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INTERNATIONAL POLYMER COLLOIDS GROUP

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NEWSLETTER

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FROM THE EDITOR'S DESK

MEMBERSHIP: TWENTY YEARS ON

The International Polymer Colloids Group was founded at a meeting at Lehigh University on 27 September, 1971. Present were Bob Fitch, Irv Krieger, Ron Ottewill, Gary Poehlein, John Vanderhoff and David Williams. Twenty years on, it is not surprising that some of our Founding Fathers are, at least in principle, retired or nearing retirement. In this issue is Sandy Dunn's report of the very successful Symposium honouring Robert M Fitch held at the recent ACS Conference in Atlanta, YA. (Sandy, himself was one of the six academics active in the field who were invited to join the Founding Six.) The Colloid and Interface Science Group of the Faraday Division of the Royal Society of Chemistry is planning to hold a meeting to mark Ron Ottewill's formal retirement from the University of Bristol from 30 March – 1 April, 1992. Jim Goodwin will be looking after local arrangements. As with Bob, it is difficult to imagine formal retirement slowing Ron down.

It is very pleasing to have Dave Bassett active in the IPCG again. Long before it became fashionable in the USA (as it has been recently) to have heart problems while jogging, Dave had developed it into an exquisite art form. Welcome back cobber.

Another of the six academics invited to join the Founding Six, Vivian Stannett, has gone into formal retirement. It is a pleasure to welcome Dick Gilbert's contribution to this Newsletter as Vivian's alternate.

The membership of the IPCG has grown over the past 20 years from the original 12 to some 50 (when alternates are included). Long may it prosper.

CONFERENCES

Professor Nomura has kindly provided the provisional programme for the International Symposium on Polymeric Microspheres to be held in Fukui, 23 – 26 October, 1991.

NEXT NEWSLETTER

Please forward contributions by airmail to reach me by **30 September, 1991.**

DH Napper
Editor

CONFERENCE SCHEDULE

1991

CONFERENCE	LOCATION	DATE
202nd ACS National Meeting	New York	25 – 30 August
Faraday Discussion of the Chemistry and Physics of Small Particles	London	18 – 20 September
Preparation of Dispersions	Eindhoven	14 – 16 October
Emulsions	Reading	18 – 19 December

1992

203rd ACS National Meeting	San Francisco	5 – 10 April
66th Colloid & Surface Science Symposium	Morgantown, WV	15 – 18 June
204th ACS National Meeting	Washington, DC	23 – 28 Ausgust

PROVISIONAL PROGRAM

INTERNATIONAL SYMPOSIUM ON POLYMERIC MICROSPHERES

DNESDAY, OCTOBER 23, 1991

:30 - Registration

M. Nomura, Presiding.
:00 - Opening Addresses:
T. Matsuo (Director, Center for Cooperative Research in Science and Technology, Fukui University)
T. Shimada (President, Fukui University)
S. Okamura (A Member of the Japan Academy)

-* Short Presentation (10 min Presentation + 5 min Discussion)
- Normal Presentation (20 min Presentation + 10 min Discussion)

M.S. El-Aasser, T. Matsuo, Presiding.
:15 - The Mechanism of Entry of Free Radicals into Latex Particles. D.H. Napper, R.G. Gilbert, I.A. Maxwell, B.R. Morrison, (University of Sydney, Australia).
:45 - The Kinetics of Emulsifier Adsorption and the Nucleation of Latex Particles. A.S. Dunn (University of Manchester, U.K.)
:15 - Particle Nucleation in Emulsion Copolymerization Containing Multi-functional Monomers. M. Nomura, K. Fujita (Fukui University, Jpn)
:45 - Reactant Partitioning in Free-Radical Heterophase Polymerization. J. Barton (Polymer Institute, Slovak Academy of Science, C.S.F.R.)

A.S. Dunn, Presiding.
:15 - Chain Transfer to Styrene Monomer to Produce Stable Radicals: Analysis of Seeded Microemulsion Polymerization of Styrene. M. Litt (Case Western Reseve University, U.S.A.)
:45 -* Studies on Mechanism and Kinetics of Emulsion Copolymerization of Vinylidene Chloride. Yu Zaizhang, Jia Hongbing, Li Bogeng, Li Baofang (Zhejiang University, P.R. China).

D.R. Napper, T. Okaya, Presiding.
:30 - The Role of Surfactant in Particle Nucleation in Emulsion Polymerization. T. Matsuo, S. Hashiya (Fukui University, Jpn.)
:00 - Shell Growth Mechanism in Emulsifier-Free Emulsion Polymerization: Morphological and Kinetic Studies. S-A. Chen, S-T. Lee (National Tsing-Hua University, R.O. China)
:30 - Development of Morphology in Latex Particles: The Interplay Between Kinetic and Thermodynamic Parameters. Y-C. Chen, V. Dimonie, M.S. El-Aasser (Lehigh University, U.S.A.)
5:00 - Emulsion Polymerization of Vinyl Esters. P.S. Martin, O.W. Smith, D.R. Bassett (Union Carbide Chemicals and Plastics Co. Inc., U.S.A.)

5:30 - Coffee Break

A. German, Presiiding.
5:45 - Miniemulsion Formation and Polymerization of Styrene. Z. Pan, H. Fan, Z. Weng, Z. Huang (Zhejiang University, P.R. China)

16:15 - Use of a ^{13}C NMR Chemical Shielding Technique to Investigate the Polymerization of Styrene Oil-in-Water Microemulsions. H.J. Yue (Air Product and Chemicals, Inc., U.S.A.), J.S. Guo, E.D. Sudol, J.W. Wanderhoff, M.S. El-Aasser (Lehigh University, U.S.A.)

I. Piirma, S. Hosaka Presiding.
16:45 - Very Small Polystyrene Latexes from Emulsion Polymerization in the Presence of Zwitterionic Surfactants. A. Guyot, C. Graillat, H. Essaddam, C. Pichot (CNRS-LMO, France)
17:15 - Mechanism and Kinetics of the Polymerization of Surface-Active Monomers. D. Cochin, R. Zana, F. Candau (CNRS-ULP, France).
17:45 -* Preparation of Reactive Latices by Copolymerization of Styrene with Novel, Water-Soluble Monomers Having an Active Ester Group. K. Nagai, H. Obata, T. Sugiura (Yamagata University, Jpn.) N. Muraoka (Sanshin Chemical Ind., Jpn.)

THURSDAY, OCTOBER 24, 1991

A. Guyot, Presidiing.
8:45 - The Role of Polyvinyl Alcohol in Emulsion Polymerization. K. Yuki, T. Sato, H. Maruyama, J. Yamauchi, T. Okaya (Kuraray, Co., Ltd., Jpn.)
9:15 - Triblock Copolymers of Polyisobutylene-Block-Polyoxyethylene-Block-Polyisobutylene(PIB-b-POE-b-PIB) as Stabilizers in Aqueous Emulsion Polymerization. I. Piirma, Bidulate Sar (The University of Akron, U.S.A.)

M.A. Winnik, H. Kawaguchi, Presiding
9:45 - Preparation of Micron-Size Monodisperse Polymer Microspheres by Seeded Polymerization Utilizing Dynamic Monomer Swelling Method (II). M. Okubo, S. Masaya, Y. Tsukuda, T. Nakagawa (Kobe University, Jpn.)
10:15 - Preparation of Monodisperse Polymer Particles by Dispersion Copolymerization of MMA with Poly(2-Oxazoline) Macromonomer. S. Kobayashi, H. Uyama, J.H. Choi, Y. Matsumoto (Tohoku University, Jpn.)
10:45 -* Preparation of Polyperfluoroalkylmethacrylate Microspheres by Dispersion Polymerization Using Graftcopolymers as the Dispersant. T. Arai, Y. Takizawa, S. Kawase (Soken Chem. & Eng. Co., Ltd., Jpn.)
11:00 -* Characterization of Latices Prepared by Surfactant-Free Emulsion Polymerization. S. Shimizu (Daikin Ind., Jpn.)
11:15 -* Monodisperse Ellipsoidal Polystyrene Latex Particles: Preparation and Characterization. C.C. Ho (University of Malaya, Malaysia), A. Keller, R.H. Ottewill (University of Bristol, U.K.)
11:30 - Intramoleculary Crosslinked Macromolecules - Characterization and Particle Properties. W. Funke, H. Bauer, B. Joos, O. Okay (Stuttgart University, Germany)

D.R. Bassett, Presiding.
13:30 -* Fluorescence Analysis for Thermo-Sensitive Hydrogel Microspheres. K. Fujimoto, Y. Nakajima, H. Kawaguchi (Keio University, Jpn.)
13:45 - Characteristics of Highly Water Absorbent Polymer Emulsion. N. Watanabe, Y. Hosoya, A. Tamura, H. Kosuge (Mitsui-Cyanamid, Ltd., Jpn.)
14:15 - Molecular Aspects of Latex Film Formation. M.A. Winnik, Y. Wang (University of Tronto, Canada)
14:45 - Water Vapor Permeability, Diffusion and Solubility in Latex Films. J. Richard, C. Mignaud, K. Wong (Rhone-Poulenc Recherches, France)

15:15 - Coffee Break

A. Hamielec, S. Omi, Presiding

5:30 - Model Prediction, Experimental Determination and Control of Emulsion Copolymer Microstructure. G.H.J. van Doremaele, A. German (Eindhoven University of Technology, The Netherlands)

6:00 - Copolymer Composition Control in Emulsion Polymerization Using Technical Grade Monomers. J.R. Leiza, G. Arzamendi, J.M. Asua, (Universidad del Pais Vasco, Spain)

6:30 - Emulsion Polymerization and Copolymerization in Continuous Reaction Systems. G.W. Poehlein, D.M. Lange. (Georgia Institute of Technology, U.S.A.)

7:00 -* A New Approach to Continuous Emulsion Polymerization. T. Imamura, K. Saito, S. Ishikura (Nippon Paint Co.,Ltd., Jpn.) M. Nomura (Fukui University, Jpn.)

8:30 - RECEPTION

FRIDAY, OCTOBER 25, 1991

W. Funke, Z. Pan, Presiding.

8:45 - A Fundamental Investigation of the Synthesis of Polybutadine Seed and Further Grafting Emulsion Copolymerization of Styrene/Acrylonitrile Mixture. J. Guillot, P. Mathey-Muller (CNRS-LMO, France)

9:15 - Crosslinking Kinetics in Emulsion Polymerization. A. Hamielec (McMaster University, Canada)

9:45 - Control of Network Structure in Emulsion Crosslinking Copolymerization. T. Tobita (Kao Co., Ltd., Jpn.)

R.E. Riman, C.F. Zukoski, Presiding.

10:15 - Chemical and Physical Aspects of Multicomponent Ceramic Oxide Precipitation Prepared via Multicomponent Alkoxide Hydrosis. R.E. Riman (Rutgers, The State University, U.S.A.)

10:45 - Precipitation of Uniform Inorganic Particles: Growth Mechanism and Colloidal Stability. C.F. Zukoski, J-L. Look (University of Illinois, U.S.A.)

11:15 - Preparation of Polymeric Microsphere-Silica Hybrid Materials by Alkoxide Process. T. Inoue, A. Kimi, Y. Kataoka (Nippon Zeon Co., Ltd., Jpn.), S. Yamazaki(National Chemical Laboratory for Industry, Jpn.)

11:45 -* Chemical Reactor System of Monosized Colloidal Oxide Particles. T. Ogihara (Fukui University, Jpn.)

R.M. Fitch, K. Higashitani, Presiding

13:30 - Laser Photoacoustic and Photothermal Spectroscopy as a Novel Characterization Method for Microparticles. T. Kitamori, T. Sawada (The University of Tokyo, Jpn.)

14:00 - Submicron Particle Size Analysis by Capillary Hydrodynamic Fractionation (CHDF) J.G. Dos Ramos (Matec Applied Sciences, U.S.A.), C.A. Cilebi (Lehigh University, U.S.A.)

14:30 - Flow Profile of Electro-Endosmosis and Effect of Chemical Coatings on the Cell Surface for Electrophoretic Light Scattering Measurement. K. Oka, W. Otani, M. Akagi, H.Kita (Otsuka Electronics Co., Ltd., Jpn.)

15:00 - Laser Manipulation and Ablation of an Individual Latex Particle in Solution. H. Misawa, M. Koshioka, K. Sasaki, N. Kitamura, H. Masuhara (ERATO, Research Development Corporation of Japan)

15:30 - Coffee Break

J.G. Dos Ramos, K. Oka, Presiding

15:45 - Dielectric Spectroscopic Characterization of Weak Acid Polystyrene Colloids. L.S. Su, S. Jayasuriya (S.C. Johnson Wax, U.S.A.), R.M. Fitch (Fitch & Associate and the University of Wisconsin, U.S.A.)

16:15 - Depletion Effect of Excess Polymer on latex Suspension. K. Furusawa (University of Tsukuba, Jpn.)

16:45 -* Electroviscus Effect in Dilute Suspensions of Ionic Polymer Latices. J. Yamanaka, S. Hashimoto, T. Yamaguchi, S. Saeki, M. Tubokawa (Fukui University, Jpn.), H. Matsuoka, H. Kitano, N. Ise (Kyoto University, Jpn.)

17:00 - Effects of Magnetic Field on Stability of Non-Magnetic Colloidal Particles. K. Higashitani, (Kyushu Institute of Technology, Jpn.)

17:30 - Superlong-Range Interactions of Colloids. S. Yoshino, (Nagoya University, Jpn.)

SATURDAY, OCTOBER 26, 1991

M. Nomura, Presiding.

Plenary Lecture

8:45 - Monosized Polymer Particles for Biochemical and Biomedical Applications. J. Ugelstad (SINTEF, Norway)

M. Litt, M. Okubo, Presiding.

9:30 - Functionalization of latex Particles by Emulsion Copolymerization in the Presence of Hydrophilic (Macro)Monomers. B. Charleux, M.T. Charreyre, A. Theretz, T.Delair, C. Pichot (Unite Mixte CNRS, France)

10:00 - Monodisperse Microspheres of the Copolymer of Glycidyl Methacrylate and its Derivatives as a Material for Biomedical Applications. S. Hosaka, Y. Murao, H. Tamaki, S. Masuko, K. Miura, Y. Kawabata (Toray Industries, Inc., Jpn.)

10:30 - Monodisperse Hydrogel Microspheres: Their Feature and Applications. H. Kawaguchi (Keio University, Jpn.)

11:00 -* Preparation of Micron-Size Monodisperse Hydrogel Microspheres and Applications. J. Hasegawa, T. Fujimoto, H. Haneda, Y. Kataoka (Nippon Zeon Co., Ltd., Jpn.)

11:15 - Synthesis and Analysis of Composite PVC-VAc Latices. S. Omi, K. Sakurai, E. Siiyama, M. Iso, (Tokyo University of Agriculture and Technology, Japan), A. Nakano, M. Nakamura (Nippon Zeon Co., Ltd., Jpn.)

11:45 -* On the Relation between the Dispersion State of Polymer Microspheres in the Coatings and the Film Properties. Y. Nakano, M. Yabuta (Kansai Paint Co., LTD., Jpn.)

12:00 - Poster Session - 13:00

14:00 - Excursion in Fukui District.(Free of Charge for Participants from Abroad)

SUNDAY, OCTOBER 27, 1991

9:00 - One Day Guided Tour to Kyoto.(Free of Charge for Participants from Abroad)

THE PREPARATION, PROPERTIES, AND APPLICATIONS OF POLYMER LATICES

Symposium honouring Robert M. Fitch at the 201st National Meeting of the American Chemical Society, Atlanta, Georgia, U.S.A., 17-18 April, 1991, sponsored by the Division of Polymeric Materials Science and Engineering and the Division of Colloid and Surface Chemistry.

There were 8300 participants (excluding exhibitors) registered for the Atlanta meeting. Sessions generally were well attended. Attendance at the POLYMER LATICES Symposium fell to 23 in the middle of the Thursday afternoon session as participants left for the Airport but was 100 or more for most of the time and included the honoree and 8 or 9 other members of the Polymer Colloids Group throughout. One of the preprinted papers (Wilkinson, Steward, & Hearn) was withdrawn but otherwise the published programme was completed with strict adherence to the time-table. About 70 attended the Symposium Dinner at Georgia Tech. Faculty House on Wednesday evening when Symposium Chairman El-Aasser presented Bob and Rita Fitch with Stetson hats of the style favoured by property owners in Nevada where they now have a third home. Although unable to be present Group Poet Irv. Kreiger sent an appropriate ode for the occasion.

Finn Hansen entitled his opening lecture 'Is There Life Beyond Micelles?' reviewing thought and theories on the mechanism of emulsion polymerisation from the earliest times to the present day and providing a good introduction to the field for its more recent entrants which was also a useful re-assessment for those about to qualify for long service awards. His conclusion was that the balance of evidence did favour micellar nucleation of latex particles when emulsifier was present above its c.m.c.

Mohammed El-Aasser presented a Lehigh paper (co-authored by Guo, Sudol, and Vanderhoff) on the mechanism of styrene microemulsion polymerisation. This produces very small (26 nm) latex particles which contain only 2 or 3 high molecular weight (2×10^6) polystyrene molecules. In contrast to a normal emulsion polymerisation the polymer molecular weight does not depend on the initiator concentration: this is because the number of latex particles ($10^{18}/dm^3$ water) is so high that polymer molecules terminate by transfer to monomer before a second initiator radical can enter the particle. The number of latex particles increases throughout the reaction giving a broad particle size distribution. Coalescence of particles appears to be negligible.

My paper gave three reasons for thinking that coalescence of latex particles nucleated from micelles might be possible contrary to the general assumption that the polymer/water interface would remain saturated with emulsifier (and the particles therefore stable) so long as micelles remained in the reaction mixture. The initial rate of expansion of the polymer/water interface when monomer solubilised in a micelle polymerises was comparable with rates of dilatation used in experiments to measure rates of adsorption of emulsifier at freshly formed water/air interfaces so that the surface potential might fall sufficient to permit particle coalescence. The rate of emulsifier adsorption depended primarily on its concentration in molecular solution which was much lower for non-ionics than ionic emusifiers even though they occupied similar areas in saturated monolayers so that coalescence was more extensive when non-ionics are used accounting for the larger particle sizes observed. Higher rates and particle numbers are observed at very low monomer/water ratios when the polymerisation rate per particle is lower permitting a higher emulsifier coverage to be maintained reducing coalescence and accounting for the larger particle number observed.

Ammerdorfer (with German, Eindhoven) had used isotachophoresis to separate according to electrophoretic mobility the oligomers formed during the persulphate initiated polymerisation of butadiene and methyl acrylate in absence of emulsifier. No appreciable amount of insoluble oligomers was formed: it was the surface activity of oligomer radicals rather than their precipitation which determined their entry rate into particles. Nuclei were formed in emulsifier-free polymerisation below the expected c.m.c. of the oligomers.

Sudol presented a paper (with Tang, Silebi, and El-Aasser) of the effects of variations of the precise method used to prepared styrene miniemulsions (50 - 500 nm droplets). No two previous workers had ever used exactly the same procedure which could explain inconsistencies in their results. The Microfluidiser-110 proved considerably more effective than the Sonifier Disruptor W-350 or the Omni Mixer for applying shear to emulsify mixtures.

Ruan (Reichold) described an automated method (which is being commercialised) which drastically reduces the 4-5 h required to measure 1200 particles in an electron micrograph to get a reliable average particle size. The particular advantage of this procedure is its ability to cope with coagulated particles. It depends on a correlation between circle diameter distribution and chord length distribution. Results using this method were in excellent agreement with those measured manually.

Jean Guillot described how T_g of copolymers depends on microstructure which determines whether blocks segregate into separate domains. Equations relating T_g to composition assume segregation: deviation of the measured T_g from the calculated value provides a measure of the compatability of the polymers.

Martin (Union Carbide) presented a paper with Dave Bassett and O.W.Smith on the retardation of the hydrolysis of vinyl acetate copolymer latices by the use of branched chain vinyl ester comonomers., to make them suitable for use as exterior emulsion paints. Although copolymerisation with vinyl versatate has long been commonly practised in Europe (Henry Warson used to show a very effective lecture demonstration) it has not caught on in the U.S. hitherto. Copolymerisation with ethylene has a similar effect but the longer chain branched vinyl esters are relatively more effective.

Vandezande (with Rudin, Waterloo) reported on the possibility of preparing vinyl acrylic latices monodisperse in particle size. Theoretically this should be achievable if the latex has a high surface potential. It was advantageous to delay addition of sodium carbonate buffer until after particle nucleation had ceased to keep the ionic strength as low as possible initially. Latices in the size range 183 - 1050 nm could be prepared with a polydispersity of 1.04.

Jean Guillot presented another paper co-authored by Pichot, Kong, and Cavaille on the particle morphology of vinyl acetate-butyl acrylate emulsion copolymers (i.e. vinyl acrylic latices). Particle morphology depends on the method of preparation (batch or semi-continuous) and affects the properties of films formed from the latices. The nature of the particle surface could be characterised by soap titration using sodium hexadecyl sulphate the adsorption area for which differs considerably between polyvinyl acetate and polybutyl acrylate, and micromechanical spectroscopy of films formed from the latices. Small Angle Neutron Scattering is also being used. Butyl acrylate is much more reactive than vinyl acetate so that semi-continuous polymerisation must be used to get particles with a homogeneous composition. Batch copolymerisation produces particles with a polybutyl acrylate core and a polyvinyl acetate shell.

Peter Lovell (UMIST) with Shah and Heatley explained how interpretation of some very minor peaks in ^{13}C n.m.r. spectra had shown that mysterious variations in the performance of emulsion adhesives prepared from a butyl acrylate-acrylic acid-methyl methacrylate terpolymer could be attributed to differences in the degree of branching of from 10 to 17 branches per 1000 C atoms. The extent of branching was primarily a function of polymerisation temperature and could be reduced by use of a lower temperature with a redox initiator.

