXPERIMENTAL

The polymer samples were kindly donated by Dr. D.R. Bassett and Dr. R. Jenkins of Union Carbide, Charleston, W.Virginia. These materials were stored under nitrogen at 4°C and the solutions were prepared in water which had been purged with nitrogen; solutions were stored with a nitrogen head space.

The small angle neutron scattering experiments were carried out at the Center for High Resolution Neutron Scattering at NIST, Gaithersburg, Maryland, using the 30m SANS instrument. Samples were examined at a temperature of 25°C, with a sample to detector distance of 15m and an incident wavelength of 12 Å. Standard computer programs were used to process the basic data in order to give the intensity of scattering, I(Q), in absolute units as a function of the scattering vector Q. The latter quantity can be defined for isotopic scatterers as, $Q = 4\pi \sin(\theta/2)/\lambda$ with θ = the scattering angle and λ = the wavelength of the incident beam.

RESULTS

Figure 1 shows the spectrum obtained on a 2.36% w/v solution of the unhydrophobed material in D_2O in the form of I(Q) against Q. For monodisperse Gaussian coils the form factor, P(Q), was given by Debye (3) as $P(Q) = 2(w-1 + \exp(-w))/w^2$ with $w = Q^2 R_g^2$ and R_g = the radius of gyration of the coil. The experimental data were found to give a good fit to the model of a Gaussian coil and this is also illustrated in Figure 1 by the continuous line. For the concentration of 2.36% w/v an R_g of 49 Å was obtained; the value actually increased with decreasing concentration (4). Extrapolation of the I(Q) data to Q = 0 for a number of concentrtions enabled a molecular weight determination of the unhydrophobed polymer to be obtained. A value of 33,000 was obtained which was somewhat lower than anticipated from the structural formula.

Figure 2 shows the results obtained on the sample with deuterated hydrophobes, i.e. with R = $C_{16}D_{33}$. The general form of the curve which is plotted as Ln[I(Q)] against Ln(Q). shows significantly different features from the results obtained on the unhydrophobed material. The overall level of scattered intensity is higher and a small maximum in intensity is apparent at Q = 0.016 $Å^{-1}$. This was interpreted as indicating a weak correlation between scattering centres separated by a distance of ca.400 Å.

The experimental results shown in Figure 3, also in the form Ln[I(Q)] against Ln(Q), were obtained by carrying out the experiments using the same material as that for the experimental results shown in Figure 2

but dissolved in a mixture of 16% D_2O and 84% H_2O. This mixture provided a medium with the same coherent scattering length density as that of the polyethylene glycol units in the polymer. Under these conditions therefore the observed scattering provides information as to the spatial distribution of the deuterated hydrophobes. The curved section at the highest Q values was interpreted as scattering emanating from small spherical units with a radius of 12 ± 3 Å; this corresponded to an apparent molecular weight of $4,400 \pm 1000$. A plausible explanation of this result is that association of some of the hydrophobic chains has occurred into small hydrophobic units, giving on average an association number of 16 ± 4.

At a Q value of ca.0.02 Å^{-1} the slope of the curve suddenly changes and an increase in intensity occurs suggesting the presence of a larger scale structure composed of the smaller units, which are weakly correlated at a distance of the order of 400 Å.

DISCUSSION

The neutron scattering data obtained provide clear evidence of the formation of associated units of the hydrophobes with end capped polyethylene glycol polymeric molecules. The material without end caps appear to form Gaussian coils in solution. It is suggested that in solutions of the end-capped materials some of these will expand to form links between the associated units whilst others may coil in such a way as to re-enter the associated unit. This arrangement which will be described in more detail in a subsequent publication (4) is in agreement with some of the suggestions of Winnik and co-workers (5).

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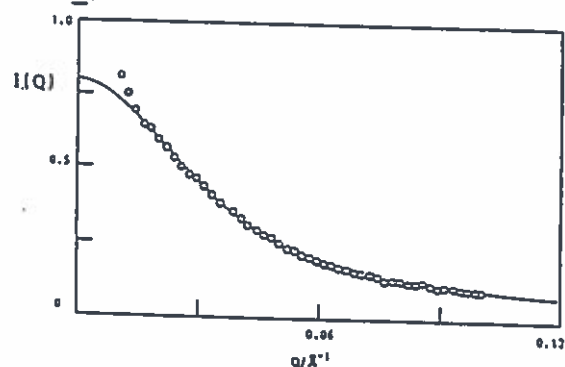
Figure 1: I(Q) against Q for an association polymer with hydroxyl end groups. Concentration = 2.36% w/v in D_2O.
O , experimental points
—— , computed curve for a monodisperse Gaussian coil, Rg = 49 Å.

Figure 2: Ln[I(Q)] against Ln[Q] for an association polymer with $C_{16}D_{33}$-hydrophobic end groups at a concentration of 2.0% w/v in D_2O.
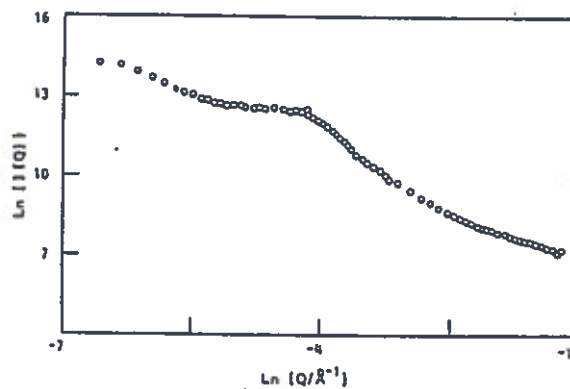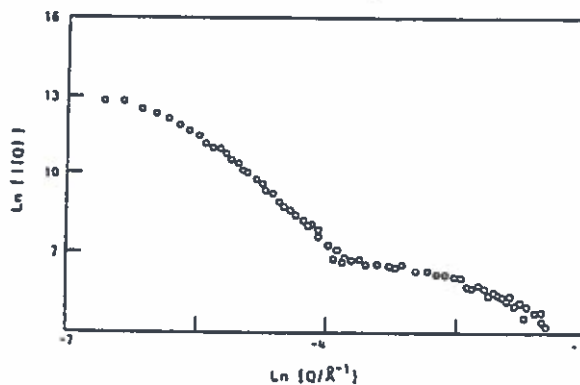

Figure 3: Ln[I(Q)] against Ln[Q] for an association polymer with $C_{16}D_{33}$-hydrophobic end groups at a concentration of 2.0% w/v in 16% D_2O.