A paper from Akron by Lafferty and Piirma concerned the morphology of butadiene-acrylonitrile core-shell particles. If the butadiene seed particles were so highly cross-linked as to be insufficiently swollen by acrylonitrile dumbell shaped particles were produced.

the use of a non-ionic initiator to reduce the polarity of the surface of the seed particles. Waters's observations on the importance of therelative volumes of the phases had been verified. Core-shell morphology could be maintained by feeding the second monomer under starved conditions to prevent the viscosity of the polymer becoming low enough for the thermodynamically favoured state with the hydrophilic polymer on the outside being attained. Cross-linking both core and shell polymers was advantageous.

John Vanderhoff concluded the first day's presentations in a paper with Park and Segall of Lehigh and Hong of the U.S.Army Aberdeen (Maryland) Proving Ground. This was a renewed attempt to find a high molecular weight polymer which could be added to jet fuel to prevent misting and fires in aircraft accidents. Copolymers of alkylaminoalkyl methacrylates and alkyl methacrylates were proposed for this purpose because they produced viscoelastic solutions at low concentrations. To get products of uniform composition semi-continuous polymerisation with emulsion addition was used. The polymerisation was unusual because very large numbers ($10^{19}/dm^3$ water) of very small (18-86 nm) particles were formed. The initial particles were single polymer molecules but growth ceased when particles contained about 10 molecules. Continued nucleation of particles permitted reaction to continue. A possible explanation for the cessation of particle growth might be that that when the concentration of positively charged amino groups on the surface of the particles increased sufficiently they formed salt with sulphate radicals which were then terminated by interaction with aqueous phase radicals before they could initiate polymerisation in the particles (this might be tested by trying an experiment with a non-ionic initiator e.g. AIBN).

Bob Gilbert opened the second day's proceedings in his own inimitable style. His co-workers Ian Maxwell and Brad Morrison, who were both presently working in the U.S., were present. He asked whether it was possible to find evidence which could refute the micellar nucleation hypothesis positively. Most observations were explicable on either theory. The skewness of early-time particle size distribution curves could arise from the equilibrium monomer concentration in small particles being lower so that they grew more slowly than larger particles. Oscillations in CSTR systems had been attributed to the dissociation of micelles not being instantaneous but could equally well be attributed to coagulation being an autocatalytic process. A forthcoming paper in 'Macromolecules' would show that oligomers became surface-active enough to enter particles at a lower degree of polymerisation than that at which they would collapse to nucleate particles homogeneously: good agreement with experiment was obtained if it was supposed that their absorption rate was fast enough not to be rate-determining. When the number of latex particles was high enough all radicals enter particles before growing large enough to nucleate new particles: this was consistent with observations on seed particle concentration required to prevent secondary nucleation. However micellar nucleation was required to account for particle number concentrations greater than $10^{15}/dm^3$ water. Entry into micelles increases the number of polymerising radicals by protecting them from premature termination in the aqueous phase. A competitive growth experiment could be used to test whether radical entry into particles was in accordance with the Smoluchowski equation $k_e = 4\pi Dr$ or whether the rate was reduced by an energy barrier in the case of ab initio polymerisations. Interpretation of the results depended on the value of k_p', the propagation rate constant for the addition of the first monomer which might be much larger than k_p: Morrison planned to attempt to measure k_p' directly.

Nomura with Ikoma and Fujita had been studying the use of azobisisobutyro--nitrile as an example of an oil-soluble initiator. Polymerisation in emulsion droplets by the bulk mechanism is important initially producing a bimodal molecular weight distribution but the low molecular weight peak becomes less prominent as conversion increases an all the monomer is absorbed by the latex particles. Only the azobisisobutyronitrile dissolved in the water phase contributes to the initiation of emulsion polymerisation (cf. Makromol. Chem. Rapid Comm. 10 (1989) 581

Tang presented another paper from Lehigh co-authored by Sudol, El-Aasser, Mary Adams (now at General Electric) and Asua (now back in Barcelona) on seeded miniemulsion polymerisation. Using a miniemulsion feed in semi-continuous polymerisation affected copolymer composition slightly and induced a lot of secondary nucleation.

Y.P.Lee (also from Lehigh but not the EPI) with Micale spoke about the rheology of ordered polymer colloids finding that approximating the surface potential outside the Stern layer by the zeta potential was liable to introduce a large error.

Slomkowski with Basinska of the Polish Academy of Sciences dealt with applications of polymer colloids in diagnostics which involves the immobilisation of proteins on their surfaces. The amount of adsorbed protein was determinable by standard methods.

John Vanderhoff opened the afternoon session by discussing the preparation of microvoid particles for use as opacifiers in surface coatings. Such materials are now commercially available e.g.'Ropaque' from Rohm & Haas. It was necessary to encapsulate a carboxyl containing polymer which swelled in alkali with a hard shell of cross-linked polystyrene or polymethyl methacrylate. After neutralising the core and drying the core collapse to leave a void within the particle. To avoid the formation of non-spherical particles it was necessary to prevent the partitioning of the second-stage monomer into the seed particles which could be done by semi-continuous polymerisation under monomer-starved conditions, Voids in the size range 134-175 nm could be produced in 370-10 070 nm particles. Their use as opacifiers when mixed with a film-forming latex would form the topic of a later publication (with El-Aasser and Park).

Okubo (with Ichikawa and Fujimura) (Kobe) described how alkali treatment could be used to induce the redistribution of buried carboxyl groups to the surface of carboxylated latex particles.

Guyot (with Espiard, Revillon, and J.E.Mark) described the use of collodal silica with or without a functionalised surface as seed particles in the polymerisation of methyl methacryate or ethyl acrylate. Encapsulation could only be achieved when the surface of the silica was first treated to make it hydrophobic: it was also essential to feed monomer semi-continuously and to use an emulsifier with a high HLB.

Partch (with Gangolli, Owen, Ljungquist, and Matijevic of Clarkson) described the production of latices of conducting polymer - polypyrrole - which is black. Its polymerisation could be initiated by solid iron compounds. Particles with magnetic cores and a conductive polymer coating had potential applications in microelectronics.

Tarcha (with Misun, Wong, and Donovan) of Abbot Laboratories Diagnostics Division described another application of polypyrrole latex although in this case it was the intense black colour of the polymer which was the property utilised. Test kits had been devised using a latex coated with antibodies which revealed a + or - sign when a drop of the patient's urine was tested.

Hou (Lehigh) with Lloyd presented a paper dedicated to the memory of his late supervisor Fred W. Fowkes on the encapsulation of pigment particles by polymer precipitation.

Ford (Olklahoma State) with Srinivasan gave apaper on the use of polymer colloids as catalyst supports (a field in which Bob Fitch had been an early contributor). These promised to avoid reaction rates being limited by diffusion by having a very high surface area. Additionally the use of an organic support promoted the adsorption of organic substrates increasing their concentration at the reaction site. The oxidation of cyclooctane using a supported molybdenum oxide catalyst was studied. Under standard conditions a dramatic improvement in the yield from 12 to 90% could be achieved by appropriate modifications to the catalyst. The catalyst latex could be recovered by filtration through a micropore filter. The use of such catalysts might eliminate the need

John Dawkins (Loughborough) gave the only paper (with Shakir) on non-aqueous polymer colloids. This was on the use of diblock polystyrene-polydimethylsiloxane or polystyrene-ethylene-propylene copoymer made by anionic polymerisation to stabilise polymethyl methacrylate or polyvinyl acetate made by non-aqueous dispersion polymerisation. Polyvinyl acetate adsorbs more stabiliser than polymethyl methacryate resulting in a thicker barrier layer as inferred from dynamic light scattering measurements.

Preprints of the papers (which were limited to 4 colums on A4) appear in Polymeric Materials Science and Engineering 64 (1991) 218-227, 271-283, 308-318, 345-357. Full texts are to be published in a volume in the A.C.S. Symposium Series after refereeing: it is hoped that the volume will appear in December.

A.S.D.

International Polymer Colloids Group Newsletter

Contribution from the Grupo de Ingeniería Química,
Facultad de Ciencias Químicas, Universidad del País Vasco,
Apdo. 1072, 20080 San Sebastián, Spain.

Reported by José M. Asua

Optimal Monomer Addition Policies for Composition Control of Emulsion Terpolymers

(Gurutze Arzamendi and José M. Asua)

An approach for the calculation of the optimal monomer addition policies for polymer composition control in emulsion terpolymerization has been developed. The model allows for the calculation of the composition of the initial charge of the reactor and the time dependent monomer addition flow rates. If the rate of heat removal of the reactor was greater than the rate of heat generation, a homogeneous terpolymer was obtained in a minimum process time when the reactor was initially charged with all the amount of one monomer plus some amounts of the other two monomers and the remaining monomers were added at controlled feed rates. The monomer to be completely included in the initial charge is the one for which a maximum z_i/Y_i ratio was obtained. Y_i is the desired molar terpolymer composition in monomer *i* and z_i the overall molar fraction of monomer *i* in the reactor that ensures the formation of a terpolymer of composition Y_i. The process time required by the classical starved process to produce a terpolymer of similar homogeneity is greater than twice of that needed by the optimal policy. A different optimal monomer addition policy was obtained when a reactor with limited capacity for heat removal was used. In this case, only a fraction of the three monomers can be included in the initial charge feeding the remaining monomers at a controlled flow rate.

A New Approach for the Estimation of Kinetic Parameters in Emulsion Polymerization Systems. II. Homopolymerization under Conditions where $\bar{n}>0.5$

(María J. Barandiaran, Mary E. Adams, José C. de la Cal, E. David Sudol and José M. Asua)

An approach for the estimation of kinetic parameters in emulsion polymerization systems in which the average number of radicals per particle exceeds 0.5 has been presented. The approach uses the time evolution of the conversion in chemically initiated systems and is based on a model that includes fundamental parameters such as the propagation rate constant, k_p, the termination rate constant in the polymer particles, k_t,the rate coefficient for initiator decomposition, k_I, and the entry, k_a, and exit, k_d, rate coefficients. It was found that when the termination in the aqueous phase is significant, k_p, k_t, k_I and k_a were accurately estimated. In addition, when the system is not completely insensitive to k_d, a rough estimation of the exit rate coefficient is possible. In the cases in which the termination in the aqueous phase is negligible, the model is not sensitive to k_a and k_d and hence, only the values of k_p, k_t and k_I can be estimated. It was found that the accuracy of the estimates is almost independent of the experimental noise level. On the other hand, the irreproducibility between runs can have a deleterious effect on the accuracy of the estimated parameters when a low number of experiments is used. More serious inaccuracies result from the poor determination of the initial polymerization time. An iterative procedure to circumvent this problem has been proposed. This procedure allows the accurate estimation of the parameters irrespective of the errors made in setting the initial time.

POLYMER COLLOIDS GROUP NEWSLETTER

Contribution from the Department of Polymerization Reactions, Polymer Institute, Slovak Academy of Sciences, Dúbravska cesta 10, 842 36 Bratislava, Czech and Slovak Federative Republic

Reporter : J. Bartoň

Polymerization in inverse microemulsion initiated by two-component initiation systems.

(V. Vašková, V. Juraničová, J. Bartoň)

The polymerization of acrylamide (AAM) and/or its copolymerization with methyl methacrylate (MMA) in inverse microemulsion toluene/water (10:1 by weight) using an emulsifier sodium bis(2-ethylhexyl) sulfosuccinate (AOT) (0,34 mol.dm^{-3} of solvent mixture) initiated by two-component initiation systems has been studied. The two-component initiation systems consisted of radical initiators with different water-solubility and of an organic aminocompound. In the Table there are given AAM polymerization initial rates R_{p0} (in mol.dm^{-3} of solvent mixture .s^{-1}) obtained during the reaction initiated by the listed two-component initiation systems.-

AIBN (2,2'-azobisisobutyronitrile) has not been found to form an effective two-component initiation system with amines, diamines and/or aminoalcohols. On the other hand water-soluble APS formed with amines and/or diamines very effective initiation systems which initiated AAM homopolymerization and/or its copolymerization with MMA in inverse microemulsion at 30°C. The rates thus obtained have been comparable with the rates of AAM polymerization initiated by APS and/or AIBN at 60°C[1,2].

Amines and diamines could be expected to form a complex with APS in the interlayer between the oil macrophase and the water microphase[1] of the inverse microemulsion. Also the rate dependence on the ratio of the components of the two-component initiation system has been observed. Only slightly less effective were in this context amino alcohols which were well water soluble and therefore could be expected to form a complex with APS in the

water microphase.

A two-component initiation systems containing oil-soluble BP in combination with amines and diethylamines have also been used to initiate AAM polymerization and/or copolymerization with MMA in inverse microemulsion at 30°C. These systems showed only poor initiating activity on rate of AAM polymerization and/or its copolymerization with MMA. The polymerization rates were approximately of three orders lower incomparison to the rate of polymerization found for systems in which instead of BP ammonium peroxodisulphate was used.

Table: Acrylamide (AAM) homopolymerization rates R_{po} (in $mol.dm^{-3}$ of solvent mixture $.s^{-1}$) estimated in inversion microemulsion toluene /water (10:1 weight) in the presence of AOT (0,337 $mol.dm^{-3}$ of solvent mixture) at 30°C. Concentrations of ammonium peroxodisulfate (APS) and/or of dibenzoylperoxide (BP) is $2,44.10^{-3}$ mol $.dm^{-3}$ of solvent mixture $[AAM]_o$ = 0,6 $mol.dm^{-3}$ of solvent mixture.

Redox system	Molar ratio of concentrations of the redox system	$R_{po}.10^3$ ($mol.dm^{-3}.s^{-1}$)
APS/MEA	1:10	1,22
APS/DEA	1:10	3,3
APS/DEA	1: 5	1,0
APS/DEA	1: 1	0,1
APS/DE(OH)A	1:10	1,7
APS/DEAN	1:10	0,05
APS/TMEDA	1:10	4,6
APS/TMEDA	1: 5	3,7
APS/TMEDA	1: 1	1,65
BP/MEA	1:10	0,002
BP/DEA	1:10	0,005
BP/DEA	1: 1	0,004
BP/TMEDA	1:10	0,003

MEA = monoethanolamine
DEA = diethanolamine
DE(OH)A = diethylaminoethanol
TMEDA = tetramethylethylenediamine

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2) V. Vašková, V. Juraničová, J. Batroň, Makromol. Chem., in press

Emulsion copolymerization of vinyl chloride and butyl acrylate
(I. Capek, Z. Mrázek)

Emulsion copolymerization of vinyl chloride and butyl acrylate initiated be ammonium peroxodisulfate at 60 °C in the presence of anionic emulsifier was investigated. Random copolymers of vinyl chloride and butyl acrylate, covering several sets of monomer compositions, are synthetized by emulsion copolymerization conducted to both low and high conversions.

The rate of emulsion copolymerization was found to decrease with increasing vinyl chloride concentration. The specific rate of butyl acrylate polymerization in the emulsion copolymerization of vinyl chloride and butyl acrylate was found to be proportional to the 0.5 power of the butyl acrylate concentration. The rate of emulsion polymerization of butyl acrylate was found to proportional to the 1.0 power of the butyl acrylate polymerization.

The particle size increases with increasing both vinyl chloride monomer concentration in the comonomer feed and conversion. In the systems with high concentration of vinyl chloride the size of polymer particles increases throughout the polymerization. In the systems with high concentration of butyl acrylate the size of polymer particles increases at low and/or at low and medium conversion with increasing conversion. The PBA particles are assumed to be formed by the micellar mechanism while those of PVC by the homogeneous nucleation.

The molecular weights of vinyl chloride/butyl acrylate copolymers decrease with increasing both initial vinyl chloride concentration and conversion. The chain transfer to vinyl chloride is very important process since their frequence relative to the chain propagation controls the molecular weight.

Variations of the experimental cumulative average copolymer composition with the comonomer feed composition and conversion were investigated. At the beginning of copolymerization copolymer enriched with butyl acrylate was formed. As reaction advances copolymer enriches with vinyl chloride. The polymer particles consist of the PBA rich-core and the PVC rich-shell.

International Polymer Colloids Group Newsletter

Alkali Stability of Vinyl Acetate / Vinyl 2-Ethylhexanoate Copolymer Latexes

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Introduction

Owing to its low cost, vinyl acetate (VAc) is an attractive alternative to methyl methacrylate for use in architectural coating latexes. Unfortunately, VAc suffers from poor hydrolytic stability, especially under alkaline conditions and, as such, sees only limited application in exterior coatings. The introduction of the vinyl esters of highly branched carboxylic acids containing nine and ten carbon atoms has enabled the formation of all vinyl emulsion based coatings, which are more suitable for exterior use and possess better alkali resistance than conventional acrylics [1]. In this study the ability of vinyl 2-ethylhexanoate (2EH) to provide protection for VAc against alkaline saponification is explored via conductometric titrations.

Experimental

VAc and 2EH were used as supplied by Union Carbide. Adequate purity (>98%) was ascertained by gas chromatography and polymerization inhibitors, usually 5 - 55 ppm hydroquinone or monomethyl ether of hydroquinone, were not removed prior to use. All latexes were prepared using a single emulsion polymerization procedure. The stabilization system comprised hydroxethyl cellulose (0.4 phm), nonionic surfactant (3.8 phm) and anionic surfactant (0.1 phm). tert-Butyl hydroperoxide (0.2 phm) in combination with sodium formaldehyde sulfoxylate (0.2 phm) was employed as the redox activated initiation system and sodium acetate (0.2 phm) as the buffer. Water was included to produce a total solids content of approximately 53%.

The alkali stability test employed here is similar to the one described previously [2]: Five grams of latex are added to 50 gms of 1 N KOH, where both are weighed to the nearest 0.01 gm. A 5 gm portion of this mixture, also weighed to the closest 0.01 gm, is diluted to approximately 80 ml with a 50/50 (w/w) triple distilled water / propanol solution and then immediately titrated with standardized 0.5 N HCl. Subsequent 5 gm portions of the latex/KOH mixture are similarly titrated at intervals of 24 and 72 hours. The total amount of saponification is the weak acid increase for these periods expressed as a percent of the weak acid present in the latex.

The titrations were performed at room temperature in a conductance cell designed and used to study micelles [3]. Conductance measurements were performed using a Leeds & Northrup # 4959 Electrolytic Conductivity Bridge operating at 1000 Hz, whose galvanometer null detector provides a sensitivity of 0.1% of the conductance reading.

Results

In Figure 1 the extent of hydrolysis for VAc/2EH copolymer latexes exposed to 1 N KOH for 24 and 72 hours is plotted against 2EH content, for 2EH contents of between 10 and 30 wt%. From the diagram it is obvious that enhanced hydrolytic stability in VAc/2EH latexes correlates with high 2EH content. It is interesting to note that in proceeding from a 90/10 to a 70/30 (w/w) VAc/2EH copolymer, the hydrolytic stability increases by a factor of between two and four.

Discussion

Several factors contribute to the stability of VAc copolymers. Given that adjacent hydroxyl groups have been shown [4] to promote hydrolysis of acetate moieties in partially hydrolyzed p(VAc), one would expect that any comonomer capable of separating the pendent acetate groups on the polymer backbone should effectively decrease the rate of saponification. Since vinyl esters possess very similar reactivity ratios, copolymerization of VAc with a more sterically hindered vinyl ester, i.e., one more resistant to hydrolysis, would be expected to decrease the rate of saponification. In other words, the comonomer would form a random copolymer with VAc, thereby spacing the VAc moieties, which in turn reduces the number and lengths of the VAc sequences and thus the extent of hydrolysis. This explanation is consistent with the behavior displayed in Figure 1, where alkali resistance correlates with the amount of comonomer, which in this instance is the more robust 2EH.

On the basis of this argument, ethylene is the comonomer of choice because its low molecular weight allows for the maximum introduction of nonhydrolyzable segments on a per weight basis. It has in fact been demonstrated that ethylene is an effective stabilizing comonomer for VAc [2]. However, it was also shown [2] that branched vinyl esters containing long pendent hydrocarbon groups are, on a molar basis, approximately five times as efficient as ethylene in providing protection from alkaline hydrolysis. This suggests that not only do the long pendent groups protect the carbonyl moieties to which they are bonded, but that they also provide an umbrella type of shield to those of their immediate neighbors.

Summarizing the structural/mechanistic aspects of alkali resistant VAc/2EH latexes, one can argue that these results are consistent with a scheme whereby the 2EH breaks up the VAc sequences and provides an umbrella like shield to adjacent moieties within the latex.

Acknowledgements

Grateful acknowledgement is made to J. H. LaPere for synthesizing the latexes and to J. E. Patrick, R. G. Ramsey and J. F. Winter for performing the alkaline hydrolysis analyses.

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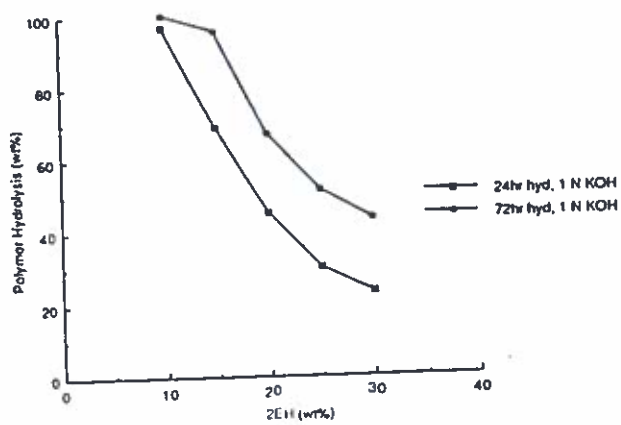

Figure 1 Hydrolysis of VAc/2EH Latexes Following Exposure to Aqueous KOH

POLYMER COLLOID GROUP NEWSLETTER

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

Françoise CANDAU

POLYAMPHOLYTES IN MICROEMULSIONS : FORMULATION AND CHARACTERIZATION

(in collaboration with J.M. Corpart, and J. Selb)

In the past decade, we have developed a method for preparing microemulsions based on acrylamide and/or sodium acrylate which produced stable microlatex polymer particles with high molecular weights[1,2]. In the present study, we extend the process to the synthesis of copolymers containing both positive and negative charges along the chain i.e. polyampholytes. Although such polymers have received little attention in the past, they have however great potential for applications, as a result of the possibility to choose the copolymer composition during the synthesis : depending on the number of ionic sites along the chain, polyampholytes exhibit behavior ranging from highly water-swollen, water-soluble to insoluble substances.

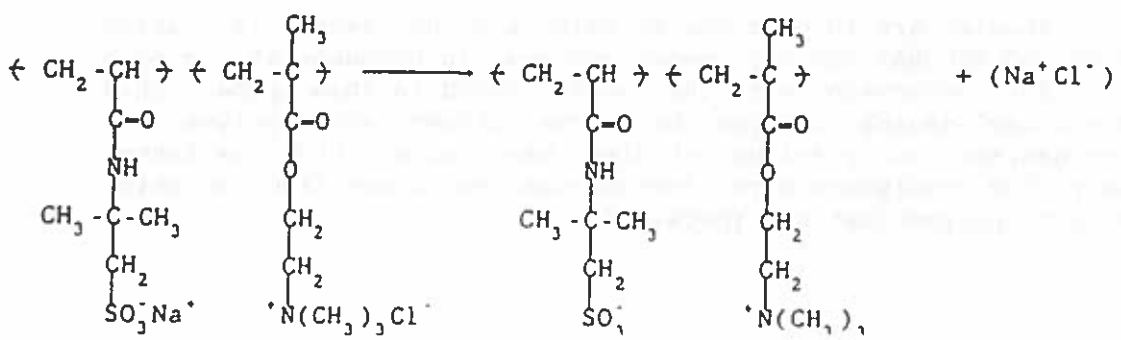
The monomers which were considered are the methacryloyloxytrimethylammonium chloride (MADQUAT) and the sodium-2-acrylamido-2-methylpropanesulfonate (NaAMPS). Both monomers play an important role in the formulation, owing to their amphiphilic and electrolytic character, as confirmed by surface tension and turbidimetry experiments. As cosurfactants, they enhance considerably the microemulsion domain and as electrolytes, they salt-out the surfactant. These effects taken together control the structural properties of the microemulsions.

A typical recipe is the following (wt/wt) : Isopar M : 44%; monomers : 22% ; water : 22% ; nonionic surfactants : 12%.

The free radical polymerization (UV irradiation, 20°C) of the polymerizable microemulsions leads to stable and clear latexes of uniform size (d = 100 nm) as determined by quasi-elastic light scattering experiments.

Copolymer Composition

A series of samples with variable amounts of the two monomers was prepared in microemulsions and polymerized up to complete conversion, according to the recipe given above. A complete analysis of the data by elemental analysis shows that the materials after dyalysis tend to self-neutralize almost completely according to :



In particular, it should be noted that the anionic and cationic monomers of samples with balanced stoechiometry (50:50) are completely paired, with no residual sodium or chloride counterions left in the solution.

Reactivity Ratios

Reactivity ratios were calculated by elemental analysis from monomer feed, and low conversion compositional data (< 10%). The Fineman-Ross, Kelen-Tüdos and Tidwell-Mortimer methods initially derived for polymerization in homogeneous solutions have been employed : this is possible because almost all of the monomers are located within the aqueous domains of the microemulsions, which allow us to neglect corrections for monomer partitioning between the oil and the water phases. Graphical evaluations of the data yield reactivity ratios r_A = 0.81 and r_M = 1.97 for NaAMPS and MADQUAT respectively. These values are indicative of a slightly blocky structure ($r_A . r_M > 1$). Figure 1 shows the monomer incorporation curve derived from Mayo-Lewis, in which mole percent NaAMPS in the copolymer is plotted versus mole percent of NaAMPS in the feed.

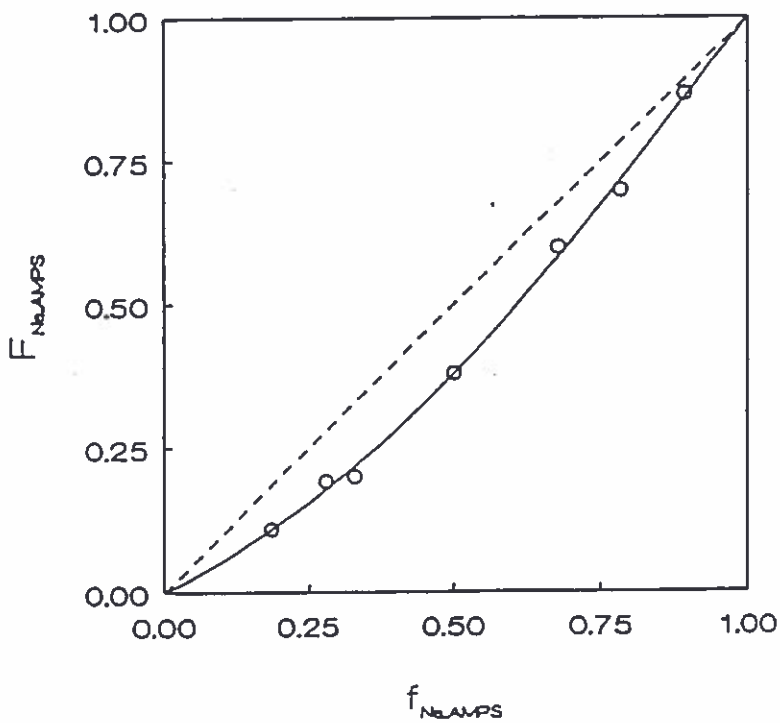


Figure 1 : Variation of average copolymer composition with feed composition for copolymers obtained at low degrees of conversion. The dotted line corresponding to ideal copolymerization ($r_A = r_M = 1$) is represented for reference.

Studies are in progress to calculate the reactivity ratios of NaAMPS and MADQUAT for copolymers prepared in homogeneous aqueous solution, for comparison with the values found in this paper. This should provide valuable information on the microemulsion polymerization mechanism, as previous studies have shown that the latter process yields copolymers more homogeneous than those from solution and emulsion polymerizations (Refs.3,4).

The weight average molecular weights of the samples have been measured by light scattering. The higher values found (M_w > 10^7), which are characteristic of polymers prepared in microemulsions make them important for applications.

The aqueous solution properties of the samples are under investigation and will be described in the next report.

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Progress in Colloid & Polymer Science Progr Colloid Polym Sci 81:81–86 (1990)

A small-angle neutron scattering study on AOT/toluene/(water + acrylamide) micellar solutions

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Abstract: The effect of the presence of acrylamide inside water-swollen micelles of Aerosol OT dispersed in toluene on the interparticular interactions and micellar size has been investigated by small angle neutron scattering. The structure factor obtained for D_2O/AOT/toluene systems (no acrylamide) can be fitted by a hard sphere model. The incorporation of acrylamide induces attractive interparticular forces. The micellar sizes obtained from the form factor are in good agreement with previous findings by quasi-elastic light scattering.

Key words: Acrylamide; aerosol AOT micellar systems; neutron scattering

Recent Publications

Polymerization of methacrylate of trimethylaminoethyl chloride in microemulsions : Formulation, characterization and rheological behavior of the microlatexes.
F. Candau and P. Buchert
Colloids Surf., 48, 107 (1990).

Synthetic polymers in water-in-oil microemulsions.
F. Candau
in *"Polymer Based Molecular Composites"* (D. Schaefer and J. Mark Eds.).
Mater. Res. Soc. Proc., Boston, 171 (1990).

Microscopic processes in microemulsion polymerizations.
F. Candau
in *"Macromolecular Liquids"* (C. Safinya, S. Safran and P. Pincus Eds.).
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Polymerization of acrylamide in a swollen lamellar mesophase.
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A small angle neutron scattering study on AOT/toluene/(water+ acrylamide) micellar solutions.
C. Holtzscherer, F. Candau and R. Ottewill
Prog. Colloid Polym. Sci., 86, 81 (1990).

Rheological studies on inverse microlatexes.
F. Candau, P. Buchert and I. Krieger
J. Colloid Interface Sci., 140, 466 (1990).

Effect of hydrophobicity of particles surface on kinetics of coagulation of free-emulsifier carboxylcontaining latexes.

V.I.Eliseeva, T.R.Aslamazova, S.V.Bogdanova, Y.I.Rabinovich, T.G.Movchun

The coagulation of carboxylcontaining styrene-methacrylate latexes in the course of polymerization in the presence of persylphate initiator was investigated. Electrosurface properties and surface tension of latexes, particle size were measured. Surfase area of particle per 1 COOH grouping was determined. Contact angle for films obtained by drying of latexes were also measured. It was found that there was no correlation between aggregative stability of particles and their zeta-potential. On the other hand it was established that latex stability decreases by increasing of surface hydrophobicity of particle (contac angle for films). The correlation dependence between contact angle for film and surface area per 1 COOH grouping was found. The authors came to the conclusions that besides electrostatic factor structural factor of stabilisation is essential for the stability of free-emulsifier carboxylcontaining latexes.

In order to confirm this suggestion the theoretical equatic of kinetics of slow coagulation of hydrophobic latexes in nearest potential well accounting the forces of structural attraction were derived. According these equations and by using of experimental results on stability of free-emulsifier carboxylcontaining styrene-methacrylate latexes parameter K characterized the value of structural forces was calculated. Dependences of K upon contact angle for films and particle surfac area per 1 COOH grouping testify the contribution of structural attraction of hydrophobic particles in their coagulation. At the same time they show theoretically the direction ofaggregative stability increasing by including hydrophilic groupings in surface of free-emulsifier latex particles.

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. 35, January, 1991, which can be found at the end of this report. Copies of any of these reports can be obtained by contacting Ms. Debra Nyby at the above address. Summaries of progress in several research areas are presented here and include areas of continuing commitment and recently established research programs.

1. Morphology of PMMA/PS Composite Particles
(Shiji Shen)

Latex systems with controlled particle morphology are the basis for many of today's advanced high performance polymer materials. Extensive studies have been carried out on the morphology of submicron size composite latex particles prepared by two-stage emulsion polymerization, ranging from core-shell to various fragmented inclusions to inverted core-shell. The ultimate particle morphology in a composite latex is found to be dictated by thermodynamic and kinetic parameters. However, the effect of the polymerization mechanism on particle morphology has not been considered as intensively.

Monodisperse microscopic poly(methyl methacrylate)/polystyrene (PMMA/PS) composite particles of 1-10μm diameter were prepared by a dispersion-emulsion two-stage polymerization. First, monodisperse PMMA particles were prepared by dispersion polymerization of methyl methacrylate in methanol using poly(n-vinyl pyrrolidone) as stabilizer. The PMMA particles were cleaned and transferred to aqueous medium and used as seed in a seeded emulsion polymerization of styrene. The resulting composite particles were characterized by transmission and scanning electron microscopy.

The PMMA/PS composite particles showed a unique morphology. Three types of PS domains were found embedded in a continuous PMMA matrix. As illustrated in Figure 1, these are referred to as the dispersed "internal" domains in the interior, the interconnected "subsurface" domains forming a spherical crust beneath the surface, and the separated "surface" domains. The formation of this striking morphology was attributed to the coexistence of different polymerization mechanisms: bulk polymerization in the interior and a combination of bulk polymerization and surface phenomena (e.g., the desorption of radicals) at the surface of the particles. This coexistence results in a radial distribution of radicals within the particles under high polymer content conditions as qualitatively depicted in Figure 2. With a varying PMMA/styrene ratio, the internal viscosity and the competition between polymerization at or near the surface differed, resulting in a series of interesting morphologies.

A mechanism for morphology development was proposed showing the simultaneous and competitive effects of thermodynamic, kinetic, and mechanistic factors.

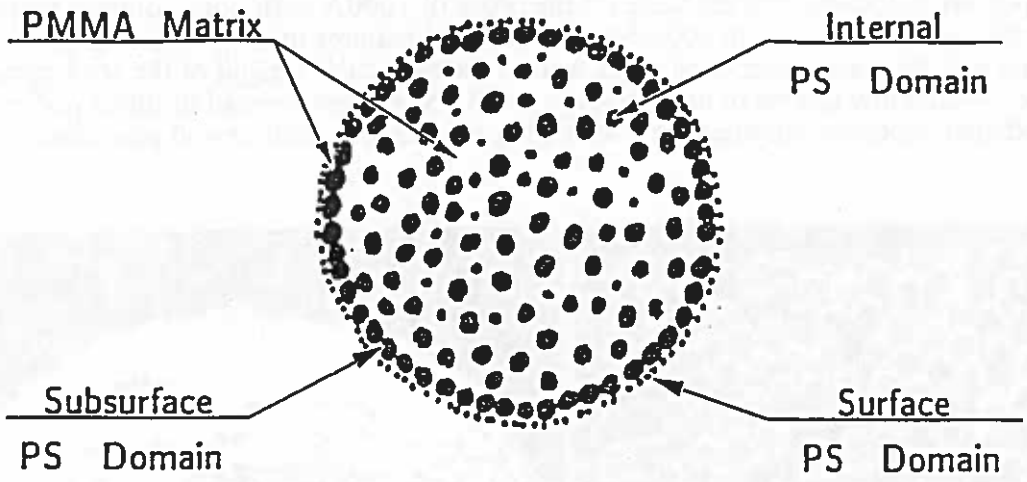

Figure 1: *Morphology of PMMA/PS (50/50 by weight) composite particles.*

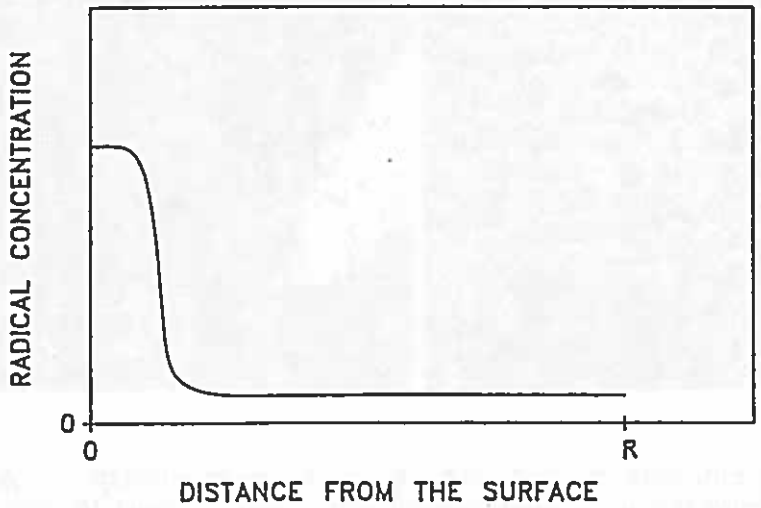

Figure 2: *Radial distribution of radicals within the particles under high polymer content conditions.*

2. Preparation and Characterization of Monodisperse Porous Polymer Particles
(Chieh-Min Cheng)

Monodisperse porous styrene-divinylbenzene copolymer particles in the size range of 10μm in diameter were prepared via seeded emulsion polymerization. Linear polymer (polystyrene seed) with molecular weights on the order of 10^6, or a mixture of linear polymer and solvent or nonsolvent were used as inert diluents. Porous structures were formed by removal of diluents by

solvent extraction after polymerization. Figure 3 shows scanning electron micrographs of 11μm porous particles. The pore shape is irregular compared to silica packing materials. The pore diameters of these porous polymer particles were on the order of 1000Å with pore volumes up to 0.9 ml/g and specific surface areas up to $200m^2/g$. The physical features of the particles depended on the diluent type and the crosslinker content, as well as the molecular weight of the seed particles. A polymer seed with a low degree of crosslinking could also be used instead of linear polymer to prepare monodisperse porous polymer particles with a smaller pore volume and pore size.

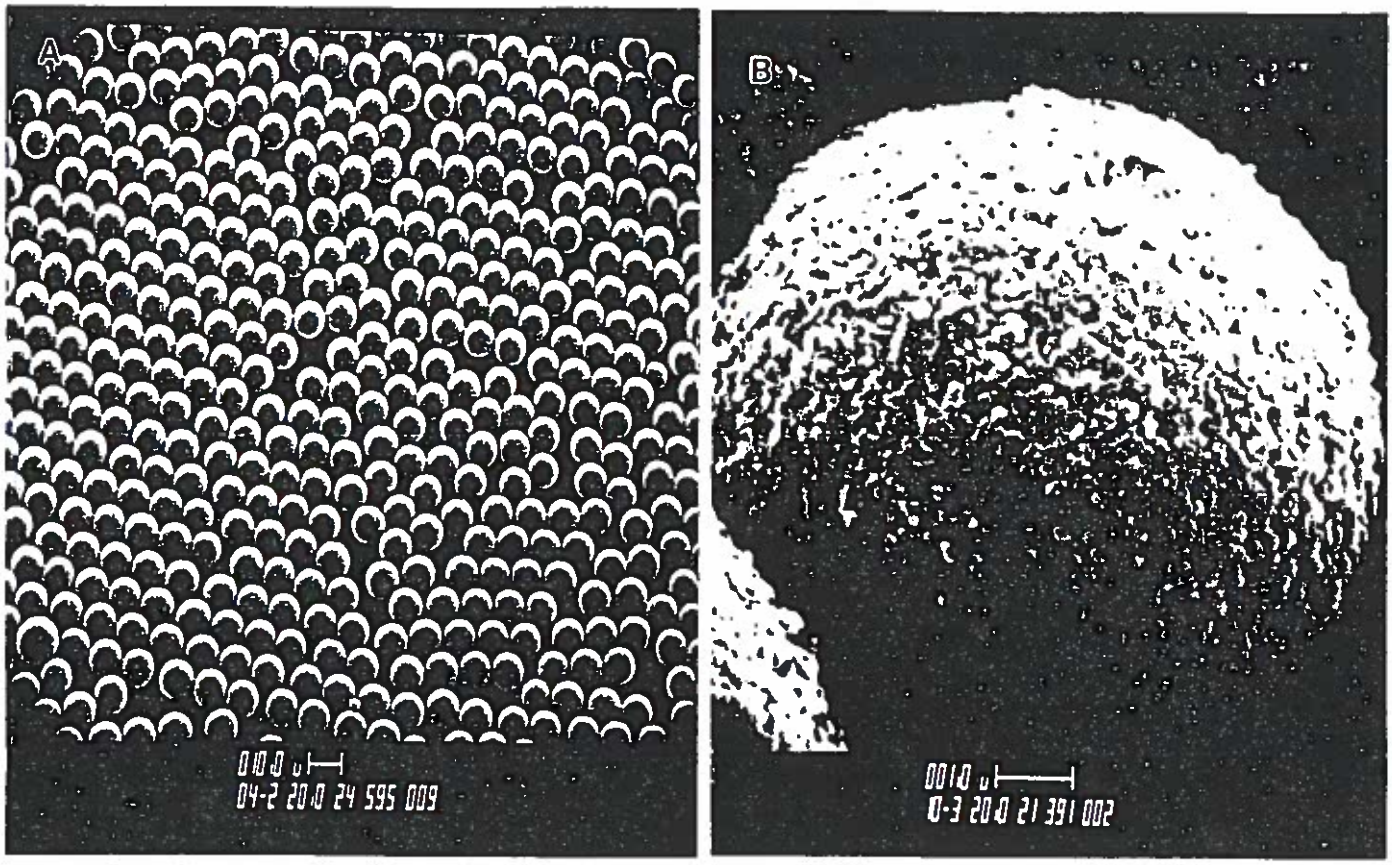

Figure 3: *Scanning electron micrographs of the 11μm monodisperse porous styrene-divinylbenzene copolymer particles: (left) magnification 400x; (right) 10,000x; diluent: linear polystyrene/n-hexane, 15% DVB, MW(linear polymer) = $1.49x10^6$.*

Mercury porosimetry and nitrogen adsorption-desorption were used together to assess pore structure and pore size distribution. The pore size distribution was very sensitive to the molecular weight of the polystyrene latex particles used as inert diluent as shown by the results given in Figure 4. The results of these measurements indicated qualitatively that the particles were macroporous in nature (average pore diameter > 500Å). As the molecular weight of the polymer decreased, the porous particles ranged in complexity across the spectrum of macro-mesopore structures. Scanning electron microscopy revealed the existence of microspheres and their agglomerates within the pores and nitrgen adsorption isotherms confirmed tht the pores were due to the interstices between these crosslinked microspheres and agglomerates.

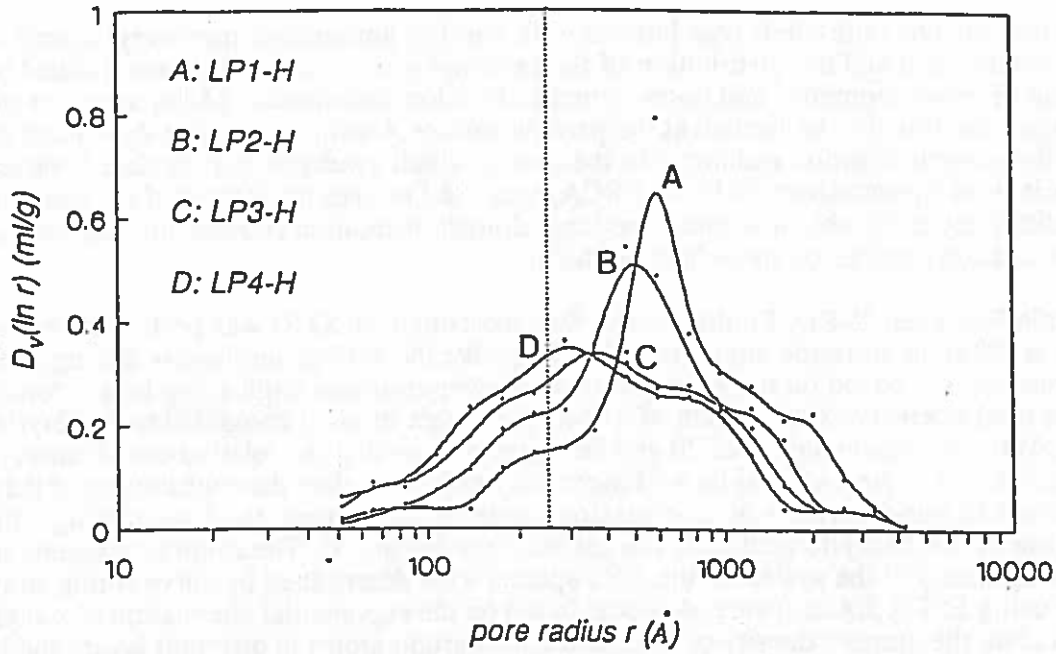

Figure 4: *Pore size distribution of monodisperse porous polymer particles prepared with linear polystyrene seed having different molecular weights (MW) and distributions (PDI): (A) LP1-H, MW=14.9x10^5, PDI=4.98; (B) LP2-H, MW=10.8x10^5, PDI=7.32; (C) LP3-H, MW=5.68x10^5, PDI=16.9; (D) LP4-H, MW=4.46x10^5, PDI=16.0 [diluent: linear polystyrene/n-hexane, 15%DVB].*

The porosity of the particles was found to be consequence of both phase separation during the polymerization and the presence of the diluents. The formation of the pore structure was investigated by changes in copolymerization kinetics, gel content, crosslinking density, particle morphology, surface area, pore volume, and pore size distribution. The sequence of events in the copolymerization was proposed to be the production, agglomeration, and fixation of the interior gel microspheres within the polymer particles. A portion of the linear polymer diluent was found to participate in the network structure while the porous matrix was formed.