POLYMER COLLOIDS NEWSLETTER CONTRIBUTION
from The University of Akron
Submitted by Irja Piirma

Emulsion Copolymerization of n-Butyl Acrylate and
Methacrylonitrile.
Reported by Carlos Pinzon

The study of the colloidal stability during and after
copolymerization of n-butyl acrylate and methacrylonitrile
gave some unusual results. While the homopolymerization of
butyl acrylate could be stabilized with 0.4% (per weight of
monomer) sodium dodecyl sulfate, the addition of the
comonomer, methacrylonitrile completely destabilized the
system. The amount of anionic surfactant had to be increased
beyond 2% to achieve stability. This was not the case when a
nonionic surfactant, Emulphogene BC-840 was employed. The
stability was unaffected by the presence of nitrile groups in
the polymer chain, although the concentration needed was
high, i.e. at least 8% (wt of monomer) in homo- and
copolymerizations. The particle size and number development
with conversion for copolymerizations (72.4% BuA and
27.6%MAN) is shown in the table below for:

	SDS Particle		BD-840 Particle	
% Conv.	Size(nm)	Number(10-14)	Size(nm)	Number(10-14)
13	52	7.4	–	–
14	–	–	80	2.3
24	55	12	119	1.2
30	62	11	130	1.1
39	–	–	141	1.1
42	62	15	–	–
52	–	–	151	1.2
57	67	16	–	–
61	–	–	161	1.2
72	71	16	–	–
82	–	–	166	
90	76	17		

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IPCG NEWSLETTER CONTRIBUTION

We have a new idea, the electrodynamic potential, which is described below in an ABSTRACT for the ACS/Washington Symposium on the Double Layer (8/21-25/94).

In earlier work on hydrodynamic and electrophoretic fingerprinting we have shown that particle size and electrophoretic mobility should be examined as a function of pH and pλ.

In the present work we combine the hydrodynamic and electrophoretic theories by defining the electrodynamic potential, g. Measuring g as a function of pH and pλ should be a powerful probe for characterization of colloids.

R.L. Rowell

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

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

POLYSTYRENE-POLY(ETHYLENE OXIDE) BLOCK COPOLYMER MICELLES IN WATER.
RELATION BETWEEN MICELLAR SIZE AND MOLECULAR CHARACTERISTICS OF THE COPOLYMER.

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Introduction

Block and graft copolymers containing hydrophilic and hydrophobic parts are investigated in numerous studies on their solid state, solution and surface properties[1,2].

According to the incompatibility of the different sequences, such copolymers are able to generate self assembling micelles in a selective solvent for one block. For example, these micelles may take up and release organic materials from water solutions so that they can find application in many fields such as latex preparation, pharmacology, ecology.

Among many known block copolymers, the polystyrene-poly(ethylene oxide) block copolymers (PS-PEO) are of great interest. Due to the presence in the same molecule of hydrophilic (PEO) and hydrophobic (PS) blocks, these copolymers form micelles in a wide variety of solvents e.g. in cyclopentane[3] or in water[4].

A part of our research is to study the PS-PEO / water system. Recently, we tried to determine experimentally the relation between the hydrodynamic radius of the micelles and the size of PS and PEO blocks in water solutions. Different theories of block copolymer micelle formation[5-7] were considered to find this relation. The whole work on this topic will be published elsewhere and we only describe in this paper the correlation between our results and the theory of Nagarajan and Ganesh.

Experimental part

Block copolymers

PS-PEO diblock copolymers were synthesized by sequential anionic polymerization in tetrahydrofuran under nitrogen at -78°C using cumylpotassium as initiator. Gel permeation chromatography and NMR were used to characterize the copolymers. The detailed procedures of the preparation and the characterization of the diblock copolymers were described elsewhere[8]. Molecular characteristics of PS-PEO block copolymers are listed in Table 1.

Micellar solutions

The concentration of the micellar solutions is 0.3 g / 100 ml. These solutions were prepared by dissolving the copolymer in tetrahydrofuran (THF), adding methanol (MeOH) then water so that the final composition of the medium is THF / MeOH / H_2O 50:25:25 volume %. This mixture is then dialyzed with water. Justifications of this procedure is given in reference 8.

Micellar size measurements

The micellar size was measured by the quasielastic light scattering using a Coultronics N4 apparatus. Each size value of Table 1 is an average of ten reproducible runs at least.

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Results and discussion

Table 1 : Molecular characteristics of the diblock copolymers
and hydrodynamic radius of the micelle obtained by dialysis procedure

COPOLYMER	$M_{n\,PS}$	$M_{n\,PEO}$	% PS (wt)	R_H (nm)
H19	50600	44000	53.5	34.3
H17	42500	15300	73.5	32.45
28	31300	51200	38.0	23.15
29	31300	80100	28.1	27.65
34	15800	24500	39.2	20.4
36	15800	58000	21.4	22.8
35	15800	261400	5.7	41.6
30	14200	29400	32.5	20.6
31	14200	53700	20.9	24.3
18	13400	22100	37.7	20.2
H13	4600	3000	60.6	13.8
37	4200	10100	29.3	11.8
38	4200	19000	18.1	14.6
39	4200	30800	12.0	19.3
HH1	4000	3950	50.0	9.2
HH2	4000	6500	38.0	11.45
HH3	4000	11000	27.0	14.55
HH4	4000	19600	17.0	16.6
HH5	4000	30800	11.0	17.9
41	3700	19800	15.6	16.2
RS1465[b]	1015	1015	50.0	7.4

Table 1 shows that the hydrodynamic radius is very dependent on the molecular characteristics of the block copolymer. Especially for the HHI series of copolymers which have exactly the same PS block (due to the polymerization procedure), an increase of the PEO content leads to an increase of the micellar size.

To correlate these values, we have used the Nagarajan-Ganesh theory[7]. For these authors, the R_H value can be related to the number of repeating units (N) in each block of the copolymer by the expression :

$$R_H = K_1\, N_A^{\alpha_1}\, N_B^{\beta_1} + K_2\, N_A^{\alpha_2}\, N_B^{\beta_2} \qquad (1)$$

A and B index correspond to soluble A and insoluble B blocks of the diblock copolymer. K_i, α_i, β_i are constants depending on the copolymer / solvent interaction parameters.

The first product of expression (1) corresponds to the radius of the core of the micelle, the second one to the thickness of the micellar shell.

There are, however two restrictions to this relation :

$$0.1 \leq N_A / N_B \leq 10$$

$$\text{and } 50 \leq (N_A + N_B) \leq 2500$$

At present, the PS and PEO / water interaction parameters are unknown. For this reason we have selected the PPO-PEO block copolymer / water system described by Nagarajan and Ganesh (PPO : poly(propylene oxide)) and assumed that α_1 and α_2 coefficients for PEO in a PS-PEO block copolymer are the same as those given by these authors for PEO in a PS-PPO block copolymer.

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Thus Nagarajan and Ganesh expression becomes for our system :

$$R_H = K_1 \, N_{PEO}^{-0.17} \, N_{PS}^{\alpha} + K_2 \, N_{PEO}^{0.74} \, N_{PS}^{\beta} \qquad (2)$$

With respect to the above restrictions, we have selected two series of copolymers with a constant PS content and plotted $R_H / N_{PEO}^{-0.17}$ versus $N_{PEO}^{0.91}$.