3. Synthesis and Characterization of Core-Shell Ionomeric Latexes
(Atul Arora)

Ionomers are defined as polymers containing hydrophobic backbone chains with a small amount of ionic groups attached to the backbone, side chains, or backbone terminals. It is generally accepted that the polar salt groups form ionic aggregates such as multiplets and clusters in the hydrophobic polymer matrix which results in a dramatic increase in the mechanical properties such as modulus, tensile strength, impact resistance, and stiffness. In this project, various core-shell latexes with polystyrene cores and styrene/butyl acrylate/methacrylic acid shells were synthesized which will be neutralized with different counterions in order to achieve ionomeric properties in the films prepared from these latexes. In addition, the influence of the composition of the second stage monomer mixture, the loci and the level of neutralization of the carboxyl groups and the size, and the degree of crosslinking of the polystyrene seed on the mechnical properties of the latex films will be investigated.

So far, various core-shell type latexes with varying amounts of methacrylic acid in the shell were synthesized and the distribution of the carboxyl groups in the shell was studied by the combination of conductometric and potentiometric titration techniques. Major amounts of carboxyl groups were found to be located at the particle surface. Owing to the time dependent nature of the conductometric titration technique in the case of alkali swellable carboxylated latexes, X-Ray Photoelectron Spectroscopy (XPS or ESCA) was used to determine the surface composition more quantitatively to be able to control the ionic domain formation process for various surface loadings of carboxyl groups on these latex particles.

Angle Resolved X-Ray Photoelectron Spectroscopy (ARXPS) was performed on one of the latexes at different emission angles in order to resolve the surface into layers having different compositions. This is based on the principle that at lower emission angles, top layers contribute more to the total intensity. XPS spectra of a core-shell latex of shell composition BA/Sty/MAA, 56/14/30, taken at emission angles of 20 and 90 degrees show that the relative contribution of the ester carbon present in the methacrylic acid increases much more than the contribution of the ether carbon present in butyl acrylate at an emission angle of 20 degrees, thus suggesting a higher concentration of methacrylic acid near the surface (see Figure 5). The relative amounts of the different components of the system in the XPS spectra were determined by curve fitting and peak integration using ESCA 300 software. A model based on the exponential attenuation of x-rays was used to calculate the number density of ester and ether carbon atoms in different layers and hence a depth concentration profile of the shell was obtained as shown in Figure 6. It can be seen that the MAA/BA ratio present at the surface of the particles is more than three times the ratio expected from the composition of the second stage monomer mixture which was fed continuously throughout the reaction. This result also corroborates the high amount of carboxyl groups found at the particle surface by the conductometric titration results. The relationship between the depth concentration profile obtained by XPS and the mechanical properties will be investigated in the near future.

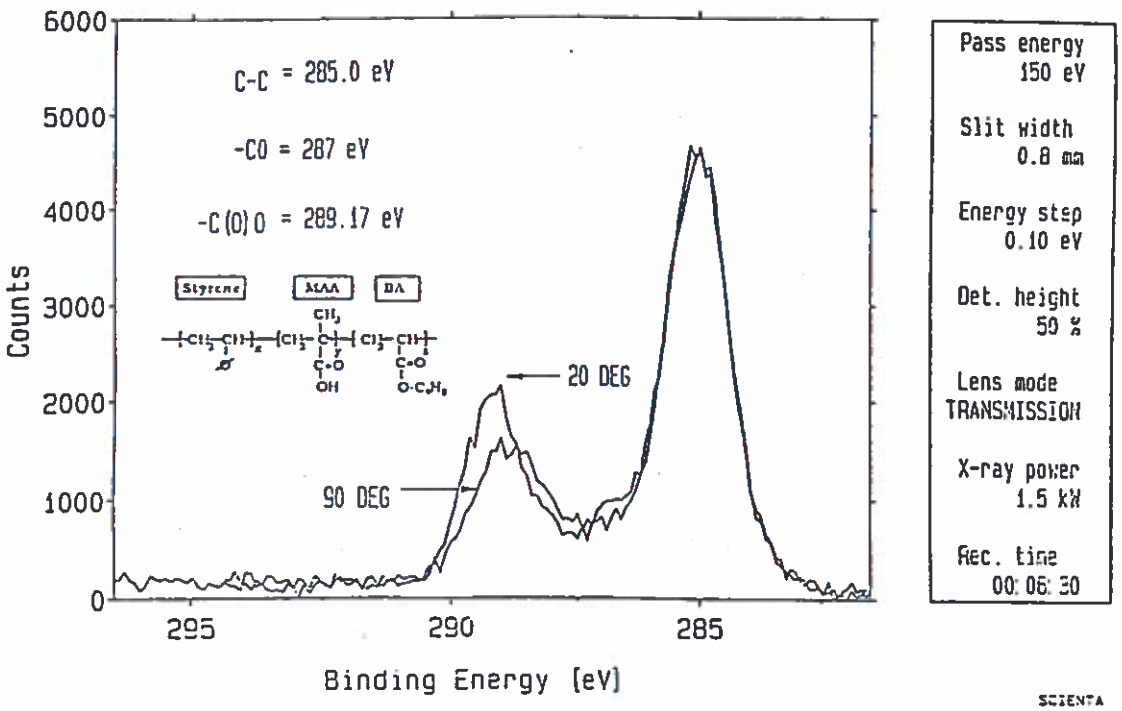

Figure 5: *XPS spectra of a core-shell latex with a PS core and a BA/Sty/MAA shell (56/14/30) taken at two different emission angles.*

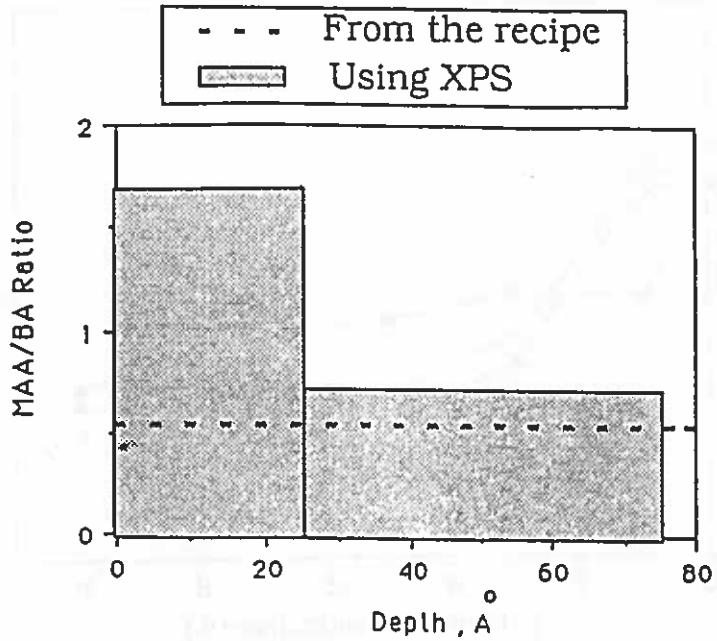

Figure 6: *Depth concentration profile of the latex of Figure 5 as determined by XPS.*

Differential Scanning Calorimetry on these core-shell latexes revealed that the glass transition temperature increases with the level of neutralization of the carboxyl groups which confirms the ionomeric behavior of these latex films. Dynamic Mechanical Analysis (DMA) and tensile testing is currently underway to study the enhancement of mechanical properties due to ionic aggregate formation.

4. The Role of Compatibilizing Agents in the Development of Particle Morphology in Composite Latexes (Wichai Chotirotsukon)

Compatibilizing agents which are block or graft copolymers are known to be used to improve the interfacial adhesion in immiscible polymer blends. They lower the interfacial tension between the polymer phases so that the degree of compatibility is increased. In composite latexes, the interfacial tension has been shown to be the main parameter controlling the degree of phase separation. So if we can incorporate the compatibilizing agent at the polymer/polymer interface in the composite latex particles, the morphology may be controlled more readily.

In this research project, the above concept is being applied to prepare composite latex particles of two immiscible polymers, poly(butyl acrylate) and poly(methyl methacrylate). The interfacial tensions between polymer solutions (in toluene) of varying concentration and a surfactant solution (5mM sodium lauryl sulfate) were measured and are shown in Figure 7. The interfacial tensions for the graft copolymer are lower than those for the poly(butyl acrylate) except at the lowest concentration measured and the values basically parallel those for the poly(methyl methacrylate). If we can modify the surface of the poly(butyl acrylate) with the graft copolymer, the interfacial tension between this and the poly(methyl methacrylate) should be decreased, thus reducing the degree of phase separation.

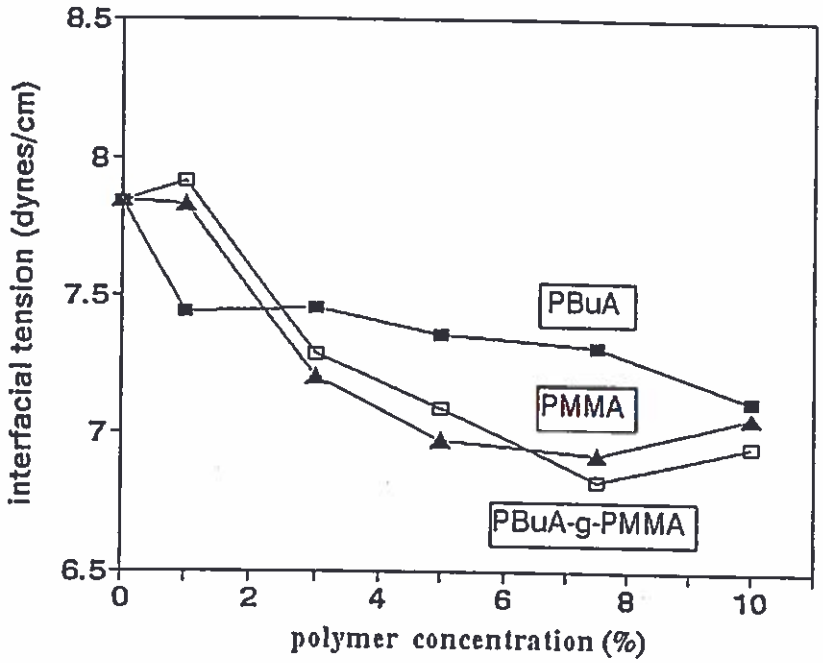

Figure 7: *Interfacial tension between polymer solutions (in toluene) and 5mM SLS.*

The compatibilizing agents were synthesized from macromonomers of poly(methyl methacrylate). This synthesis was carried out either prior to seed preparation or by *in situ* polymerization during seed preparation. This poly(butyl acrylate) seed was made by the miniemulsion polymerization process for subsequent incorporation of the second stage polymer (poly(methyl methacrylate)). The particle size distribution of the seed was determined by transmission electron microscopy (TEM). A smaller particle size and broader distribution was found for the poly(butyl acrylate) latexes produced when the macromonomers were included in the miniemulsion recipe.

The morphology of the composite latex particles will be investigated by TEM to determine the effect of the type and amount of compatibilizing agent. Differential Scanning Calorimetry (DSC) and Dynamic Mechanical Spectroscopy (DMS) will be used to study the degree of compatibility.

5. Role of the Interphase Region in the Transport of Small Molecules Through Polymeric Systems (C. Rodrigo Correa C.)

The interest that exists in the study of the transport of small molecules through polymer films (membranes) is due to the fact that a number of important theoretical and practical applications depend wholly or in part on such phenomena. The transport of small gas molecules through a polymer film is sensitive to the molecular structure and to the degree of intermolecular entanglements in the film. Transport phenomena studies in polymers have been used as tools for investigating polymer properties. These studies provide a means of detecting small morphological changes by means of a large change in the transport properties.

Changes in morphology with processing conditions and phase ripening on aging are considered as major characteristics of heterogeneous polymeric blends. From the practical point of

view, heterogeneous polymeric systems are advantageous because, as has been demonstrated experimentally, the dispersed phase improves the toughness of brittle polymers or has a reinforcing effect. A common way to obtain heterogeneous polymeric systems which are stable and reproducible is by stabilization of the phases, which is known as compatibilization or alloying. However, these methods of stabilization involve addition of an agent which will modify the interfacial properties of the polymeric system and simultaneously generate an interphase region. In the case of composite materials in which the filler (discontinuous phase) is dispersed in a polymer matrix (continuous phase), a similar interfacial region exists. Mechanical properties of the filler-matrix composite depend not only on the properties of each component but also on the nature of the filler surface, the nature of the bonds between filler and matrix, and the mechanism of load transfer at the interface or in the interphase region. Therefore, the inherent problem of these systems is the continuous-discontinuous phase interface which is considered a critical link that provides the structural integrity. Conventionally, the interface is considered to have zero thickness. Theoretical studies have shown that insertion of an interphase region can improve impact strength without decreasing the elastic mechanical properties of the polymeric system.

An interesting question is whether the characteristics of the interphase region significantly affect transport processes. This aspect is especially relavent since some of the observed experimental findings could be explained based on these effects. A possible approach to resolve this question is illustrated in Figure 8. This approach consists basically of two experimental steps. A discontinuous phase (filler or polymer) with known characteristics is blended with a well charcterized polymer. After blending, a heterogeneous film is formed with a well-defined interface between the two phases. Such a sharp interface is due to the incompatibility between the phases. Secondly, if the same discontinuous phase is used but compatibilized, alteration of the interfacial characteristics is expected. A blend of this material with the same continuous phase under the same conditions will produce another heterogeneous system. Any comparative experiments conducted on these two systems will be useful in evaluating the importance of the interphase region.

In this work the following approach is being taken. Core-shell latex particles, prepared by emulsion polymerizaton, are being used as a model to simulate the interphase region. Model polymer films with differing morphologies can be prepared from latexes, these being similar to those found in filled systems or in polymer alloys. The resulting filled barrier systems lend themselves advantageously to theoretical treatment since the transport properties of their isolated polymers can be determined and calculated from data on homogeneous films. Multiphase polymer films comprised of high and low permeability polymers of various compositions cast from latex mixtures are being used.

Poly(n-butyl methacrylate) with a glass transition temperature of about 27°C is used as a high permeability rubber and poly(vinylidene chloride) as the low permeability polymer. Poly(vinylidene chloride) is recognized as an outstanding barrier polymer but the homopolymer is highly crystalline and as such is undesirable as a non-Fickian diffusion model. The crystallinity can be destroyed by incorporation of 15 mole % of a methacrylic comonomer, in the present case n-butyl methacrylate, which does not substantially change the barrier properties but renders the polymer to be in the rubbery region at room temperature. Thus, the second polymer will be poly(vinylidene chloride-co-n-butyl methacrylate). The model heterogeneous system is illustrated in Figure 9. This system was selected because its glass transition temperature is in a convenient range and a great deal of kinetic information exists on the copolymerization of these two monomers. In addition, the thickness and transport characteristics of the simulated interphase (the shell) can be altered by changing the monomer ratio in the copolymer. Since the polymer is nonpolar and amorphous, the free volume theories are expected to be applicable in the temperature range above the glass transition.

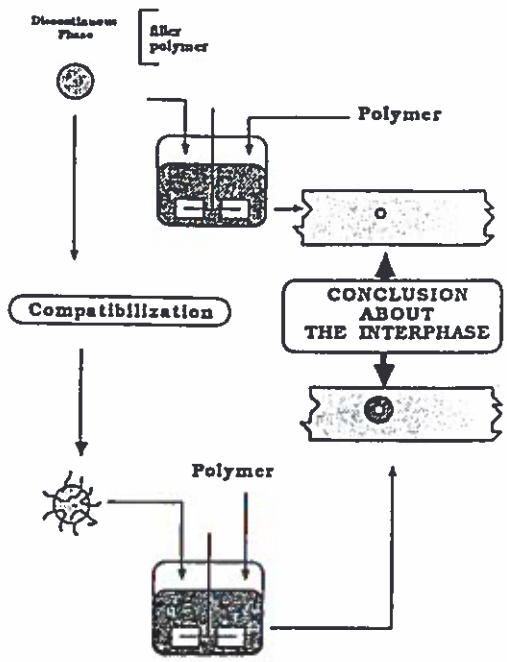

Figure 8: *Conventional Approach.*

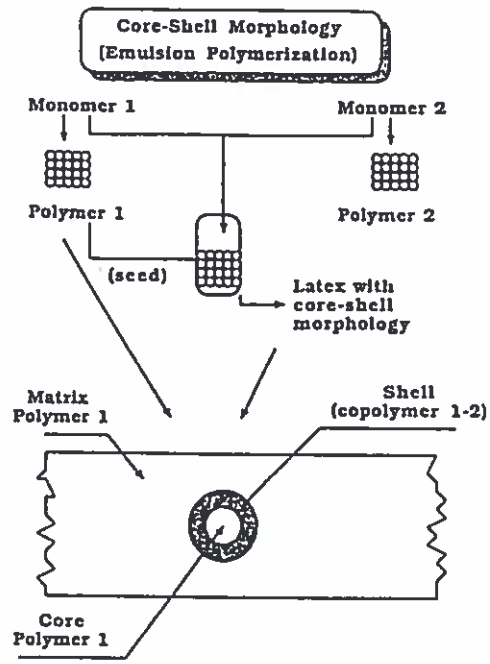

Figure 9: *Simulation of the Interphase.*

Some initital results are presented in the following. Figure 10 shows the glass transition temperatures of the vinylidene chloride/n-butyl methacrylate copolymers as a function of their composition. The variation of the permeability coefficient of nitrogen for films cast from latex blends of poly(n-butylmethacrylate) and vinylidene chloride/n-butyl methacrylate copolymer latexes is shown in Figure 11. A mathematical model is currently being developed to describe the permeability in heterogeneous polymeric systems for comparison to these findings.

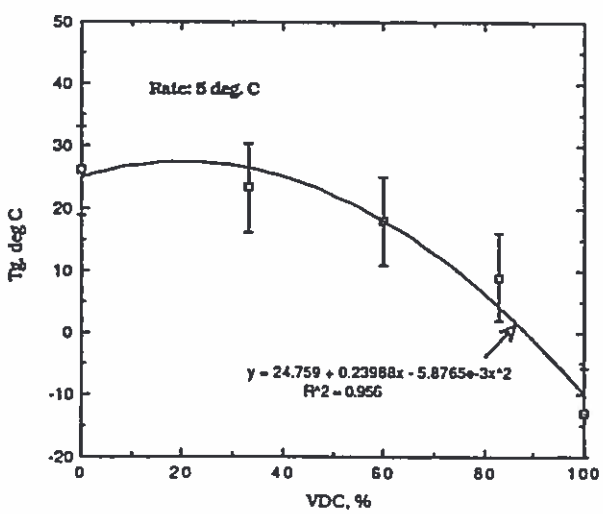

Figure 10: *Variation of T_g of the vinylidene chloride/n-butyl methacrylate copolymer.*

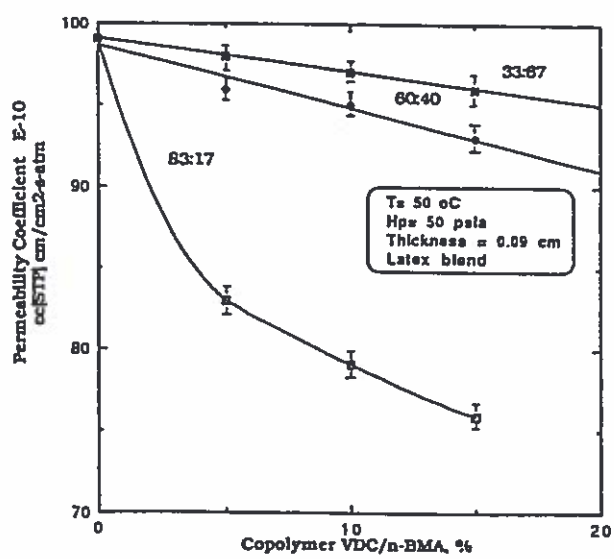

Figure 11: *Permeability coefficient of films vs composition of latex blends of poly(n-butyl methacrylate) and 3 copolymers of vinylidene chloride/n-butyl methacrylate.*

6. The Role of Water Soluble Oligomers in Emulsion Polymerization
(Claudia Kokkeler)

In the preparation of styrene-butadiene (SBR) or acrylonitrile-butadiene (NBR) carboxylated latexes, acrylic and/or methacrylic acid as well as acrylamide comonomers are generally used. Nucleation of particles in systems with such water soluble comonomers starts with the formation of water soluble oligomeric radicals. These radicals can grow to some critical size at which point they precipitate to form primary particles (i.e., homogeneous nucleation) [R.M. Fitch and C.H. Tsai, in "Polymer Colloids", R.M. Fitch, ed., Plenum Press, New York, 1971, p.73]. These particles are stabilized by surfactant, ionic charges from the initiator end-groups, and ionic charges from the carboxyl groups. Oligomeric radicals formed thereafter can: 1) grow to the critical size and form particles; 2) be captured by existing particles; or 3) terminate in the water phase. When a termination event (e.g., with another oligomeric radical) takes place , the resulting oligomer can be located in the water phase (serum), absorbed at the particle surface, or buried in the particle. Oligomers will affect the incorporation of the water soluble monomers in the latex particles and thus the final latex properties.

The objectives of this research are to determine the rate of formation of oligomers, their characteristics (e.g., solubility, composition) and their effect on the final latex properties as a function of the process parameters.

A model latex was prepared of styrene, butadiene, and acrylic acid as given in Table 1. The reaction was carried out via batch polymerization in 30 ml glass pressure bottles. Reaction times (0 to 24 hrs) and reaction temperatures (70, 80, or 90°C) were varied. With the initiator concentration used in this recipe, the reaction rate was found to be too high to enable investigation of the initial stages of the polymerization process. Therefore, reactions were carried out with 1/2 and 1/3 of the original initiator concentration. Separation of the serum from the polymer particles was achieved by ultracentrifugation (37000 rpm, 20 hrs). The particles were then coagulated in three freeze-thaw cycles and the polymer removed. The solids content of the serum was determined for the reaction employing 0.025 g ammonium persulfate and is shown in Figure 12. This reaction was essentially complete in 4 hrs. The solids content was found to be constant, within the experimental error, at about 1.29%. The solids content would be 1.8% if no reaction occurred.

Table 1: Recipe for Model Carboxylated Styrene/Butadiene Latex*

Component	Amount (g)
Distilled-deionized water	16.5
Sodium lauryl sulfate	0.17
Sodium hydroxide	0.08
Styrene	3.98
Butadiene	2.97
Acrylic acid	0.29
Ammonium persulfate	0.05

2.3% on monomer

* total solids = 30%; oil/water ratio = 0.411

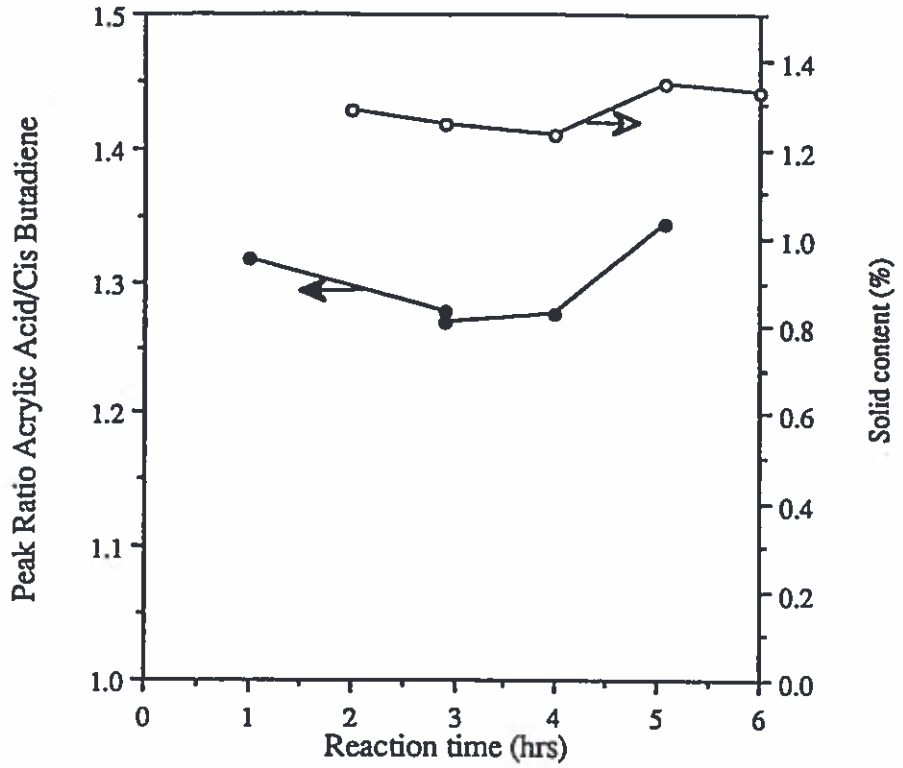

Figure 12: *Serum analysis as a function of reaction time: open circles represent the solids content of the serum; closed circles, the peak ratio of acrylic acid/cis-butadiene by FTIR.*

Fourier Transform Infrared Spectroscopy was used to determine the oligomer composition. Characteristic infrared peaks for a styrene-butadiene-acrylic acid terpolymer were determined. In the spectrum of the serum, the bands for the cis C=C stretch of butadiene (at 1640 cm^{-1}) and the acrylic acid group (at 1560 cm^{-1} in the presence of Na ions) in the oligomers can be located. The characteristic peak for styrene at 698 cm^{-1} could not be found. This can be explained by the higher water solubility of the butadiene (15 mM) compared to styrene (3.5 mM) [J.W. Vanderhoff, *J. Polym. Sci., Polym. Symp.*, **72**, 161 (1985)]. The ratio of acrylic acid to butadiene content in the oligomers is also shown in Figure 12. More experiments are to be done to determine significant trends in the amount of acrylic acid vs butadiene in the oligomers.

Papers Recently Presented

The following were presented at the Spring Meeting of the ACS in Atlanta, GA, April 1991:

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

"Miniemulsion Polymerization -- A Study of Preparative Variables", P.L. Tang, E.D. Sudol, C.A Silebi, and M.S. El-Aasser.

"Small-Particle-Size Poly(Alkylaminoalkyl Methacrylate-co-Alkyl Methacrylate) Latexes", J.W. Vanderhoff, J.M. Park, I. Segall, and S.H. Hong.

"Seeded Emulsion Polymerization Utilizing Miniemulsions", P.L. Tang, E.D. Sudol, M.S. El-Aasser, M.E. Adams, and J.M. Asua.

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

"Emulsion Polymerization and Latex Technology", E.S. Daniels, V.L. Dimonie, O,L. Shaffer, E.D. Sudol, and M.S. El-Aasser.

"Emulsion Coplymerization of Poly(Alkylaminoalkyl Methacrylate-co-Alkyl Methacrylate)", J.W. Vanderhoff, J.M. Park, and I. Segall.

"The Rate of Transport of Monomer Into Latex Particles ---- A Mimetic Membrane Effect?", J.W. Vanderhoff, A. Klein, and J.-I. Kim.

The following papers were presented at the Fall Meeting of the AIChE in Chicago, IL, November 1990:

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

"Monodisperse Macroporous Styrene-Divinylbenzene Copolymer Particles", C.-M. Cheng, M.S. El-Aasser, and J.W. Vanderhoff.

"Effect of 1-Pentanol and Sodium Dodecyl Sulfate Concentrations on the Partitioning Behavior in Styrene Oil-in-Water Microemulsions", J.S. Guo, M.S. El-Aasser, E.D. Sudol, H.J. Yue, and J.W. Vanderhoff.

Recent Publications

"Mathematical Modeling of Seeded Miniemulsion Copolymerization for Oil-Soluble Initiator", V.S. Rodriguez, J.M. Asua, M.S. El-Aasser and C.A. Silebi, *J. Polym. Sci.*, **29**, 483-500 (1991).

"Effects of Electrolyte on the Electrokinetic Properties of Toluene-in-Water Miniemulsions", R.J. Goetz and M.S. El-Aasser, *J. Colloid and Interface Sci.*, **142**, No.2, 317-325 (1991).

"Role of Itaconic Acid in Latex Particle Nucleation", M.R. Lock, M.S. El-Aasser, A. Klein, and J.W. Vanderhoff, *J. Appl. Polym. Sci.*, **42**, 1065-1072 (1991).

"Interfacial Phenomena Controlling Particle Morphology of Composite Latexes", Y.C. Chen, V.L. Dimonie, and M.S. El-Aasser, *J. Appl. Polym. Sci.*, **42**, 1049-1063 (1991).

"Optical Microscopy of Lyotropic Mesophases in Dilute Solutions of Sodium Lauryl Sulfate-Lauryl Alcohol (or Cetyl Alcohol)-Water Systems", C.C. Ho, R.J. Goetz, M.S. El-Aasser, J.W. Vanderhoff and F.M. Fowkes, *Langmuir*, **7**, 56 (1991).

"Infrared Studies on the Grafting Reactions of Poly(vinyl alcohol)", N.J. Earhart, V.L. Dimonie, M.S. El-Aasser and J.W. Vanderhoff, in Polymer Characterization, ACS Advances in Chemistry Series, **19(227)**, 175 (1990).

"Phase Compositions of Styrene Oil-in-Water Microemulsions", J.S. Guo, M.S. El-Aasser, E.D. Sudol, H.J. Yue and J.W. Vanderhoff, J.S. Guo, M.S. El-Aasser, E.D. Sudol, H.J. Yue and J.W. Vanderhoff, *J. Colloid and Interface Sci.*, **140**, 175 (1990).

"Measurement of Permeability, Diffusion and Solubility Coefficients. A Testing Method", C.R. Correa-C. and A. Klein, *Polymer Testing*, **9**, 271 (1990).

"Preparation of ABS (Acrylonitrile/Butadiene/Styrene) Latexes Using Hydroperoxide Redox Initiators", E.S. Daniels, V.L. Dimonie, M.S. El-Aasser and J.W. Vanderhoff, *J. Appl. Polym. Sci.*, **41**, 2463 (1990).

"Evaluation of Alkylated Diphenyl Ether Disulfonate Surfactants in 60:40 Styrene-Butadiene Emulsion Copolymerization", J.W. Vanderhoff, V.L. Dimonie and M.S. El-Aasser, *J. Appl. Polym. Sci.*, **41**, 1549 (1990).

Recent Ph.D. Dissertations

"The Fundamental Thickening Mechanism of Associative Polymers in Latex Systems: A Rheological Study" by Richard D. Jenkins.

"Formation and Stabilization of Oil-in-Water Miniemulsions" by Richard J. Goetz.

Copies of the Abstracts are available upon request.

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Lehigh University

Graduate Research Progress Reports
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Contribution to the International Polymer Colloids Group Newsletter

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Catalytic effect of ionenes adsorbed on latices in the oxidation of thiols

Introduction

In our laboratory the thiol oxidation reaction has been used as a model system for studying macromolecular effects on catalytic groups:

$$4\ RSH + O_2 \rightarrow 2\ RSSR + 2\ H_2O$$

RSH: thiol, usually 2-mercaptoethanol.

This reaction is catalyzed by cobaltphthalocyanine tetra(sodiumsulphonate) (CoPcTS, Figure 1).

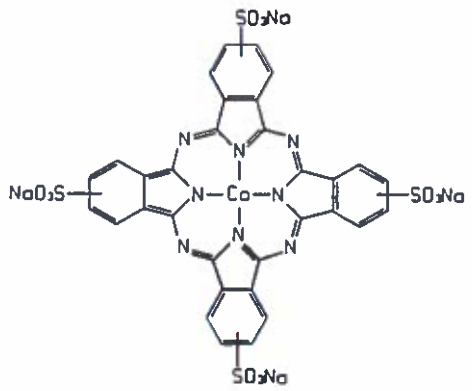

Figure 1: Structure of Cobaltphthalocyanine tetra(sodiumsulphonate) (CoPcTS)

The thiol oxidation is carried out under basic conditions because the thiolate anion is the active species.

A strong (50 fold) increase in the catalytic activity of the CoPcTS catalyst is found

when polycations are added to the reaction mixture. At first it was thought that this increase was due to an increase in the local concentrations of both CoPcTS and the thiolate anion by the polycations. However, the increase in the catalytic activity is too large to be attributed to a concentration effect alone. It was found that the CoPcTS forms dimers or even higher aggregates whereas the formation of catalytically inactive, oxygen bridged dimers is prevented in the presence of polycations [1].

After this effect was found attempts were made to immobilize ionenes (poly(quaternary ammonium)salts) (Figure 2) on resins in order to facilitate separation of reaction products and catalyst [2]. However, when using this type of support mass transport limitations were observed and therefore it was decided to immobilize ionenes on much smaller particles, viz. latices. Because of the very small particle size of latices a large surface area is obtained, without pores, and therefore occurrence of mass transport limitations is very unlikely in this case.

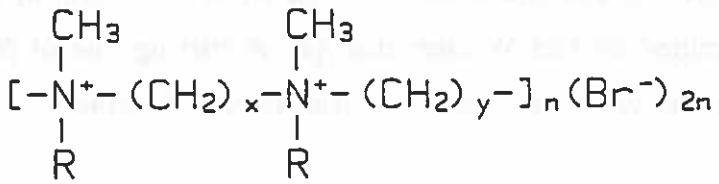

Figure 2: Structure of x,y-ionene

Three different ways to immobilize ionenes on latices have been considered:

1-preparation of an anionic latex followed by immobilization of the ionene through electrostatic interaction;

2-preparation of a functionalized latex followed by reaction of the functional group with an ionene;

3-use of ionene-containing macromonomers, surfactants or macroinitiators in the emulsion polymerization of vinyl momomers

In this paper the preparation of anionic copolymer latices of styrene and sodium styrene sulphonate, the immobilization of ionenes on these latices by electrostatical interaction, and the performance of the so prepared catalysts in the autoxidation of 2-mercaptoethanol will be described.

Experimental part

2,4-ionene was synthesized according to Rembaum et.al. [3]. The molecular weight of the product was determined by potentiometric titration of the amine end groups with 0.1 M hydrochloric acid. The latices were prepared by emulsifier free emulsion copolymerization of styrene and NaSS as described by Kim [4].

To a stirred solution of 0.3 g ionene (number averige molecular weight 11.5 10^3) in 100 ml water, 100 ml latex (10 % solids) was added in about 20 minutes, using a dropping funnel. The resulting ionene/latex complex was purified by repeated ultracentrifugation till no desorbed ionene could be detected in the serum. This detection was carried out according to the method given by Van Streun [2]; detection limit $[N^+] = 3\ 10^{-7}$ M.

The catalytic activity of the latices were measured at 25 °C and at an oxygen pressure of 1 atm, as described by Van Welzen et.al. [1]. A stirring rate of 2600 rpm was found to be sufficient to prevent gas-liquid mass transport limitations [1].

Results and discussion

No coagulation was observed during the immobilization of the ionenes on the latices, although this process involves a charge inversion. The latex/ionene complex was ultracentrifugated and redispersed several times. Already after four cycles no free ionene could be detected in the serum. The nitrogen content of the latex/ionene complex was below the detection limit of elemental analysis (i.e. less than 0.2 wt%) and therefore other methods were employed to determine the amount of ionene present on the latex surface. By adsorption of CoPcTS, which adsorbes 1 : 4 to ionene, it was found that the latices contained at least 0.03 % nitrogen. At least, because the fraction of N^+ that takes part in the bonding with the sulphonate groups is not availlable for the adsoption of CoPcTS (and will therefore also not contribute to the cocatalytic activity).

The (co)catalytic activity of the latices in the oxidation of 2-mercaptoethanol was

found to be a function of the initial pH of the reaction mixture, as can be seen in Figure 3. Similar to the homogeneous CoPcTS/ionene system [1] an optimal pH of about 9 was observed.

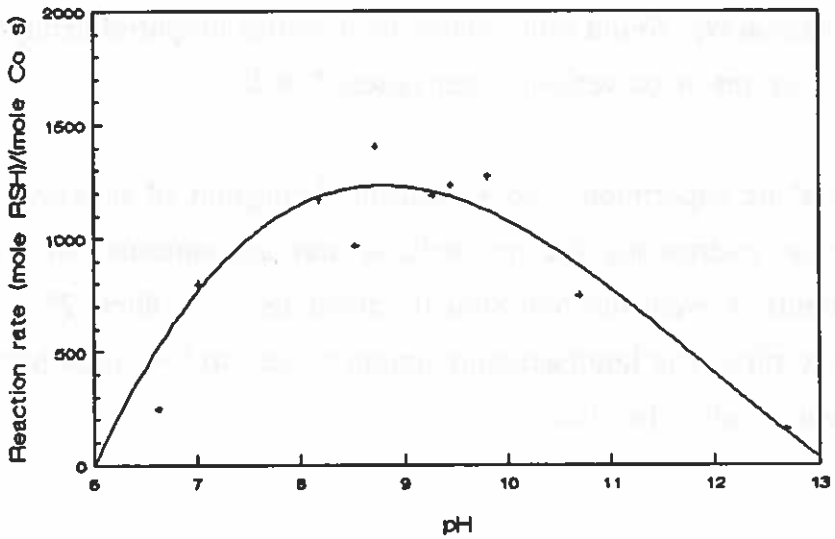

Figure 3: pH-optimum of the latex cocatalyst

In Figure 4 the effect of the latex concentration on the catalytic activity at a constant CoPcTS concentration of 10^{-7} mol l^{-1} is shown. An optimum was observed at 2.5 ml latex (2.1 % solids), this is equal to a N^+/Co ratio of between 12 and 538. These values were calculated using the detection limit of the elemental analysis and the adsorption of CoPcTS as upper and lower limit for the N^+ content of the latex respectively. For the homogeneous CoPcTS/ionene system an optimal N^+/Co ratio of 200 [1] was observed so the N^+/Co optimum of the latex catalyst lies in the same range.

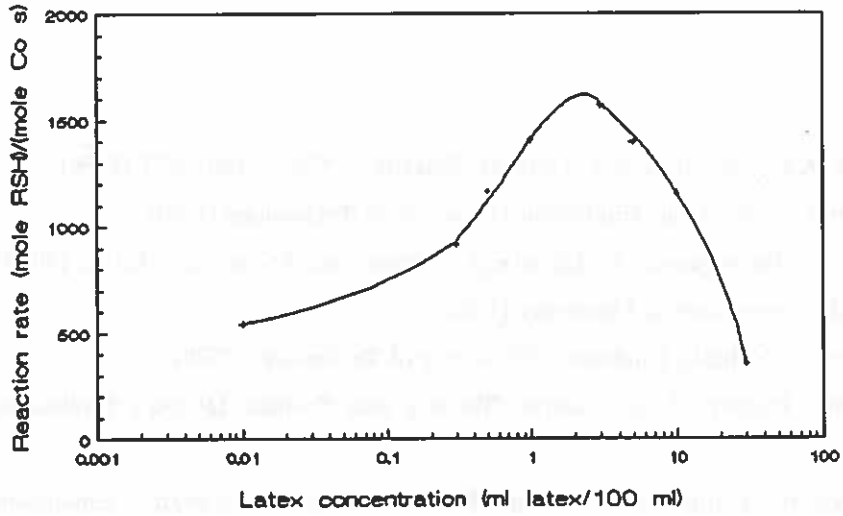

Figure 4: Influence of latex concentration on catalytic activity

The optimal turn over frequency (T.O.F.) of the latex catalyst was calculated to amount to 1700 mole O_2 per mole Co per second, which is lower than observed for the homogeneous system (4000 mole O_2 per mole Co per second) [5]. However, the present latex catalyst was found more active than earlier prepared catalysts, supported on macroporous resins or on various other latices [2,6,7].

During the catalytic experiments no significant desorption of ionene was observed. Scanning electron microscopy did not indicate any agglomerates of latex particles. Reuse experiments showed that only slow deactivation takes place: 25 % deactivation after 14 catalytic runs. The homogeneous system proved to be somewhat more stable: 15 % loss of activity after 14 runs.

Conclusions

Latex supported thiol oxidation catalysts can be prepared by adsorption of ionenes on anionic latices. The so prepared catalysts are very active, even more than the heterogeneous catalysts investigated earlier.

The latex catalysts proved to be very stable. Even at the high stirring rates applied during the catalytic experiments neither desorption of the CoPcTS/ionene complex nor coagulation of the carrier latex could be detected. During repeated catalytic runs only slow deactivation of the catalyst was observed.

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Macromolecules, 1990, *23*. 4206

^{1}H and ^{13}C NMR Investigation of the Intramolecular Structure of Solution and Emulsion Styrene–Methyl Acrylate Copolymers

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Received March 17, 1989; Revised Manuscript Received February 27, 1990

ABSTRACT: The intramolecular structure (triad distribution and tacticity parameter, σ_{SM}) of homogenous styrene (S)–methyl acrylate (M) copolymers, obtained by low-conversion solution polymerization, has been studied by ^{1}H and ^{13}C NMR. With the set of reactivity ratios $r_S = 0.73$ and $r_M = 0.19$ and classical formulas, based on Alfrey–Mayo (AM) kinetics, it was possible to verify the experimentally observed triad distributions. For the methoxy proton region in the ^{1}H NMR spectra it is difficult to make a correct peak assignment. Two different assignments can fit the observed data on triad level. The well-known Ito–Yamashita (I–Y) assignment leads for the random copolymers to a high degree of coisotacticity ($\sigma_{MS} = 0.9$), contrary to the value obtained for alternating copolymers ($\sigma_{MS} = 0.5$). An alternative assignment is possible, which results in $\sigma_{MS} = 0.3$. In order to discriminate between the two assignments, three 2D NMR COLOC experiments were carried out in an attempt to establish the connectivity over three bonds of the carbonyl C=O resonances and the protons of the OCH_3 resonances. However, the correctness of neither of the two ^{1}H assignments of the methoxy resonances could be rigorously proved by means of the 2D NMR COLOC experiments. The cumulative triad fractions and the molar composition of copolymers, obtained up to very high conversion by means of both solution and emulsion batch processes, could be adequately described by models, on the basis of instantaneous distributions according to AM kinetics. In the case of the emulsion copolymerization it is shown that the model for predicting the sequence distribution should account for the monomer partitioning between the oil and water phases. The agreement found between predicted and observed triad distributions was quite satisfactory for both polymerization processes. It was shown that (statistical) emulsion copolymers have the same degree of coisotacticity as the statistical solution copolymers, regardless of whether or not the I–Y assignment is used for the alternative assignment.