Indeed, if N_{PS} is constant for a given copolymers series, the expression (2) becomes :

$$R_H / N_{PEO}^{-0.17} = K_3 + K_4 \, N_{PEO}^{0.91} \qquad (3)$$

where $K_3 = K_1 \, N_{PS}^{\alpha}$ and $K_4 = K_2 \, N_{PS}^{\beta}$ are constants in this case.

Using a linear regression for this plotting, we have calculated K_3 and K_4 as shown in Table 2.

Table 2 : K_3 and K_4 determination from $R_H / N_{PEO}^{-0.17} = f \, (\, N_{PEO}^{0.91} \,)$

COP	N_{PS}	N_{PEO}	N_{PEO} / N_{PS}	$N_{PEO} + N_{PS}$	R_H (nm)	K_3	K_4	r^a
34	152	557	3.66	709	20.4			
36	152	1318	8.67	1470	22.8	42.36	0.055	0.9674
30	136	668	4.91	804	20.6			
31	136	1220	8.97	1356	24.3			
37	40	229	5.72	269	11.8			
38	40	432	10.8	472	14.6			
HH1	38	90	2.36	128	9.2	15.69	0.109	0.9332
HH2	38	148	3.89	186	11.45			
HH3	38	250	6.57	288	14.55			

a : linear regression coefficient

The expressions of K_3 and K_4 can be written as :

$$\log K_3 = \log K_1 + \alpha \log N_{PS}$$

$$\text{and} \quad \log K_4 = \log K_2 + \beta \log N_{PS}$$

By substituting in these new expressions K_3 and K_4 values of Table 2, as well as the average values N_{PS} for each series of copolymers, we obtained :

$$\alpha = 0.75 \qquad \beta = -0.53$$
$$K_1 = 0.98 \qquad K_2 = 0.76$$

Finally, the relation between the hydrodynamic radius and the molecular characteristic of the diblock copolymer becomes:

$$R_H = 0.98 \, N_{PEO}^{-0.17} \, N_{PS}^{0.75} + 0.76 \, N_{PEO}^{0.74} \, N_{PS}^{-0.53} \qquad (4)$$

If we now plot R_H versus $(0.98 \, N_{PEO}^{-0.17} \, N_{PS}^{0.75} + 0.76 \, N_{PEO}^{0.74} \, N_{PS}^{-0.53})$ for all the copolymers of Table 1, we obtain Figure 1.

4

$$0.98 \ N_{PS}{}^{0.75} \ N_{POE}{}^{-0.17} + 0.76 \ N_{PS}{}^{-0.53} \ N_{POE}{}^{0.74}$$
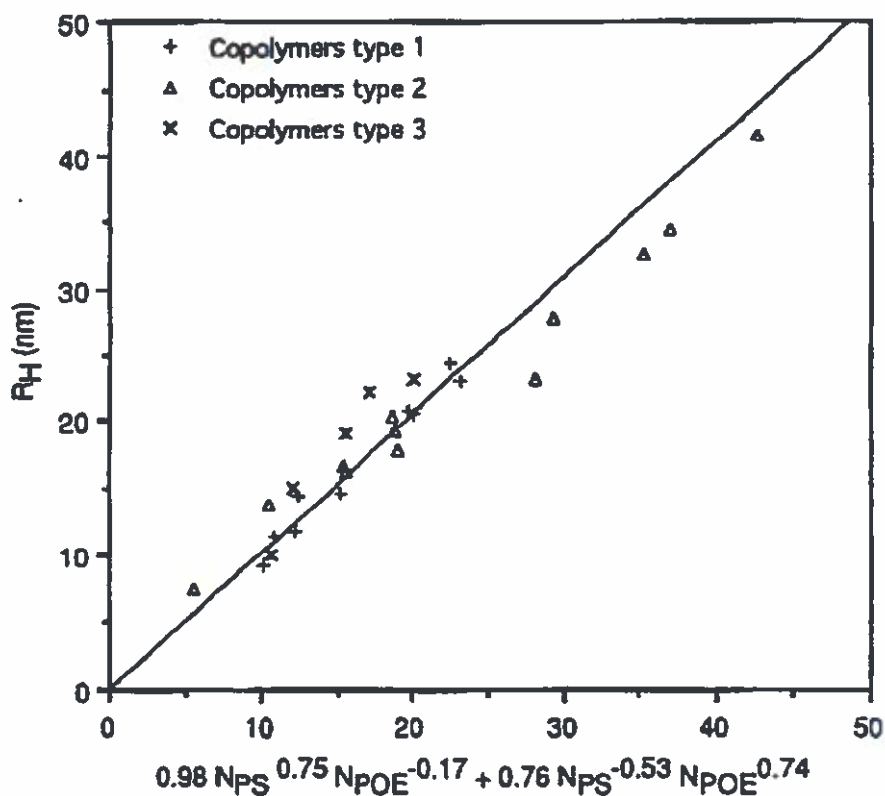
Figure 1 : Relation between R_H and (N_{PEO}, N_{PS})
for diblock PS-PEO copolymers micelles

Three types of copolymers are plotted in Figure 1.
- type 1 : copolymers which were used to determine the relation (4). (see also Table 2)
- type 2 : copolymers which were not used for this determination due to the restrictions given by Nagarajan and Ganesh. (upper part of Table 3)
- type 3 : five copolymers which were independently analyzed by Winnik's group[9]. (lower part of Table 3)

Table 3 : Molecular characteristics of copolymers which were not used
for the determination of the relation (4)

COPOLYMERE	N_{PS}	N_{POE}	N_{POE} / N_{PS}	N_{POE} + N_{PS}	R_H (nm)
H19	486	1000	2.05	1486	34.3
H17	409	348	0.85	757	32.45
28	301	1164	3.86	1465	23.15
29	301	1820	6.04	2121	27.65
35	152	5841	39.08	6093	41.6
18	129	502	3.89	631	20.2
H13	44	68	1.54	112	13.8
39	40	700	17.5	740	19.3
HH4	38	445	11.7	483	16.6
HH5	38	700	18.42	738	17.9
41	35	450	12.85	485	16.2
RS1465	10	23	2.3	33	7.4
32	113	886	7.84	999	23.0
23	108	398	3.68	506	22.0
41	35	450	12.8	485	19.0
40	35	236	6.74	271	15.0
JLM5	16	154	9.62	170	10.0

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One can notice a good agreement with Winnik's values. The more, it appears that all the copolymers we have analyzed follow the general relationship (4) even those which are off the limits given by Nagarajan and Ganesh.