Recent dissertation:

G.H.J. van Doremaele, Model prediction, experimental determination, and control of emulsion copolymer microstructure, Ph.D. thesis Eindhoven University of Technology, 1990, ISBN 90-9003718-7.

Macromolecules **1991**, *24*, 1473–1479

Characterization of Intramolecular Microstructure of Styrene–Methyl Methacrylate Copolymers: New ^{1}H NMR Assignments Supported by 2D-NOESY NMR

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Received June 5, 1990; Revised Manuscript Received September 17, 1990

ABSTRACT: The methoxy ^{1}H NMR signals in the δ 2.10–3.70 region for statistical styrene–methyl methacrylate copolymers have been reassigned for several methyl methacrylate centered triad/pentad resonances. Former literature assignments for statistical copolymers were inconsistent with experimental results. New peak assignments are completely based on pentad sequence distributions. Supporting evidence for these reassignments is 2-fold: First, comparison of theoretically calculated and experimentally observed peak areas, and the use of various independent procedures for the determination of the coisotacticity parameter σ, yields consistent results ($\sigma = 0.44$). Second, 2D-NOESY (Nuclear Overhauser effect spectroscopy) NMR experiments were carried out for alternating as well as for statistical copolymers. The results supported the proposed reassignments.

Macromolecules 1991, *24*, 1622–1628

Kinetic Aspects of the Emulsion Polymerization of Butadiene

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Received March 19, 1990; Revised Manuscript Received August 10, 1990

ABSTRACT: Kinetic information on particle growth is obtained for the ab initio emulsion polymerization of butadiene. It is shown that the decrease in particle number by coagulation (induced by the high ionic strength) hardly affects polymerization rate, since the average number of radicals per particle ($\bar{n}$) increases with particle size. From a rate analysis of intervals II and III it follows that the system is "zero–one" ($\bar{n} \leq 0.5$), i.e., termination is not rate-determining. Zero–one kinetics, in combination with a low initiator efficiency, explains the small effect of initiator concentration on polymerization rate. The radical loss mechanism responsible for the zero–one kinetics could not be established unambiguously, but chain transfer/desorption processes involving polybutadiene, thiol, surfactant, and the Diels–Alder dimer 4-vinyl-1-cyclohexene were all refuted on experimental grounds. Desorption of monomeric species seems a reasonable explanation, given the rather low estimate for the propagation rate coefficient.

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April 11, 1991

Professor Dr. H. Napper
School of Chemistry
University of Sidney
New South Wales 2006
Australia

Dear Professor Napper:

Vivian Stannett asked me to write you regarding a possible contribution for the Polymer Colloid Group Newsletter from North Carolina State University. May I suggest the following:

Preliminary investigations have indicated that high molecular weight ($\bar{M}w \sim 500,000$) polyacrylonitrite may be prepared by inverse emulsion polymerization. A narrower molecular weight distribution ($\bar{M}w/\bar{M}n=1.5$) than the most probable was obtained. Proper selection of the oil phase to adjust the partition of acrylonitrile between the oil and water phases was required.

Best regards.

Sincerely,

Richard D. Gilbert

RDG/cmt

cc: V. T. Stannett

RECEIVED
23 APR 1991

CONTRIBUTION TO POLYMER COLLOID GROUP NEWSLETTER SPRING 1991

from

FINN KNUT HANSEN
UNIVERSITY OF OSLO, DEPT. OF CHEMISTRY
P.O.BOX 1033 BLINDERN, 0315 OSLO 3, NORWAY

In connection to the ACS symposium "Preparation, Properties and Applications of Polymeric Latices" in the honor of Bob Fitch, I have once more tried to review the "state of art" in Particle Nucleation. An attempt to reevaluate the mechanism of micellar nucleation has led to the following extended abstract.

THE FUNCTION OF SURFACTANT MICELLES IN LATEX PARTICLE NUCLEATION.

The theory for particle nucleation in emulsion polymerization, traditionally described by the Smith-Ewart (S-E) and Roe theories, has been generally advanced by the work of Fitch & Tsai and Hansen & Ugelstad. These mechanisms have been joined by the label "HUFT" theory, and include the possibility for particles to be formed by 3 different mechanisms, i.e. precipitation of growing oligomers from the water phase (homogenous nucleation), adsorption into emulsifiers micelles as in the S-E-theory (micellar nucleation), and initiation in monomer droplets. The theory also includes the possibility for limited coagulation of the small primary particles, especially in emulsifier-free and low emulsifier cases.

In the last decade, Gilbert & Napper and coworkers have done considerable work in order to discriminate between the nucleation mechanisms. Especially the amount of experimental data has been considerably increased, and quantitative calculations on limited coagulation seem to confirm the theory. However there still seems to be some controversy over the role of the emulsifier micelles, the main question being if and to what degree these are the main locus for nucleation at supermicellar surfactant concentrations. Also the role of water phase termination and the magnitude of the termination constant have been questioned.

When evaluating the role of emulsifier micelles, the full consequences of the Hansen & Ugelstad adsorption equation should be kept in mind; up to now this seems to have been overlooked. This equation describes the <u>net</u> adsorption rate of diffusing molecules (i.e. radicals) into spherical particles of any size, composition and surface potential:

$$\rho_A = 4\pi D_w N r C_w \frac{aD_p(X \coth X - 1)}{D_w + W' a D_p(X \coth X - 1)} = 4\pi D_w N r C_w F \qquad (1)$$

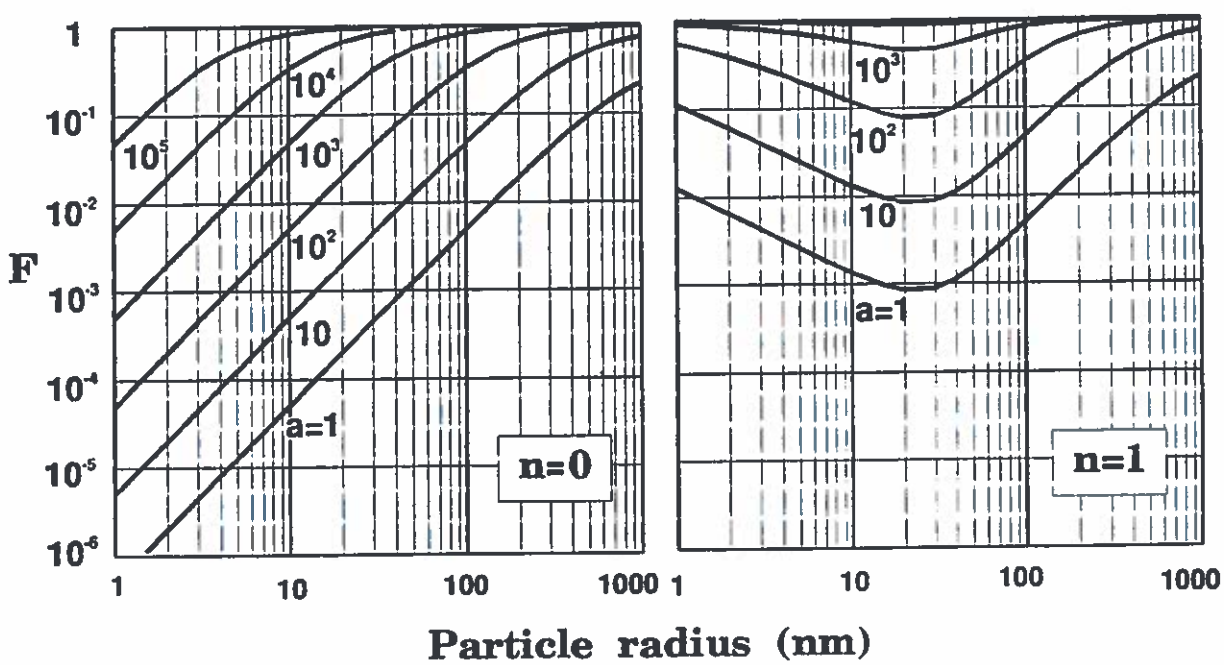
where $X = r\,(k/D_p)^{1/2} = r\,((k_p[M]_p + nk_{tp}/N_A v)/D_p)^{1/2}$

The parameter k is the first order rate constant for reaction of a radical inside a particle. The fraction, denoted by F, is the efficiency factor, describing to what degree absorption is lowered compared to irreversible diffusion. The equation may seem complex, but by inserting realistic values for the parameters, some simple limiting cases appear. Also by plotting F

as a function of particle radius r and the distribution constant a, the true implications of this equation appear. This has been shown in the figure, for particles and micelles without any radicals (n=0), and for particles which contain 1 radical (n=1). The figure (n=0) shows that for relatively small particles, all other than very water insoluble molecules are adsorbed at a **much lower rate** than by irreversible diffusion. The slope +2 (n=0) or -1 (n=1) in the log/log plots corresponds to the equation

$$F = ar^2k/3D_w \qquad \text{meaning that} \qquad \rho_A = (4\pi/3)r^3NakC_w \qquad (2)$$

The slope +2 corresponds to the case where $k = k_p[M]_p$, the rate constant for propagation in particles, whereas the slope -1 corresponds to $k = k_{tp}/N_Av$, so that F becomes proportional to 1/r and ρ_A becomes **independent of particle size.** Equation (2) which is valid for all cases in these figures where F<<1 (say <0.1) corresponds the situation where adsorption in micelles and small particles is **not controlled by diffusion, but by the rate of reaction inside the particles.** This means that radicals are adsorbed at a gross rate equal to the diffusion rate (with F=1), but are **desorbed** again at the same rate, if they do not react inside the particle.



The situation during the particle nucleation period of any monomer where micelles are present, may be visualized by the following:

1. Radicals are created by splitting of the water soluble initiator and add monomer in the aqueous phase because they are not oil soluble (a<<1).

2. Soon the radicals will become partly oil soluble (a≈1) and may absorb into micelles or adsorb at their surface (producing some sort of mixed micelle) at a **net** rate proportional to a and **proportional to the propagation rate.**

3. Reaction in the micelle will lead to an oligomer with one more monomer unit. The value of a for this chain will be larger, but as long

as a is less than the value required for irreversible absorption (ca. 10^6), it will have a chance to desorb again. This must also be the case if the radicals are merely adsorbed, in parallel to the (fast) exchange of surfactant between the surface and solution.

3. We will therefore have a situation where radicals pass through the micelles at a high rate, and eventually increase their chain length by propagation both in the aqueous an in the oil phase. Micelles may therefore be visualized not only as a source of surfactant, but as a **source of total increase in the monomer concentration in the aqueous phase** leading to increased propagation.

The ratio between the rates of particle nucleation in micelles to that in the aqueous phase may simply be taken as the ratio of propagation in these two phases of an oligomer of one less the critical chain length. For monomers of low water solubility (for instance styrene), and thus a low critical chain length in the region 2-5, the difference in a between the different chains is very large, and this model is applicable. For monomers of higher water solubility, such as MMA, VAc or VC, the picture becomes cluttered when a is increasing and F approaches 1 for several oligomers. Still the qualitative picture stays the same. For these monomers also desorption of monomer (or similar) radicals produced by chain transfer becomes important for the nucleation, and these will probably have a lower critical chain length.

We can calculate the ratio between propagation in micelles and water by assuming the equilibrium distribution between the phases both of monomer and of radicals:

$$\rho_{pp}/\rho_{pw} = a_R a_M V \qquad (3)$$

where a_R and a_M are the distribution constants for radicals and monomer, respectively and V the volume fraction of micelles. If V=0.01 (1%) and a_M=1300 (styrene) we see that ρ_{pp}/ρ_{pw} >>1 for all radicals except the smallest, and increases with increasing chain length. Therefore, it seems highly probable that the dominating place for particle nucleation is the micelles. For more water soluble monomers like VAc with a_M=28, the picture becomes somewhat different. A monomer radical with the same value of a will have a propagation ratio of 28*28*0.01=7.8 . Higher radicals will have higher ratios, so that even for these monomers it may seem that micelles should be the dominating source for nucleation as indicated by seed experiment with MMA. Because the number of radicals in the water phase (at the steady state) is usually much smaller than the mumbler of micelles, only few of the micelles can have a propagating radical, even if most of the radicals are distributed in micelles.

The final particle number is reached both as a result of competition between nucleation and adsorption of radicals in particles already formed, as a result of adsorption of surfactant on the new particles and the possibility for limited coagulation of the particles. The depletion of surfactant due to particle growth is according to the S-E-theory. The new particles that contain 1 radical will terminate rapidly because of the increased adsorption rate as shown in Figure 1(ii), and this will hinder the maximum in rate that is predicted by the S-E-theory.

April 26, 1991

Contribution to Polymer Colloids Group Newsletter

by
Mamoru Nomura

Department of Materials Science and Engineering
Fukui University, Fukui, Japan

As have been already announced, "International Symposium on Polymeric Microspheres" will be held in Fukui in Oct. 23(wed)-26(sat), 1991 in cooperation with Lehigh University(EPI), McMaster University(MIPPT) and CNRS(LMO). Provisional program is included for reference in this contribution. In answer to the request by potential contributors, We have decided to provide the Poster Session, so that we are still accepting papers to be presented in the Poster Session. 2nd circular will be soon issued and sent to those who are planing to attend or are interested in this symposium. Special typing sheets and "Instruction for Authors" will be sent by the end of May to those who submitted the papers. We hope that many of the IPCG members will participate in this symposium. Those who are interested in attending this symposium, please contact the symposium secretariat, Professor M. Nomura.

A paper entitled "Kinetics and mechanism of emulsion polymerization initiated by oil-soluble initiators. 2. Kinetic behavior of styrene emulsion polymerization initiated by 2,2'-azoisobutyronitrile." is in the process of printing in J. Polymer Sci. Chem Ed.

A paper entitled "Kinetics and mechanism of particle formation and growth in the emulsion polymerization of styrene initiated by 2,2'-azoisobutyronitrile" has been submitted in the ACS Atlanta meeting. The emulsifier used was NaLS. This paper provide the experimental data which support that:

(1) Polymer particles are produced from the emulsifier micelles.
(2) The loci of polymerization shifts from the monomer droplets to polymer particles at comparatively early stage of the reaction.
(3) The radicals which participate in the polymerization in the polymer are those stemming from the initiator dissolved in the water phase.
(4) The polymerization in the monomer droplets proceeds according to suspension polymerization kinetics and radical desorption into and entry fro the water phase can be neglected.

This paper is scheduled to be finally published in a special book of ACS Symposium Series.

CONTRIBUTION TO POLYMER COLLOID GROUP NEWSLETTER

FROM CNRS/LYON

(SUBMITTED BY C.PICHOT)

Studies on the surface-active and stabilizing properties of zwitterionic emulsifiers (C. GRAILLAT, F.MELIS, LMO)

More work has been recently developped so as to understand the role played by zwitterionic emulsifiers in the formation of latex particles during emulsion polymerization.A comparaison was made between a carboxybetaine (with an intercharge distance of 3 methylene), two sulfobetaines (N-N-dodecyldimethylammoniopropane sulfonate (NC12) and the 3-N-acetyl-N-(dodecyldimethyl ammoniumethyl)aminipropane sulfonate (OXC18)) and two ionic surfactants (SDBS and SDS).At fist, micellar solutions were examined at 60°C by QELS ,under optimal purifying conditions and using a high power laser (working at $\lambda = 514$nm). Results, as below reported, seem to show that stable micelles are obtained with zwitterionic emulsifiers together with a narrow size dispersity (as indicated by the variance).This is not the case with anionic emulsifiers showing wider size distribution and no measurable size value (in the case of SDS). When emulsion polymerization was carried out in the presence of NC12 upon varying the styrene concentration (0 - 40g/l), it was found that the number of polymer particles was near the initial expected number of micelles with a similar particle size dispersity (0.02).These preliminary results might suggest differences in the nucleation mechanism for sulfobetaines, compared to SDS, which could be correlated with the stability of the micelles as well as the strong adsorption energy of those surfactants at the styrene - water interface(as experimentally observed).

Emulsifiant	carboxybetaine	NC12	OXC18	SDBS	SDS
Size (nm)	3	5	6	4	< 2
variance (μ^2/Γ^2)	0.028	0.024	0.038	0.056	-

Characterization of films obtained from latexes prepared by emulsion polymerization using high resolution solid-state ^{13}C NMR (M. HIDALGO, J.GUILLOT, M-F LLAURO-DARRICADES, H.WATON, R. PETIAUD, LMO/SCA/CNRS)

Recent studies have been investigated in cooperation with NMR specialists(SCA/CNRS) in order to use high resolution solid-state ^{13}C NMR so as to discriminate latex films having the same composition consisting in PS inclusions in a poly (butyl acrylate) matrix.The method was based on the measurement of $T1\rho(H)$ values and latexes were prepared owing to various polymerization pathways.It was clearly shown that fims issued from core-shell latexes can be differentiated from those formed from the coalescence of the corresponding homopolymers whereas similar behaviors were exhibited through dynamical mechanical spectroscopy.Moreover, an interphase has been evidenced in the film obtained with the core-shell latex.

Adsorption of proteins onto amphiphilic acrylic acid copolymers - stabilized polystyrene latex particles(A.THERETZ, F.BETTON,H.ELAISSARI, C.PICHOT,UM CNRS/bioMERIEUX)

The adsorption behavior of bovine serum albumine (BSA) onto amphiphilic polyelectrolyte-stabilized polystyrene latexes has been investigated. Special attention was first paid to the preparation of the lauryl acrylate (LA)- acrylic acid (AA) radical - initiated copolymers which were characterized with regards to monomer sequence distributions (LA) and molecular weight .Adsorption of this copolymer (5 % weight in LA) was then carried out onto a negatively - charged polystyrene latex at a selected pH so as to ensure complete surface coverage. In a last step, the adsorption of the BSA onto these hairy-like latex particles have been examined as a function of Ph and buffering conditions and compared with bare particles.

Nucleation of emulsion polymerization in the presence of small silica particles (P. ESPIARD, A. REVILLON, A. GUYOT(LMO) and in collaboration with J.E . MARK(Univ. of Cincinatti - Ohio USA)
(Abstract of a paper given at the recent ACS Meeting - April 1991)

Several silica were used : either non functionalized silica from commercial origin or prepared according to the Stöber method, or functionalized silica prepared upon surface coverage of non functionalized silica with functional coupling agents such as $X(CH_2)_3Si(OR)_3$ where X is either a methacryloyl group or the precursor amino group for an azo compound. Some organophobic silica can be prepared via a sol-gel process from cohydrolysis and cocondensation of tetraethoxysilane (TEOS) and the functional coupling agent with water in inverse microemulsion in the presence of a suitable surfactant. The average diameter of the silica particles is in the range 20-90 nm. When the silica is hydrophilic, encapsulation with polymer upon emulsion (co)polymerization of highly hydrophobic monomers (styrene, butyl acrylate) is not observed : a regular latex is produced independently from the silica, even if coverage of silica with surfactant has been previously carried out. Partial success has been obtained using limited amounts of methylmethacrylate. Very good results have been obtained for ethylacrylate polymerization with a semi-continuous feed process, provided a suitable non ionic surfactant is used. The dispersability of functionalized silica is poor, but may be improved after a suitable treatment with ammonia, and a combination of an alcohol and a non ionic surfactant. Then, each latex particle is nucleated by the silica, again in the case of ethylacrylate.

Recent Papers:

Structural morphology of polystyrene-polybutylacrylate polymer-polymer composites studied by mechanical spectroscopy
J.Y. CAVAILLE, R. VASOILLE, G. THOLLET, L. RIOS and C.PICHOT - Colloid Polymer J in press , april 1991

Ordering of latex particles during film formation
M. JOANICOT, K. WONG, J. MAQUET, Y. CHEVALIER, C. PICHOT, C. GRAILLAT, P. LINDNER, L . RIOS and B. CABANE
- Prog.Colloid Polym. Sci. 81, 175(1990)

Preparation and characterization of low size polystyrene latex particules with various strong acid surface charges
C. GRAILLAT - C. PICHOT - A. GUYOT - Colloids and Surfaces, in press (May,1991).

Stability of polystyrene latexes covered with zwitterionic - sulfobetaine type emulsifiers
C. GRAILLAT - B. DUMONT - P. DEPRAETERE - V. VINTENON - C. PICHOT - Langmuir. in press (Avril,1991).

Radical - initiated copolymers of styrene and p. formyl styrene.
I - Synthesis and characterization of solution copolymers
B. CHARLEUX - C. PICHOT - M. F. LLAURO (In press, Die Makromolekulare Chemi(1991).

II - Preparation and characterization of emulsifier - free copolymers latexes.
B. CHARLEUX - P. FANGET - C. PICHOT. (In press , Die Makromolekulare Chemie 1991).

Synthesis and characterization of emulsifier- free quaternarized vinylbenzylchloride latexes
B. CHARLEUX, C. GRAILLAT, Y. CHEVALIER, C. PICHOT, A. REVILLON
in press-Colloid and Polym.Sci. (avril 1991)

Swelling of polybutadiene as latex particles and cast films by styrene and acrylonitrile monomers
P. MULLER and J. GUILLOT in Polymer 199,32, n°5,934 (1991)

Newsletter Contribution from The University of Akron
by Dr. I. Piirma
Institute of Polymer Science
Akron, Ohio 44325-3909

Polymerization of Butadiene and Acrylonitrile
Report by Sam Laferty

A two stage polymerization was used in this study. In stage one, an azeotropic composition of butadiene and acrylonitrile was emulsion polymerized. In stage two the butadiene-acrylonitrile copolymer (BD-AN) was used as a seed particle for the polymerization of acrylonitrile and methyl acrylate copolymer (AN-MA). The acrylonitrile to methyl acrylate ratio used was 75:25 by weight. The weight ratio of seed polymer to second stage monomers is 1:10. The methyl acrylate was used to make the acrylonitrile melt processable. Normally acrylonitrile polymer is paracrystalline and not melt processable. The surfactant used was sodium dodecyl sulfate.

The second stage latex particles formed could be one phase or two polymer phases depending on the crosslink density of the seed latex used. The second stage latex was characterized by DMTA (dynamic mechanical thermal analysis), TEM examination of the particles, and by TEM examination of thin sections of bulk polymer sliced with a microtome. All three methods confirmed that one phase and two phase latex particles could be formed. Other variables on the second stage polymerization were studied. The effect of temperature, surfactant, water, co-surfactants, and chain transfer agent on the second stage polymerization were noted. The dou bling of the chain transfer agent concentration or the addition of BC-840 nonionic surfactant could change the second stage morphology of two phase particles from hemisphere to core-shell. This may be due to changing the interfacial tension between the two copolymers or between one copolymer and the aqueous phase.[1]

1. J. Berg, D. Sundberg, and B. Kronberg, *Polym. Mat. Sci. & Eng.*, 54, 367 (1986).

Aqueous Phase Polymerization of Chlorotrifluoroethylene

David Murray and Irja Piirma
The University of Akron

We are beginning to investigate the aqueous phase polymerization of chlorotrifluoroethylene (CTFE) due to several unique characteristics of this system in comparison to typical emulsion polymerization systems. First, CTFE's low water solubility combined with its insolubility in its own polymer creates questions about the exact polymerization locus and mechanism. Secondly, CTFE's semicrystalline nature along with the fact that all polymerization occur below the melting point of the polymer creates questions regarding the important factors controlling the crytallization process. Thirdly, the low boiling point of the monomer results in the rapid evaporation of the monomer after sampling. This allows for the study of particle size characteristics at low conversion without interference of monomer droplets.

A study of the variables influencing the kinetics of the aqueous phase CTFE polymerization has begun using ammonium perfluorooctanoate as the surfactant. The percent conversion versus time curves show typical emulsion polymerization characteristics with a linear rate region from about 10 to 90% conversion.

The rate of polymerizations shows a strong surfactant concentration dependance. This dependency of rate on surfactant concentration appears to be a function of surfactant concentration. The rate of polymerization depends on the initial surfactant concentration to the 0.8 to 1.5 power depending on the surfactant concentration level. The polymerization rate was found to be independent of the initial monomer concentration.

The number of particles formed in the polymerization was found to depend on the initial surfactant concentration to the 3.0 power. The number of particles formed during polymerization changed rapidly over the first 10% conversion and then remained constant.

Work is now in progress which focuses on the early stage nucleation of the PCTFE particles with emphasis on comparing the nucleation process with current theories.

Ph. HEIM, P. TANGBORIBOONRAT and G. RIESS

Ecole Nationale Supérieure de Chimie Mulhouse
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Phase transfer of natural rubber and acrylic latex - development of an emulsion-suspension polymerization process *

A phase transfer technique has been firstly developed by Heim (1) to determine the surface charge of crosslinked synthetic latex such as polystyrene, poly(butyl acrylate) and poly(methyl methacrylate). This technique involves the titration of the anionic stabilized latex with cationic surfactant aqueous solution in the presence of a non-water miscible organic solvent. At a certain concentration of added cationic surfactant (critical transfer concentration, CTC), which is just sufficient to form a hydrophobic layer, the latex particles would be transfered from aqueous phase into organic phase. The titration end point is obtained by observing instantaneously the translucent mixture and finally the clear aqueous phase. The phase separation occured immediately, when the agitation was stopped.

The critical transfer concentration was calculated from the following equation,

$$CTC = \frac{V \times C}{10 \times TS \times m}$$

where,

CTC = critical transfer concentration (mol of cationic surfactant used per gram of dry latex),
V = volume of cationic surfactant used at titration end point (ml),
C = cationic surfactant concentration (mol/l),
TS = solid content of latex (%),
m = weight of latex sample.

Table 1 shows the CTC values of different types of polymer latex. From this table, it can be seen that the CTC values were proportional to the quantity of surface charge of latex particles calculated from the anionic surfactant, SDS, used for the synthesis of latex (Q1). The quantity of negative charge at the particle surface from the decomposition of initiator, $K_2S_2O_8$ (Q2), had little effect on the CTC

values. The determination of CTC by phase transfer technique can be used in all types of polymer latex.

The CTC values were constant and dependent on neither the structure of cationic surfactant nor the mass of latex particles (wt %). The particles can be transfered until wt % was about 70%. The phase separation, however, occured at a certain volume fraction of organic phase of each wt%.

Table 1 : CTC values of different types of synthetic latex using MMA as organic solvent and dodecyldimethylethyl bromide as titrant.

Latex	Q*1 (x 10^{-6})	Q**2 (x 10^{-6})	CTC*** (x 10^{-6})
PBA	10.2	30	11.7
PS	27	40	29
PMMA	99	9.9	85
PB	28	30	29
PBA-co-PS	11	30	14.2

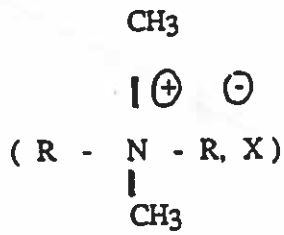
*Q_1 mol of anionic surfactant, SDS, used for the synthesis of latex per gram of dry latex

**Q_2 mol of negative charge from the decomposition of initiator per gram of dry latex

***CTC mol of added cationic surfactant per gram of dry latex

After phase transfer, the particles were homogeneously dispersed and swollen in the organic phase. The stability of particles in this phase came from the polymer - solvent interaction. The organic phase containing the swollen particles was then separated by centrifugation. The swelling ratio would be determined by measuring the size of swollen and unswollen particle.

In the present work, we intend to show that this phase transfer technique can be applied to characterize the surface of γ - radiation vulcanized natural rubber latex (RVNRL) (2). It was found that the negatively charged natural latex, derived from an absorbed layer of a protein-lipid complex, can be transfered in organic phase by titration with quaternary ammonium salts.

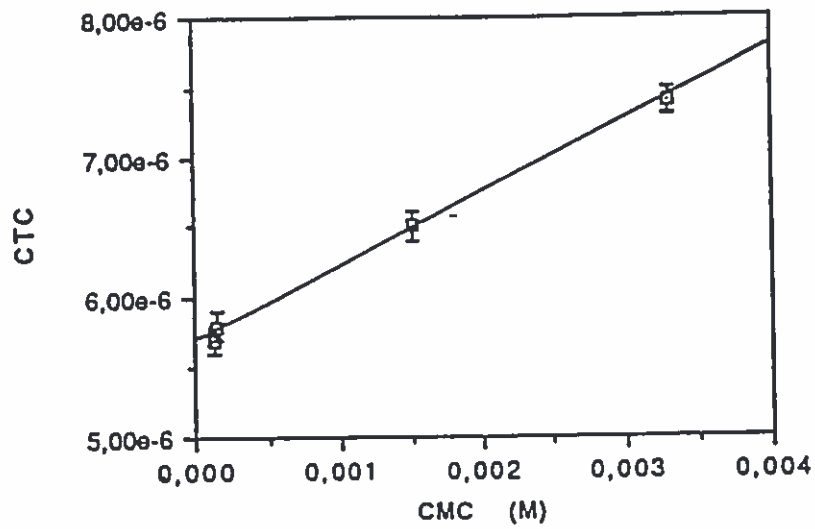


The CTC values are presented in Table 2. From these results, the CTC values depended on the structure of quaternary ammonium salts. They increased when decreasing of carbon chain length of surfactants (CMC increase) and they were constant (reproducible) for each cationic surfactant. Figure 1 shows the relation between the CTC values and CMC of surfactants. We can explain by considering the effect of cationic surfactants on the conformation and aggregation of protein at the surface of rubber particles (3).

Table 2 : CTC values (mol of cationic surfactant per gram of dry latex) of γ-radiation vulcanized natural rubber latex using toluene as organic solvent (wt% = 3,3)

CATIONIC SURFACTANT	CMC ($\times 10^{-3}$ M)	CTC ($\times 10^{-5}$)
Benzyldimethyloctadecyl ammonium chloride	0,12	5.7 ± 0.1
Benzyldimethyloctadecyl ...	0,15	5.8 ± 0.1
Benzyldimethyloctadecyl ammonium chloride	1.5	6.5 ± 0.1
Benzyldimethyloctadecyl ammonium chloride	3.3	7.4 ± 0.1

Figure 1: Relation between the CMC (M) of cationic surfactants and the CTC values (mol of cationic surfactant per gram of dry latex) of γ-radiation vulcanized natural rubber latex.



Like in the case of synthetic latex, the mass of latex (wt%) and the volume of organic phase had no effect on the CTC values. The phase separation occured at $f \leq 0.5$ for all wt%.

The quantity of surface charge of natural latex can be calculated from the CTC. This quantity is certainly an average surface charge for the given latex because the latex particles are not uniform in size.

The transfer technique can also be used to isolate the rubber particles from an aqueous serum phase or to prepare polymer blends such as rubber modified polystyrene.

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* Paper presented at the "REGIO MACRO III" meeting in Strasbourg (February 26-27, 1991).

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ELECTROPHORETIC FINGERPRINTING FOR SURFACE CHARACTERIZATION OF COLLOIDAL PARTICLES

by

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INTRODUCTION

The zeta potential has been widely used as a characterizing parameter in colloid science (1). The zeta potential is the average potential at the surface of shear surrounding a moving colloidal particle so that it links the hydrodynamic radius with various theoretical models of the structure of the double layer. It is calculated from the measurable electrophoretic mobility $u_\varepsilon = v_\varepsilon/E$ which is the particle velocity under unit field strength.

In earlier work (2,3) we reported on modern instrumentation for measurement of the distribution of the electrophoretic mobility. Here we show that the average electrophoretic mobility may be represented as a function of two variables of state: the pH and the pλ which is the negative log of the specific conductance (S/m). The representation of u_ε as a function of pH and pλ is called "electrophoretic topography" and yields a template or "fingerprint" (4,5) as well as details on the fine structure (2,3), i.e., the electrophoretic mobility distribution at a point in the pH-pλ domain.

EXPERIMENTAL

The apparatus, a Pen Kem System 3000 Automated Electrokinetics Analyzer, is described elsewhere (2) and full experimental details may be obtained in (2,3,4 and 5).

RESULTS

In Figure 1 we show the template and fingerprint for a polystyrene latex containing acidic surface groups (carboxyl, R-CO_2H) and basic surface groups (amidine, R-C(NH)(NH_2)) so that the latex is zwitterionic. The behavior is dominated by the carboxyl group over a wide area in the pH-pλ domain. The dashed envelope curve defines the locus in the pH-pλ domain above which the mobility can be measured. The lower domain is shown by the curve-fitting program but it is inaccessible because changing the pH changes the conductance at the same time. Interesting features are the carboxyl-dominated ridge of stability over several orders of pH and the pronounced acid peak in mobility arising from protonation of the amidine group. The isoelectric line at pH 4 is independent of pλ over more than two orders of magnitude giving a classic "isoelectric point." At high pλ, extrapolation of the pH-pλ behavior predicts a migration of the isoelectric line toward more positive mobility or higher surface positive charge. Since double-layer compression acts to lower the mobility, the prediction is for specific adsorption of potassium ion at high pλ.

The fingerprint and template for the TiO_2-KCl system is given in Figure 2. Comparison of the two fingerprints (Figs. 1 and 2) readily shows the characteristic identity of each.

A set of fingerprints are shown in Figures 3 and 4 for two dispersions of carbon black which had a common ancestry. The oxidized carbon black powder, BLACK PEARLS® was manufactured by oxidation of the parent material, the non-oxidized REGAL 660®. Both materials were obtained from the Billerica, Massachusetts Research Laboratory of the CABOT Corporation. The pronounced differences in the fingerprints show the characteristic identity of each.

Finally, we note that each fingerprint is unique in this small catalog of four quite different colloidal systems.

ACKNOWLEDGEMENT

This work was supported by grants from the CABOT Foundation and a contract with the AMOCO Corporation. Technical assistance and instrument support was provided by Pen Kem, Inc. The work is based on the Ph.D. thesis of S.-J. Shiau, presently at DuPont Taiwan Ltd., 7th Fl. International Bldg., 8 Tung Hua North Rd., Taipei, Taiwan, R.O.C.

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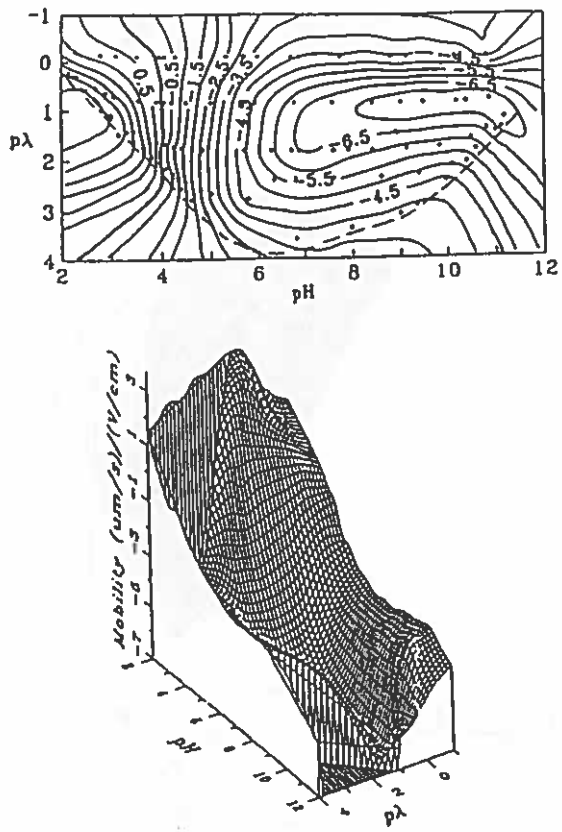

Figure1. The electrophoretic fingerprint and template of the carboxyl-amidine zwitterionic latex (PL-7).

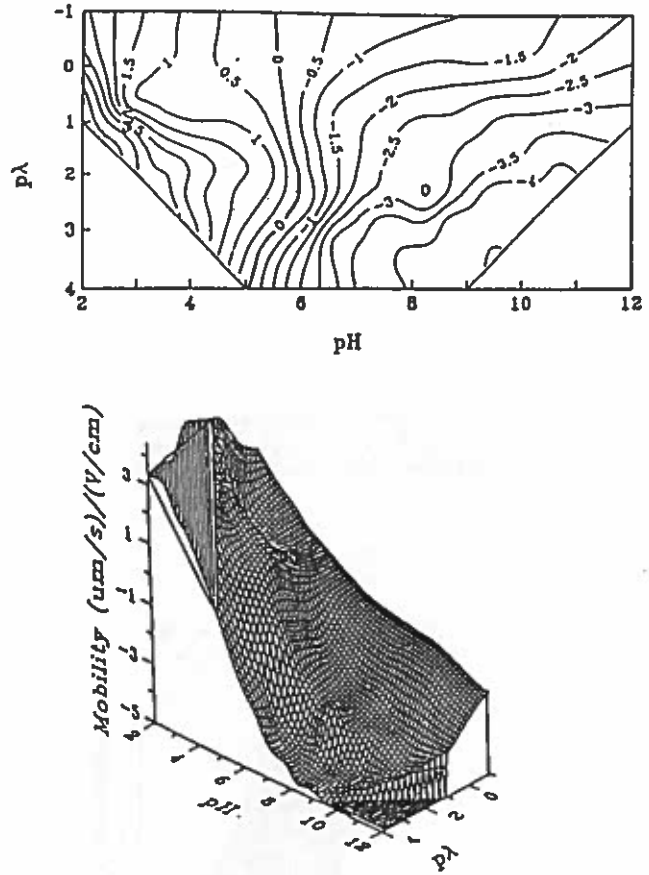

Figure 2. The electrophoretic fingerprint and template of the titanium dioxide-KCl system.

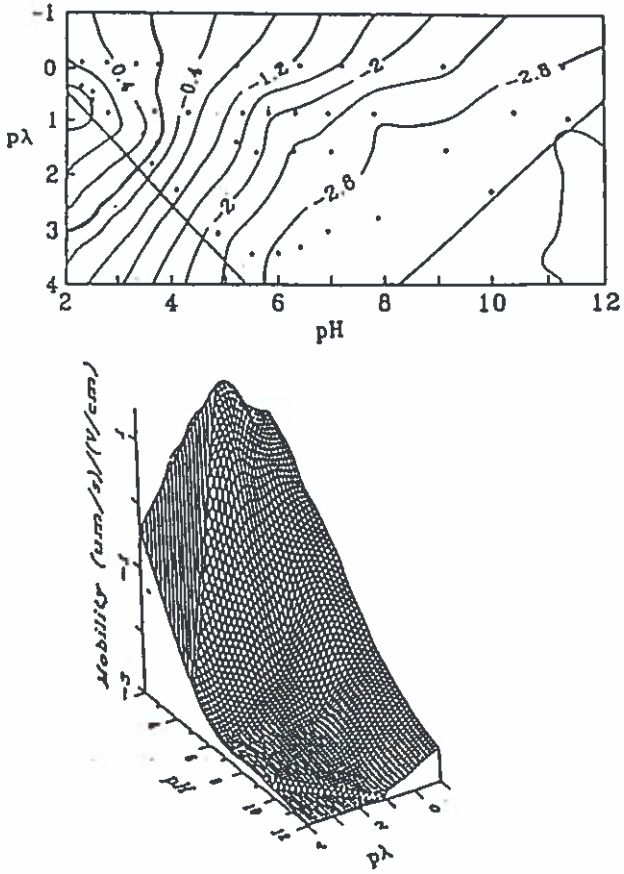

Figure 3. The electrophoretic fingerprint and template of the BLACK PEARLS® (oxidized carbon black) dispersion.

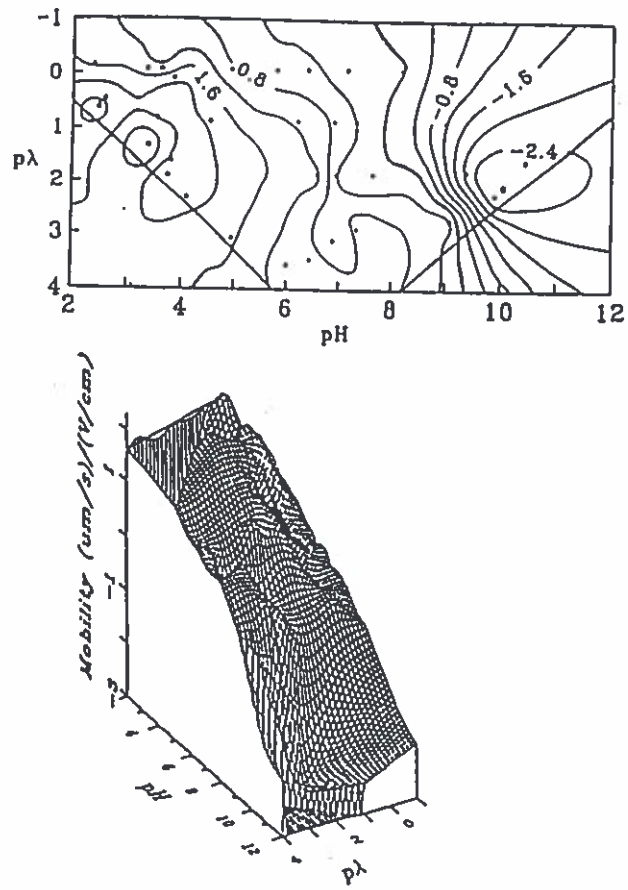

Figure 4. The electrophoretic fingerprint and template of the REGAL 660® (non-oxidized carbon black) dispersion.

April 10, 1991

CONTRIBUTION TO THE INTERNATIONAL POLYMER COLLOIDS GROUP NEWSLETTER

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17 APR 1991

NMR linewidth study of a latex interpenetrating network

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

Key words: Latex; structure; NMR spectroscopy; interpenetrating network; NMR linewidth

Conclusions

1. The temperature dependence of CMR linewidths is useful for examining composite polymer structure. The morphological changes in a latex interpenetrating network caused by variation in crosslink concentration were detected with linewidth data having a sensitivity exceeding electron microscopy and differential scanning calorimetry.
2. CMR linewidths obtained at low frequency, 15 MHz, are relatively insensitive to changes in sample form, minimizing the influence of variations in magnetic susceptibility on these data.
3. Two linewidth parameters, the spectral collapse temperature, and a breakpoint temperature defining the onset a limiting slope of the curve vary systematically with the IPN structure.
4. These data can be related to motional processes on a segmental scale in polymer networks, characterizing both the relative mobility of specific carbons and the effects of swelling and

VISCOMETRY AS A DETECTION SCHEME FOR PARTICLES IN SEPARATION TECHNIQUES FOR SIZE DISTRIBUTION ANALYSIS

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Viscometry was investigated as a possible size and composition independent detector for hydrodynamic chromatography. The specific viscosity was found to be linear with latex concentration from 0.01 to 0.4% solids, did not depend on particle composition, and was independent of particle size above roughly 100 nm. However, the specific viscosity increased 30% as the diameter of the latex decreased from 100 nm to 30 nm. This size dependence was ascribed to the presence of a surface layer on the latex in solution. Although the size dependence would not preclude its application, the utility of the viscometer was limited by low sensitivity and long time response.

CONCLUSION

The application of viscometric detection to colloidal particle separation techniques has been found to be more complex than the Einstein viscosity law suggests. Although viscometric detection was found to meet one of the two criteria of the ideal particle quantitation detector, independence from particle composition, an increase in η_{sp} of 30% as the diameter of the latex decreased from 100 nm to 30 nm was observed. Evidence from photon correlation spectroscopy and viscometry suggests this size dependence is the consequence of a 1.5 nm thick surface layer in HDC eluent. This size dependence does not preclude the application of viscometry for particle quantitation, particularly for particles with diameter greater than 100 nm where the η_{sp} was observed to be constant within 10% out to particle diameters of 913 nm. However, the minimal sensitivity and long time response of current pressure transducer technology limit the utility of viscometer for use with HDC. If more sensitive transducers were developed, viscometry should be reconsidered as this detection scheme could greatly enhance the accuracy of size determinations using particle size separation methods by providing composition, and at least above 100 nm in diameter, size independent detection.