Conclusions

By using the theoretical correlation between the hydrodynamic radius and the molecular characteristics of the copolymer given by Nagarajan and Ganesh, we have found an experimental relation of the same form. This relationship holds for PS-PEO diblock copolymers with a large range of molecular weights and compositions such as :

$$2000 \leq M_{nCOP} \leq 95000 \quad \text{and} \quad 5 \leq \% \, PS \leq 75$$

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**CONTRIBUTIONS TO THE IPCG NEWSLETTER
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ABSTRACTS OF RECENT PAPERS

The Role of Water in Particle Deformation and Compaction in Latex Film Formation. P.R. Sperry, B.S. Snyder, M.L. O'Dowd, and P.M. Lesko. Submitted to *Langmuir.*

The particle deformation and compaction stage of latex polymer film formation was investigated via Minimum Film Formation Temperature (MFT) measurements; variables included polymer composition, particle size, time, and, especially, water content in the film deposition and drying environments. Water content of the system ranged from very low (latex film predried well below the MFT before imposition of the temperature gradient, with low relative humidity maintained throughout) to very high (wet latex cast on the gradient bar and high humidity maintained during drying). A film predried well below the MFT - an turbid deposit owing to interparticle voids - exhibits a "dry MFT" transition, from turbid to clear film, as it is heated. With hydrophobic polymer compositions, the dry MFT is virtually identical to that from a wet casting, indicating that so-called capillary forces associated with presence of liquid water have little if any role. With hydrophilic compositions the "wet MFT" is lower than the dry by as much as 10°C or more; this is ascribed simply to plasticization by water. Dry MFT values decrease with log time similar to the WLF glass temperature - time shift, consistent with viscoelastic relaxation driven by interparticle van der Waals attractive forces/polymer-air surface tension such as described by the Johnson-Kendall-Roberts model of particle adhesion and deformation. For a given polymer composition, the dry MFT increases with particle diameter; the time dependent MFT data correlate with a simple model of surface tension driven collapse of the interstitial voids.

Effect of Microstructure on the Viscosity of Hard Sphere Dispersions and Modulus of Composites. W.B. Russel (Princeton University, Department of Chemical Engineering) and P.R. Sperry, Accepted by *Progress in Organic Coatings.*

Results from theory and experiment in the literature for the viscosity of dispersions of monodisperse hard spheres are contrasted to highlight the effects of particle microstructure, such as ordered spatial distributions versus random or partially aggregated dispersions. Hard spheres, comprising a simple ideal limit with no interparticle forces other than infinite repulsion at contact, are achieved experimentally by either minimizing van der Waals attractions or negating them with short range repulsions. For dispersions, the balance between viscous forces and Brownian motion, as gauged by the Peclet number Pe, determines the microstructure and hence, the viscosity. This results in a progression from isotropic equilibrium at Pe = 0, a small perturbation oriented in the principle direction of strain for Pe << 1, two-dimensional anisotropy for Pe >> 1, and a return to isotropy, albeit hydrodynamically dominated, at Pe = ∞. The viscosities for hard spheres vary in the order η_{hyd} (Pe = ∞) > η_0 (Pe << 1) > η_∞ (Pe >> 1) > η'_∞ (Pe = 0). The first three represent steady shear viscosities, while the last results from high frequency, small amplitude oscillations. At low Peclet numbers, aggregation due to short range attractions and long range repulsions increase the steady shear viscosity. With permanent aggregates the effect persists to Pe = ∞, with the data available for η_{hyd} indicating a monotonic increase with degree of aggregation. Hence, these results for hard spheres generally represent limiting cases. A fundamental connection also exists between composites of hard particles in an incompressible, elastic continuous phase and dispersions of spheres with a corresponding microstructure. The analogy between Hookean elasticity and Stokes flow means that the static shear modulus of the former, normalized by the modulus of the continuous phase, equals the high frequency limiting relative viscosity of the latter. A combination of data and rigorous theory demonstrates that the modulus of a composite decreases in the order - simple cubic > random > body centered cubic > face centered cubic, that is, in order of increasing distance between nearest neighbors at the same volume fraction.

MODELING OF LATEX PARTICLE MORPHOLOGY
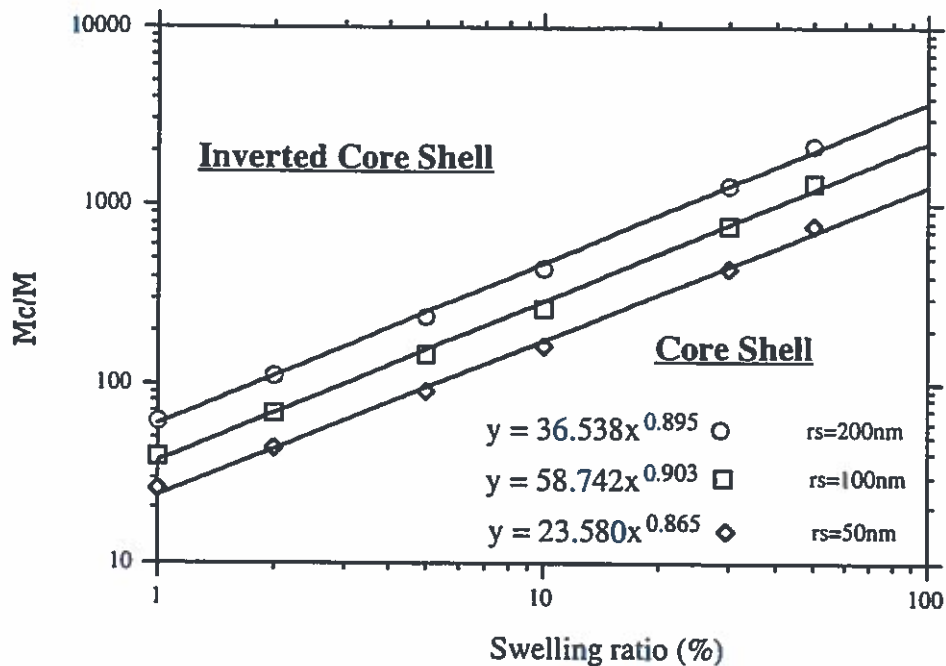*Yvon Durant and Eric Sundberg*

Effect of crosslinking

We have considered the effect of crosslinking the seed latex particle on the ultimate equilibrium morphology of the particle. Our standard free energy analysis has been modified to take the elastic free energy into account and the resulting expression becomes

$$G = Gs + Ge + Go \qquad (1)$$

where G is the total free energy of the particle, Gs is the interfacial energy, Ge is the elastic free energy stored in the particle, and Go is the reference free energy. In this work we only considered core/shell (CS), inverted core/shell (ICS), and occluded structures (OCC). The elastic term can be analyzed by considering the elastic restoring forces present in the particle as a result of some new configuration. If the ultimate morphology is to be CS, then the original, crosslinked seed polymer must be deformed from its original shape of a sphere into an outer shell. The free energy due to the restoring force can be written according to the statistical analysis of isolated chains and results in an expression which is dependent upon the degree of crosslinking, the phase ratio of the second stage polymer, and the original particle size of the seed. The importance of this last dependency is to be underscored as the free energy analysis has now lost its particle size independence.

· The results of our calculations show that it only takes a very small degree of crosslinking to make the elastic term significantly large as compared to the interfacial terms. This has the effect of creating sort of a contour map (crosslink density vs. swelling ratio for second stage monomer) in which the space is divided into a zone in which CS structure is preferred and one in which ICS is preferred. The dividing line is dependent upon the seed latex particle size. In the figure shown below one can see that for a seed particle of 100nm with 1000 monomer units between crosslinks, a second stage swelling ratio 30% leads to an ICS structure. If the crosslinking is increased to an effective Mc/M of 100, the equilibrium morphology shifts to core/shell. Alternatively, if the swelling rato is increased to100%, the morphology also shifts to CS. Thus we predict that increases in seed latex particle size, crosslinking and swelling ratio all lead to the tendency towards CS structures, even though the interfacial forces would have created an ICS structure if left to act alone.

Swelling ratio (%)

The chart shows axes MclM (y-axis) vs Swelling ratio (%) (x-axis), with labels "Inverted Core Shell" and "Core Shell", and equations:

$$y = 36.538x^{0.895} \quad \circ \quad rs=200nm$$
$$y = 58.742x^{0.903} \quad \square \quad rs=100nm$$
$$y = 23.580x^{0.865} \quad \diamond \quad rs=50nm$$

We have carried out a number of experiments in which PMMA seed latices were uniformly crosslinked to various levels, swollen with styrene to different extents, and polymerized under batch conditions. The electron micrographs support the predictions described above showing the very strong influence of crosslink density.

Surfactant Concentration Effect on Particle Morphology

Surfactant concentrations are normally kept below the CMC during polymerization. In this region, the interfacial tensions vary substantially with surfactant concentration and morphology predictions need to be sensitive to this effect. We have measured the variation of polymer/water interfacial tensions on the concentration of SDS (see results of interfacial tension studies described below) in order to derive relationships between the two. In the figure shown below we have simulated a series of experiments in which the SDS concentration was varied from 0% to 100% of full coverage for a seed latex of PS produced with persulfate initiator and swollen with MMA monomer to a phase ratio of 200%. One can readily see that as the surfactant level increases, the morphology shifts from nearly CS to more moonlike structures. This is due to the increasing importance of the polymer/polymer interfacial energy as the difference between the polymer/water interfacial tensions become smaller with increases in SDS concentration.

0%	10%	15%	25%	50%	100%
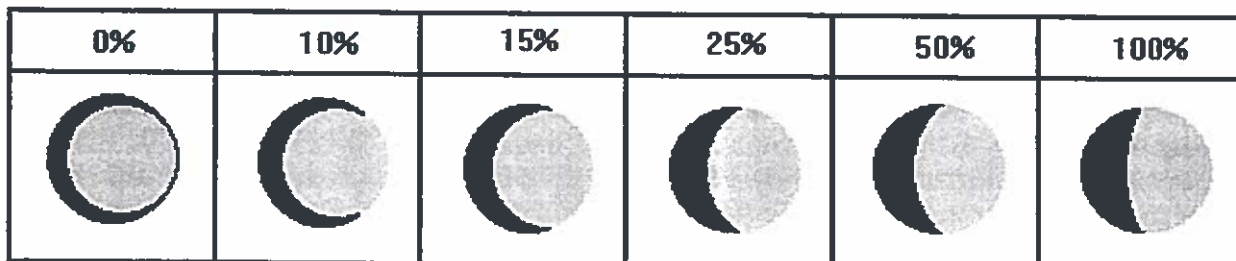
INTERFACIAL TENSION STUDIES
Yvon Durant and John Learson

In-situ Measurements of Latex Particle/Water Interfacial Tensions

The abstract shown below is for a paper that is in print in the Journal of Applied Polymer Science and should be published in the next 6 months.

On the determination of the interfacial tensions for latex particles.
Yvon G. Durant, Donald C. Sundberg, J. Guillot.

The possibility of measuring *in-situ* the interfacial tension at the monomer swollen polymer/water interface of synthetic latices is considered in detail. Experimental measurements of certain liquid or vapor phase properties of the latex can, in principle, yield values of the desired interfacial tension. This technique requires the evaluation and comparison of the Flory-Huggins term and the Morton term of the thermodynamic expression for the chemical potential of the monomer in the latex particle. While each term can be evaluated, it turns out that the relative magnitudes of the two terms are such that unrealistically high precision is required in the experimental measurements for this technique to be useful for obtaining reasonably accurate interfacial tensions. At saturated swelling conditions with highly surface active emulsifiers (e.g. Sodium Dodecyl Sulfate) the interfacial tension values obtained have a precision of only about +/- 50%. The reliability of these appoximate values degrades rapidly as one moves away from saturation conditions, so as to render *in-situ* experimental techniques inappropriate for gaining accurate knowledge about the surface energy at the latex particle/water interface at any monomer/polymer ratio.

The Effect of Monomer on the Polymer/Water Interfacial Tension

It is usually the case that monomer has a lower interfacial tension against water containing surfactant than does its polymer. Thus we expect to see significant effects of monomer on the interfacial free energies that we use to predict the equilibrium morphology as a function of monomer conversion. As such we have sought to measure these effects and to develop interpretive models to allow us to make predictions. Our studies concentrated upon the effect of the type of monomer (in terms of its polarity) and its concentration in the polymer phase The measurements were done using SDS in the water phase at a concentration above its CMC. The two figures below show the type of results that one obtains for two monomers (or solvents) of increasing polarity when the polymer is non-polar. In this case we have used PDMS at 3900 molecular weight to serve as a simple polymer of low viscosity. The interfacial tension values were obtained from our pendant drop apparatus which has an absolute accuracy of 1%. In the case of MMA monomer the deviation from linear behavior is significant and the dotted line represents our thermodynamic model (based on the Prigogine-Marachal treatment) using a polymer solvent interaction parameter which is concentration dependent. This makes a very significant improvement in the predictions over that obtained using a fixed value of the interaction parameter.

Interfacial tension (mN/m) vs **Volume fraction of MMA**

PDMS 3900

Concentration of SDS : 0.5 wt%

Decane
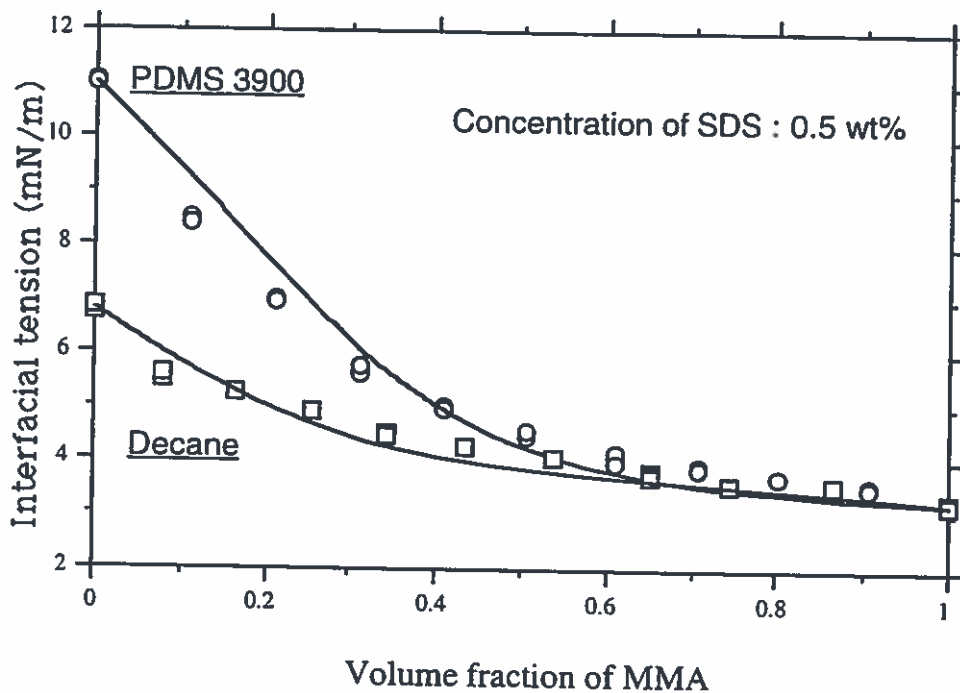
Competitive Adsorption of Surfactants

We report here the beginning of a study of competitive adsorption of two surfactants at the polymer/water interface. In this portion of the study we have chosen to work with SDS and various chain length nonyl phenyl ethylene oxides (NP-X). The results shown below are limited to the case for which there is no monomer present and for which the polymer is PDMS (extremely non-polar). The inclusion of monomer causes the NP-X component to partition into the monomer swollen polymer phase and dramatically complicates the analysis. We have developed three dimensional interfacial tension surface profiles for the combinations SDS/NP-30 and SDS/NP-100 and find striking behavior. The plot shown below is for SDS/NP-30 in which one can see that at the chosen level of total surfactant, a very small addition of NP-30 to a pure SDS solution causes a dramatic lowering of the interfacial tension. This highly non-linear behavior will have a significant impact upon the modelling of latex particle morphology in such systems.

Weight fraction of SDS in a solution at 4.52E-4 g/g
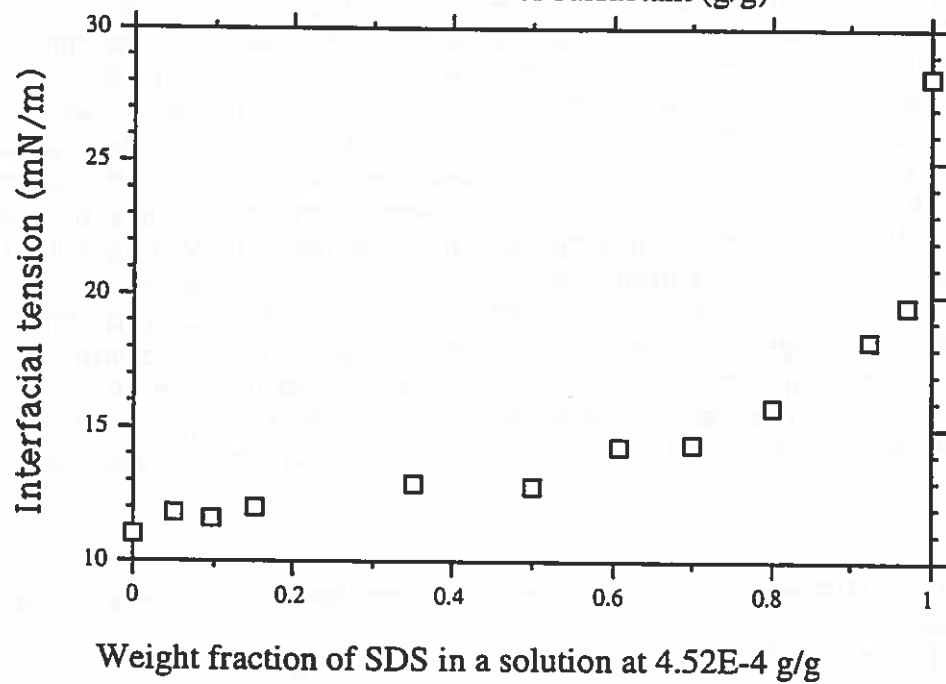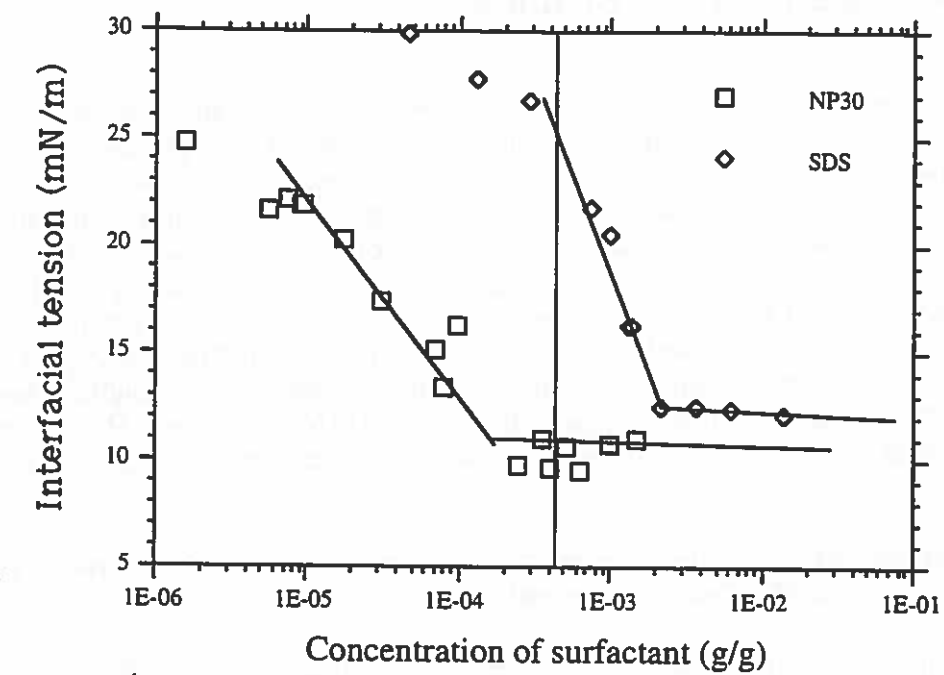
GRAFT COPOLYMERIZATION STUDIES
Naï-Jen Huang

We have recently completed a study of free radical graft copolymerization in solution polymerization. This was done in order to avoid the greatly complicating factors of phase separation and high viscosity present in bulk and emulsion polymerizations. Our objective was to develop a standard modeling structure and to evaluate the basic rate coefficients which describe the reactions leading to the measurable results of graft efficiency, graft ratio, graft frequency and polymer molecular weight. Along the way we have had to develop a new method to measure the graft efficiency and have used this to complete a study of the grafting of styrene, methacrylate and acrylate monomers onto the different isomers of polybutadiene (cis, trans, and vinyl) using both benzoyl peroxide and AIBN initiators. Below we have listed the abstracts of several papers which have been submitted for publication.

A Gel Permeation Chromatography Method to Determine Grafting Efficiency During Graft Copolymerization

A new method of measuring the efficiencies of free radical grafting reactions is presented. This technique utilized the compositional analysis capability of dual detector (UV and RI) gel permeation chromatography in which the mixture of polymer resulting from the graft copolymerization reaction is also subjected to separation by molecular size. Sample of the reaction mass drawn from a reactor are diluted with GPC eluent and injected directly into the chromatograph without any other preparative step. Grafting efficiency, graft ratio, molecular weight distributions, and the frequency of graft chains along the backbone polymer are simultaneously determined. Low molecular weight diluents (residual monomer, solvent, initiator, etc.) are readily separated from the polymer within the GPC, allowing for the determination of the fractional conversion of graft monomer (to grafted and ungrafted polymer) from the same analysis. This simple technique overcomes the need to separate or purify the polymer mixture prior to analysis, as required for most other methods. Experimental results are presented for the grafting of styrene onto cis-polybutadiene. Gelled samples cannot be analyzed by this new technique.

Fundamental Studies of Grafting Reactions in Free Radical Copolymerization.
1. A Detailed Kinetic Model for Solution Polymerization.

Graft site initiation occurs by primary radical and/or polymeric radical attack on the backbone polymer. The controlling mechanism is determined by the structure of the backbone and activity of the free radicals. The efficiency of incorporating monomer into the graft chains depends upon the graft site initiation mechanism and the mode of polymer chain termination (recombination or disproportionation). A kinetic analysis results a series of uniquely different expressions describing the graft efficiency, Φ, corresponding to different combinations of graft site initiation and chain termination mechanisms. The dependency of Ø upon monomer, initiator and backbone concentrations is different from case to case. The complete kinetic model is capable of

predicting reaction rate, graft efficiency, graft frequency, graft ratio, and molecular weight averages and distributions. Simulations are provide to compare predicted results with experimental data for two different system which show contrasting mechanisms of graft site initiation and mode of termination.

Fundamental Studies of Grafting Reactions in Free Radical Copolymerization.
2. Grafting of Styrene, Acrylate and Methacrylate Monomers into cis-Polybutadiene Using AIBN Initiator in Solution Polymerization.

Grafting can be initiated by primary and/or polymer radical attack on the backbone polymer and it is well known that AIBN does not readily promote grafting, even when using polybutadiene. We have studied the grafting of several different monomers onto cis-polybutadiene using AIBN initiator and find dramatically different results among the monomers. As expected, styrene grafts at very low levels due to the inactivity of the initiator radicals <u>and</u> the polystyryl radicals. Methacrylate monomer grafts at a slightly higher level due to its more reactive polymer radical, while acrylate monomer readily grafts onto the polybutadiene because polyacrylate radicals are quite reactive. The use of a kinetic model allowed the evaluation of rate coefficients for graft site initiation to be in the relative order or 0.1 : 1.0 : 10.0 (L/mole/sec) for styrene:methacrylate:
acrylate monomers. The model also provided successful interpretations of the grafting data and its dependence upon the concentrations of monomer, initiator and backbone polymer.

Due to the relatively high reactivity of the polyacrylate radicals, the benzene solvent acted as a chain transfer agent in this system. This affected the molecular weight of both free and grafted acrylate polymer and also surpressed the graft level. Polyacrylate radicals attack the cis-polybutadiene backbone by abstracting an allylic hydrogen and also adding across the residual double bond. The latter mechanism is responsible for the majority of the grafting; the hydrogen abstraction leads to relatively inactive radicals which cause a retardation in the overall reaction rate.

To the "Polymer Group"

from John Ugelstad, Department of Industrial Chemistry, NTH, Trondheim, Norway.

The main activities of the Trondheim group are for the moment:

1. Preparation of monodisperse macroporous particles for size exclusion chromatography.

2. Preparation of macroscopic particles for immunofluorometric assays using flow cytometry.

3. Preparation of magnetic particles for different applications within cell separation, microbiology and molecular biology.

4. Preparation of magnetic particles for use as contrast agent in MRI.

5. Preparation of Paste PVC by polymerization of VC by the miniemulsion method.

Ad 1: The main activity within this field is connected with preparation of particles with very high degree of crosslinking and a predominance of extremely large pores.
We have worked with two types of particles i.e. particles with hydrophobic surface, made from styrene with 80% crosslinker and particles with very hydrophilic surfaces also these with 80% crosslinker. Pore size distribution of such particles,15 micron size are shown below. The large pores are obtained without use of polymeric porogen, which is important for effective extraction of porogen. The hydrophobic particles perform very well in analysis of very high molecular weight polyethylene. The high degree of crosslinking allows operation at high temperature in "strong" organic solvents. Effective separation up to $20 \cdot 10^7$.
The hydrophilic particles have been used successfully in separation of very high molecular weight polysacharides.
Two papers dealing with these particles have been submitted.

Cumulative size distribution of 15 μm particles.

2
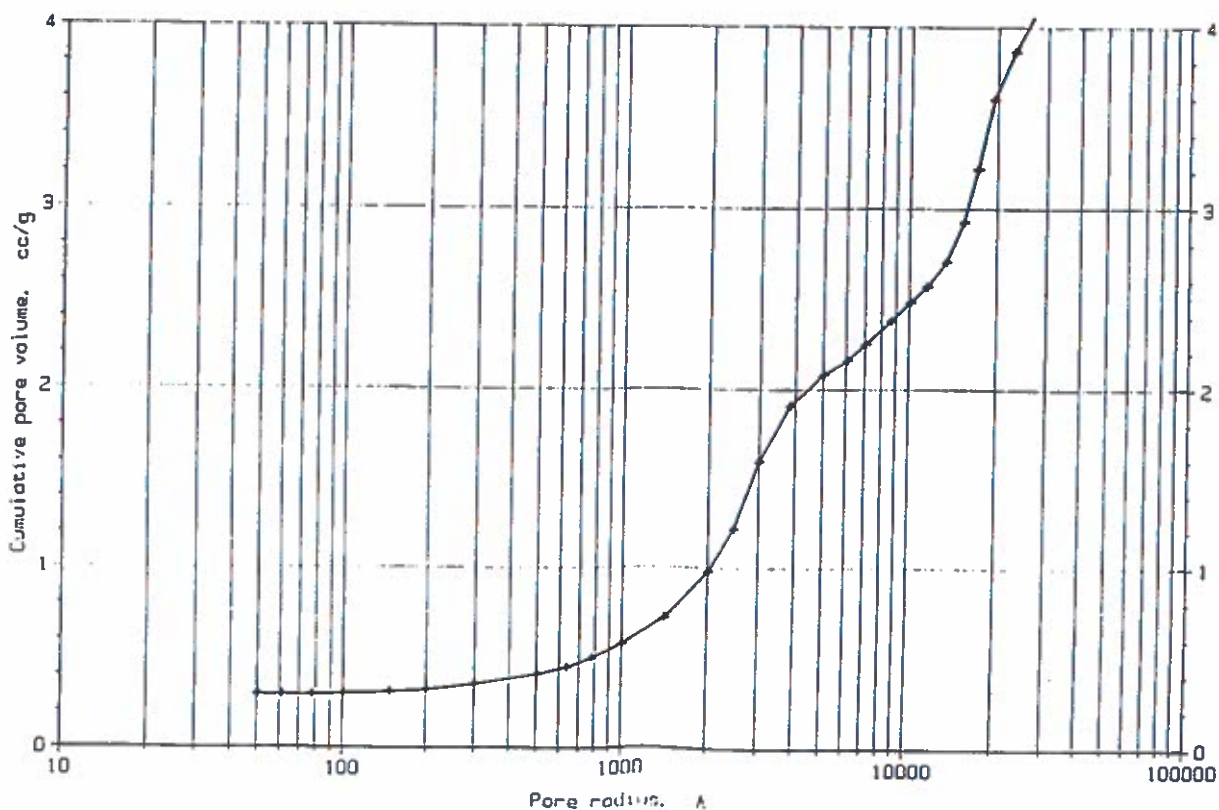
Ad 2. In cooperation with the Institute of biophysics we have developed monodisperse particles, both compact and macroporous for application in immuno-fluorometric analysis, a method which has been developed at this institute. In "normal" particle immunoassays one has to isolate and wash the particles after incubation which may be a tedious and time consuming process. In immunofluoro-metric assays by flow cytometry the isolation and washing steps are avoided.

Flow cytometry can read homogenous particle assays directly since only negligible amounts of medium fluorescence will be excited from the particle sensing volume of the flow cytometer.

Another important feature of flow cytometry is the ability to detect single particle light scattering and fluorescence simultaneously. Thus particles of different size can be distinguished by the light scatter measurements and at the same time the fluorescence of each particle type registered, making multiparameter analysis possible. In this case the monodispersity in size is essential. The extreme monodispersity of our particles make them especially suited for such multianalyzis.

References:

1. T Lindmo et al.: Immunometric assay by flow cytometry using mixtures of two particle types with different affinity. J. Immunol. Methods:*126*,183 (1990).

2. J.Frengen et al.: Homogenous immunofluorometric assays for AFP based on macroporous monosized particles and flow cytometry. Clin. Chem. *39*, 2174 (1993).

3. J.Frengen et al. Demonstration and minimization of serum interference in immunometric assays based on flow cytometry.

4. . J. Frengen et al. Sequential binding assay extending the working range beyond seven decades. J. Immunol. Meth., submitted.

5. J.Frengen et al. Dual analyte assay based on particle types of different size read by flow cytometry, submitted.

Ad 3. Papers dealing with our magnetic particles in medicine and biochemistry is increasing exponentially. Up to now more than 1200 papers dealing with applications of the particles within these fields have been published.

Especially there has been a great increase in the use of the magnetic particles within molecular biology.

At the second John Ugelstad conference, which was being held at MIT in Boston a year ago, most of the papers dealt with application of our magnetic particles within DNA technology.

The book containing the main lectures at this conference is available from DYNAL AS, Oslo, Norway.

Our work at the polymer institute and SINTEF in Trondheim in connection with the magnetic particles has of course chiefly been concentrated on the preparation of different particles for different applications.

We have, however, found it necessary to establish a laboratory for direct work with cells also here at our institute in Trondheim. Especially we have been working with methods to prevent nonspecific binding of cells to the magnetic particles and moreover

we have worked with positive separation of cells. These fields are in some respect connected. We have now succeeded in developing a method which combines an effective selective extraction of cells and an effective loosening of particles from the cells after separation. Likewise we have reduced non specific binding of cells quite dramatically. We have applied for patents on these methods.

Ad 4. We have finished our work on particles for magnetic resonance imaging (MRI). The particles are applied as a contrast agent in the abdomen in order to overcome problems with lack of contrast between bowel and adjacent organs.
These particles are prepared in a somewhat different way than our other magnetic particles. They are 2.8 μm particles with a layer of magnetite. The agent is administered orally and will behave as an inert substance in the gastrointestinal tract. The particles will greatly reduce the spin-spin relaxation time. This leads to a local signal loss which gives a negative black contrast in the area of interest. The method has been shown to be very useful in identifying relapse of cancer in the abdomen. A short review of the method with literature references is given in the review papers given below.(6,7)

There has recently been published several review papers on the use of our particles in general and on our magnetic particles:

6. J. Ugelstad et al.: "Monodisperse polymer particles: "Preparation and new biochemical and biomedical applications" .
In "Advances in Biomagnetic Separation" Eaton publishing Co. (1994) p 1-20.

7. J Ugelstad et al: "Magnetic Polymer Particles, New Applications in Biochemistry and Medicine". Blood Purification. In press.

8. Ø. Olsvik et al. "Magnetic separation techniques in diagnostic microbiology".
Clinical Microbiol.Reviews Jan. 1994, p 43-54

Ad 5. Bård Sæthre has finished his thesis: " Mechanisms and kinetics in mini-suspension polymerization of vinyl chloride."
The polymerization was performed in an isothermal calorimeter.Initiators with different solubility from highly water insoluble initiators to completely water soluble ones were applied. Also a number of red-ox. systems were used. The aqueous emulsions of monomer droplets were prepared by the diffusion method where the monomer is added to a fine emulsion of a Y compound. The size of the particles was determined by light scattering and by electron microscopy. Qualitatively the size and size distribution of the particles is comparable to that of the monomer droplet emulsion as obtained theoretically from calculations based on size and size distribution of the Y droplets and of model experiments with 1-2 dichlorethane. The results indicated that all the monomer droplets got initiated and were transformed to particles. The equalization of monomer droplets during polymerization was found to be small even in the case of water soluble initiators.
Parts of the thesis will be submitted for publication.

Trondheim 26/4   John Ugelstad