TAIL-EDGE PICKING, BACK-TRAP MOTTLE AND FOUNTAIN SOLUTION INTERFERENCE OF MODEL LATEX COATINGS ON A SIX-COLOR PRESS PREDICTED BY LABORATORY TESTS

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ABSTRACT

Important properties of coatings for six-color, sheet-fed offset performance include: (a) tail-edge picking resistance, (b) back-trap mottle resistance, and (c) fountain solution/ink receptivity. This study found that certain laboratory print tests could predict how a series of model latex coatings would perform on a six-color, sheet-fed press with respect to the properties mentioned above. In addition, by using this model latex series in which all variables were held constant except the styrene (S)/butadiene (B) ratio, it was possible to establish the effects of changing latex composition on press performance of the coatings. The details of the effects of latex composition change on press performance and laboratory print testing as well as the correlation between the laboratory and press results will be discussed in this paper.

CONCLUSIONS

The tail-edge picking, back-trap mottle and fountain solution interference performance of model latex coatings on a 6-color sheet-fed offset press were accurately predicted by laboratory print testing.

Tail-edge picking on the press correlated with the ink tack build rate of the coatings, as determined by ECC International Ltd. Back-trap mottle and water interference on the press were accurately predicted by N. Plowman Associates, Inc.

Latexes with lower styrene/butadiene ratios resulted in the highest resistance to tail-edge picking. The latex with the highest styrene/butadiene ratio gave severe tail-edge picking requiring press clean-up.

Fountain solution interference during ink transfer appeared to decrease with increasing latex S/B ratio.

The best resistance to back-trap mottle was obtained with the coating that contained the lowest styrene/butadiene ratio latex while a higher S/B ratio latex coating resulted in the highest level of back-trap mottle.

TIP-SURFACE FORCES DURING IMAGING BY SCANNING TUNNELING MICROSCOPY

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ABSTRACT

The effect of compressive and shear forces between tip and surface during the operation of the Scanning Tunneling Microscope is illustrated with examples obtained both in air and vacuum environments. We show that at typical gap resistances used in STM ($\leq$ 20 GΩ) these forces can have significant effects. Compressive or repulsive forces give rise to anomalous topographic corrugations (elastic deformations) as well as to permanent damage (inelastic or plastic deformation). These forces also cause the anomalously low values obtained in measurements of the tunneling barrier height. The effects of shear forces when imaging weakly bound material will also be demonstrated.

1. INTRODUCTION

The existence of forces between the tip and the surface in the Scanning Tunneling Microscope has been recognized since the invention of the instrument.[1] The measurement and control of these forces led to the development of a new instrument, the Atomic Force Microscope.[2] Due to tip-surface forces, there can be gross distortions in STM images and damage to the surface in the extreme of large forces (plastic deformation), and more subtle effects that affect image interpretation when the forces are smaller and their action reversible (elastic region). The anomalous atomic corrugation observed in graphite[3,4] is one of the best known examples of the effects of compressive forces. Mamin *et al.* have linked the abnormally high corrugations on graphite to a contamination-mediated deformation of the graphite surface. They have shown that corrugations of < 1Å and current *vs.* distance curves steeper by two orders of magnitude than in air can only be obtained by cleaning tip and sample in UHV.[5]

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* This paper will be published in the Journal of Vacuum Science and Technology in May/June 1991

Contributions to the International Polymer Colloids Group Newsletter from the Institute for Surface Chemistry

April, 1991

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Flocculation of polystyrene latexes with cationic polyelectrolytes

Effect of Cationic Polyelectrolyte Characteristics,and Flocculation Conditions on Properties of Polystyrene Latex Flocs

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(Submitted to 11th Scand. Symp. on Surface Chemistry, Bergen, Norway, June 21-15)

ABSTRACT

Cationic polyelectrolytes with different charge densities (between 4 and 100 % cationic monomers) and different molecular weights (105 and 106) were used to flocculate negatively charged monodisperse polystyrene latex. Effects of ionic strength, particle concentration and flocculation conditions were also investigated. The flocs were characterised in an instrument set-up containing in series: a stirred jar, a Photometric Dispersion Analyzer (PDA), a flow-through microscope with video camera, a Couette shear cell, a second PDA, a tube flocculator and a third PDA. In this equipement the flocculation kinetics, the floc structure, the shear resistance and the ability for reflocculation after high shear could be followed. The structure was further investigated by SEM on freeze-dried flocs.

The flocs obtained with low charge density polymers at low ionic strengths had good shear resistance but limited ability to reflocculate after rupture. They consisted of small compact microflocs with almost close-packed primary particles connected into more open macrostructures. The perimeter fractal dimension was lower than with polymers of higher charge density indicating a smoother floc surface. The results could be explained by a bridging mechanism.

With high polymer charge density the flocs were less shear resistant but had better ability to reflocculate. The structure had voids on all length scales and the perimeter fractal dimension was higher indicating a more "stringy" structure. This is in accordance with a patch mechanism. At medium charge density where there was a good geometrical fittnes between surface and polymer charges the smallest flocs were obtained. This is due to limited contributions of bridging and patch mechanisms. At higher ionic strengths there were less differences between flocs obtained with different polymers, probably because a coagulation type of structure was obtained in all cases.

Flocculation of polystyrene latex with cationic polyelectrolytes. Part 1. Adsorption and optimal flocculation concentrations.

Leif Eriksson and Barbro Alm, Institute for Surface Chemistry, Box 5607, S-114 86 Stockholm, Sweden
(Submitted for publication)

ABSTRACT
We have studied adsorption of cationic polyelectrolytes with different charge densities on negatively charged particles. At low ionic strength we found almost stoichiometric relation between maximum amount of adsorbed cationic groups and negative surface groups when the mean distance between charged groups were the same on the polymer and on the surface.

At lower and higher charge densities the number of cationic groups were higher. On the lower side this was due to formation of loops and tails and at the higher there is a surplus of cationic groups at the adsorption site even if the polymer remains in a flat conformation. At the highest charge density the particle surface cannot be fully covered when ionic strength is low due to strong repulsion between different polymers.

We also found that the length of the side chain carrying the quarternized nitrogen was important for the ability of the polymer to cover negative surface sites.

In the flocculation studies the optimal flocculation concentrations and zero charge concentrations decreased with increasing ionic strength at low polymer charge densities and increased somewhat at high.

Effect of Cationic Polyelectrolyte Characteristics, Ionic strength and Concentration of Anionic Particles on Flocculation Kinetics and Floc Properties.

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(Particulate Science and Technology, submitted)

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ABSTRACT
Cationic polyelectrolytes with three different charge densities (low, medium and high) and two molecular weights (105, 106) were used to flocculate negatively charged monodisperse polystyrene latex. Varied on two levels were also particle concentration and ionic strength.

The observed effects on flocculation kinetics, floc size, shear resistance and ability to reflocculate could be explained as a result of different flocculation mechanisms. At low polymer charge density a bridging mechanism resulted in compact, shear resistant flocs with limited ability to reflocculate after floc rupture. At higher charge densities neutralization/mosaic patch formation gave fractal flocs with less shear resistance but better ability to reflocculate.

Associative thickeners

Rheology and Adsorption Behaviour of some Model Associative Thickeners

M. Hulden and E. Sjöblom

(Abstract of paper presented at the 64th Colloid and Surface Science Symposium, Bethlehem, USA, 18-20 Jure 1990)

The rheology and adsorption behaviour of some hydrophobically modified ethylene oxide urethane block copolymers (HEUR) have been studied. The results are compared with those for some commercial HEUR-thickeners and ethyl hydroxyethyl cellulose. Aqueous solutions of HEUR exhibit a sharp increase in the viscosity above a critical concentration. This is in contrast to EHEC solutions, showing a more gradual viscosity increase. The critical concentration decreases with increasing molecular weight. Further, the efficiency and the "associative character" increases with increasing hydrophobicity of the hydrophobic modification in the order Cl7 l<Cl5<Cl8. Addition of surfactants to solutions of HEUR increases the viscosity, which reaches a maximum and then is reduced. The reduction is more pronounced with ionic surfactants compared to nonionics. In comparison, addition of an electrolyte, e.g. Na2S04, does not influence the viscosity.

Combination of the thickeners with model latexes shows a complex behaviour. The viscosity is affected by the latex particle size, the amount of acrylic acid comonomer in the latex and the surfactant type and concentration.

Qualitative information on the adsorption was obtained by electrophoretic mobility measurements. Both HEUR and EHEC adsorb on surfactant free latex. A monolayer coverage of nonylphenol poly(ethylene oxide) on the latex shifts the adsorption towards higher thickener concentrations. On the other hand, if the latex is stabilized with sodium dodecyl sulphate no adsorption takes place. Further, the HEUR thickeners do not adsorb on TiO2 coated with A1203. This is the case both for bare pigment and pigment dispersed with the sodium salt of a polyacrylic acid.

The Adsorption of Surfactants and Polymers in Latex Paints

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Ago Saarnak, Scandinavian Coatings Research Institutete, H0rsholm, Danmark.

(Paper to be presented at the 13th Congress of the Federation of Scandinavian Paint & Varnish Technologists, May 12-1~1991, Stockholm, Sweden)

ABSTRACT

The adsorption of nonylphenolethoxylate (NPEOlo) and sodium dodecyl sulphate (SDS) to poly(butyl methacrylate) (PBMA) latex was investigated. It was found that NPEOlo was very effective at restricting the SDS access to the

latex surface. These results support the similarity between the processes in competitive adsorption and mixed micelle formation. The addition of organic solvents (such as coalescent agent) affect the adsorption process in the same manner as they affect the critical micelle concentration. It was found that ethyl hydroxyethyl cellulose (EHEC) and a sodium salt of polyacrylic acid (PAA) do not adsorb on the latex surface in the presence of surfactant.

SDS, EHEC and PAA adsorb to a TiO2 pigment coated with Al203, but NPEOlo does not. Studies of the competitive adsorption of PAA and EHEC showed that the adsorption of PAA is not influenced by EHEC. However, the adsorption of EHEC is reduced in the presence of PAA. The final amount of EHEC on the surface is dependent on the order of addition of PAA and EHEC.

The rheological properties, hiding power, gloss and water uptake of various paints was analysed in terms of the adsorption studies. Special attention was paid to the effect of the order of addition of PAA and EHEC on the paint properties.

CONTRIBUTION TO THE INTERNATIONAL POLYMER COLLOIDS GROUP NEWSLETTER

IPOC Polymer Colloid Research
Reporter: Klaus Tauer

Influence of Polymerization Temperature on Latex and Polymer Properties

1. Temperature Dependence of the Mean Degree of Polymerization in the Emulsion Polymerization of Styrene

There is a lack in experimental results regarding the dependence of emulsion polymerization kinetics as well as latex and polymer properties on polymerization temperature. We have investigated emulsion polymerization of styrene regarding the dependence of mean degree of polymerization (P_N) and particle number (N) on polymerization temperature over a range from ambient to 100 °C with different initiator-emulsifier-systems (IES) (table 1). The polymerizations were carried out with the following recipe: 100 g of water as dispersion medium , 3 g of styrene (28,85 mmole) as monomer, 6,5 mmol initiator and different amounts of emulsifier (ref. table 1). The mean degree of polymerization was calculated from viscosimetric data [1].

Table 1: Polymerization recipes
X_I - amount of initiator per polymerization
X_S - amount of emulsifier per polymerization

Abbreviation IES	Initiator	X_I (g)	Emulsifier	X_S (mg)
PEGAS	PEGAS[1)]	5,00	none	/
PEGA-100 E30	PEGA[2)]	3,70	E30[5)]	100[7)]
PEGA-10 E30	PEGA	3,70	E30	10[8)]
KPS-100 E30	KPS[3)]	1,77	E30	100[7)]
KPS-100 LS	KPS	1,77	SDS[6)]	100[7)]
KPS-5 LS	KPS	1,77	SDS	5[8)]
KPS	KPS	1,77	none	/
AIBN-100 E30	AIBN[4)]	1,07	E30	100[7)]

1) Surface active initiator perpared from AIBN and poly(ethylene glycole) 200 with sulfate end groups; concentration above CMC [1]
2) Initiator prepared from AIBN and poly(ethylene glycole) (molecular weight 200) with hydroxyl end groups; lower surface activity than PEGAS [1]
3) Potassium peroxidisulfate
4) Azo-bis(isobutyronitrile)

5) Sodium alkyl sulfonate
6) Sodium lauryl sulfate
7) Emulsifier concentration above CMC
8) Emulsifier concentration below CMC

These investigations offer the possibility to a considerably variation of the reaction conditions without changing the recipe. In this part we reporting results concerning the overall activation energy of the mean degree of polymerization ($E_{A,P}$). The results are interpreted in form of ARRHENIUS-plots.
The classical radical polymerization theory leads to equation (1) for a roughly estimation of $E_{A,P}$ if chain transfer and physical reactions influencing P_N are neglected.

$$E_{A,P} = E_{AW} - 0,5\ E_{AA} - 0,5\ E_{AZ} \qquad (1)$$

E_{AW} - Energy of activation of chain growth
E_{AA} - Energy of activation of chain termination
E_{AZ} - Energy of activation of initiator decomposition

Using well known values for E_{AW} (25 kJ/mole), E_{AA} (2,5 kJ/mole) and E_{AZ} (120 kJ/mole) $E_{A,P}$ should be in the order of -35 kJ/mole mainly influenced by E_{AZ} .
However the experimental results (figures 1-3) show much more differentiated pictures. Two main differences are obviously: the shapes of the ln P_N - 1/T - curves and the order of magnitude of the $E_{A,P}$-values. The shape of the curves seems to be influenced mainly by the emulsifier concentration, whereas the value of $E_{A,P}$ seems to be determined by the nature of the employed initiator.
Regarding the shape of the ln P_N - 1/T - curves are observed two different cases. The IES PEGAS, PEGA-10 E30, PEGA-100 E30, KPS-100 E30 and KPS-100 LS (figures 1,2) show over the investigated temperature range two activation energies. Thereby is the energy of activation in the higher temperature range in every case less negative than those in the range of lower polymerization temperatures. The other IES (KPS, KPS-5 LS, AIBN-100 E30) show only one activation energy over the whole range of polymerization temperatures.
It seems possible to explain the observed change in the energies of activation with increasing polymerization temperature by an enhanced formation of surface active oligomers with raising temperature, which subsequently leads to an enhanced formation of mixed micelles or mixed adsoprtion layers. In all IES which show two $E_{A,P}$-values the formation of mixed stabilizing systems is possible. In the cases of the other IES this is generally not possible (KPS, AIBN-100 E30) or not in such an extent (KPS-5 LS) possible. From a mechanistical point of view the mixed stabilizing systems can influence the initiator decomposition or the radical absorption in such a way that $E_{A,P}$ becomes less negative. The value of E_{AZ} (initiator decomposi-

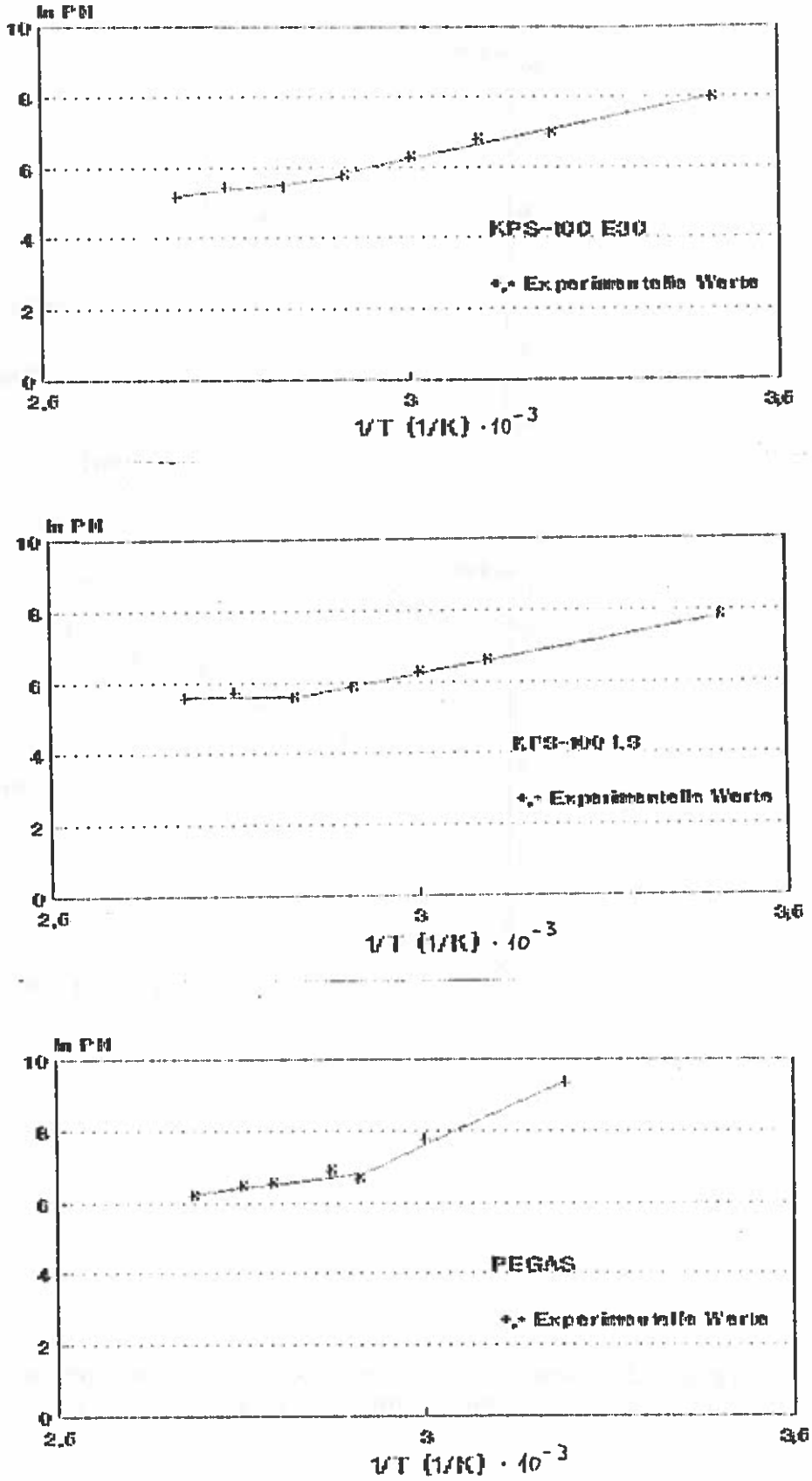
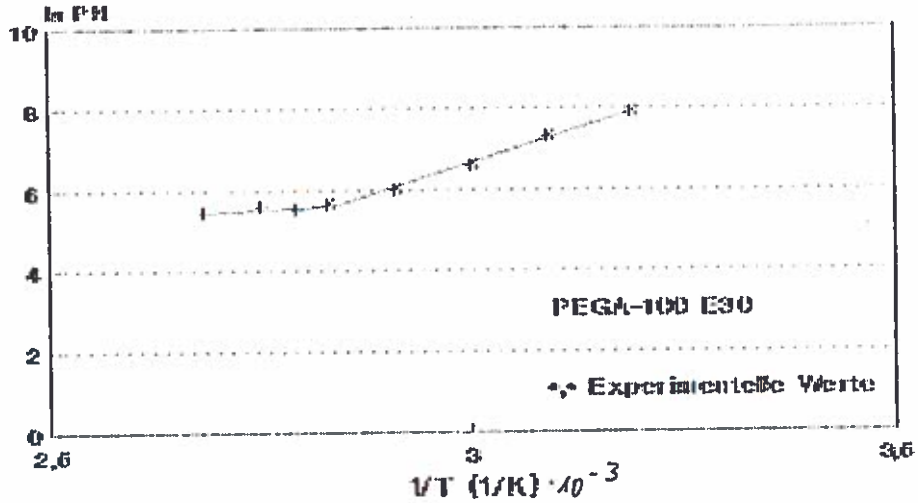


Figure 1: ARRHENIUS-plots for the mean degree of polymerization IES: KPS-100 E30, KPS-100 LS and PEGAS



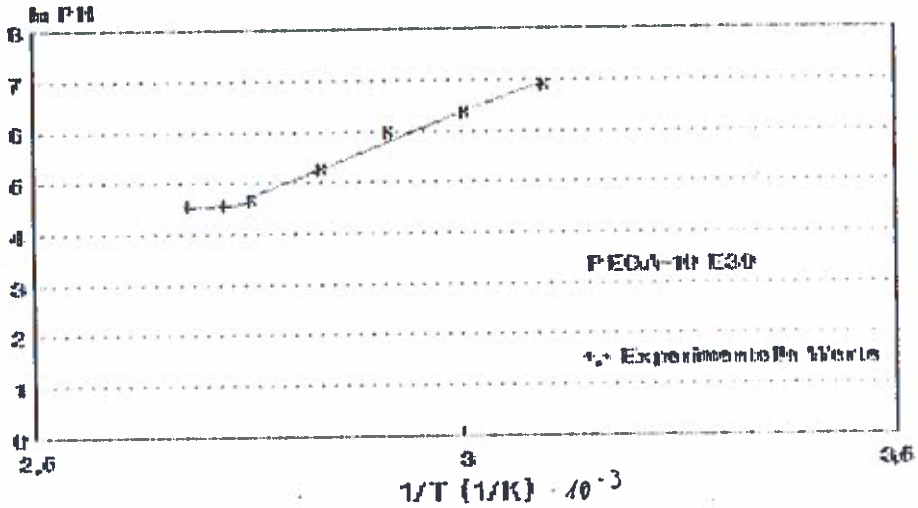


Figure 2: ARRHENIUS-plots for the mean degree of polymerization IES: PEGA-100 E30 and PEGA-10 E30

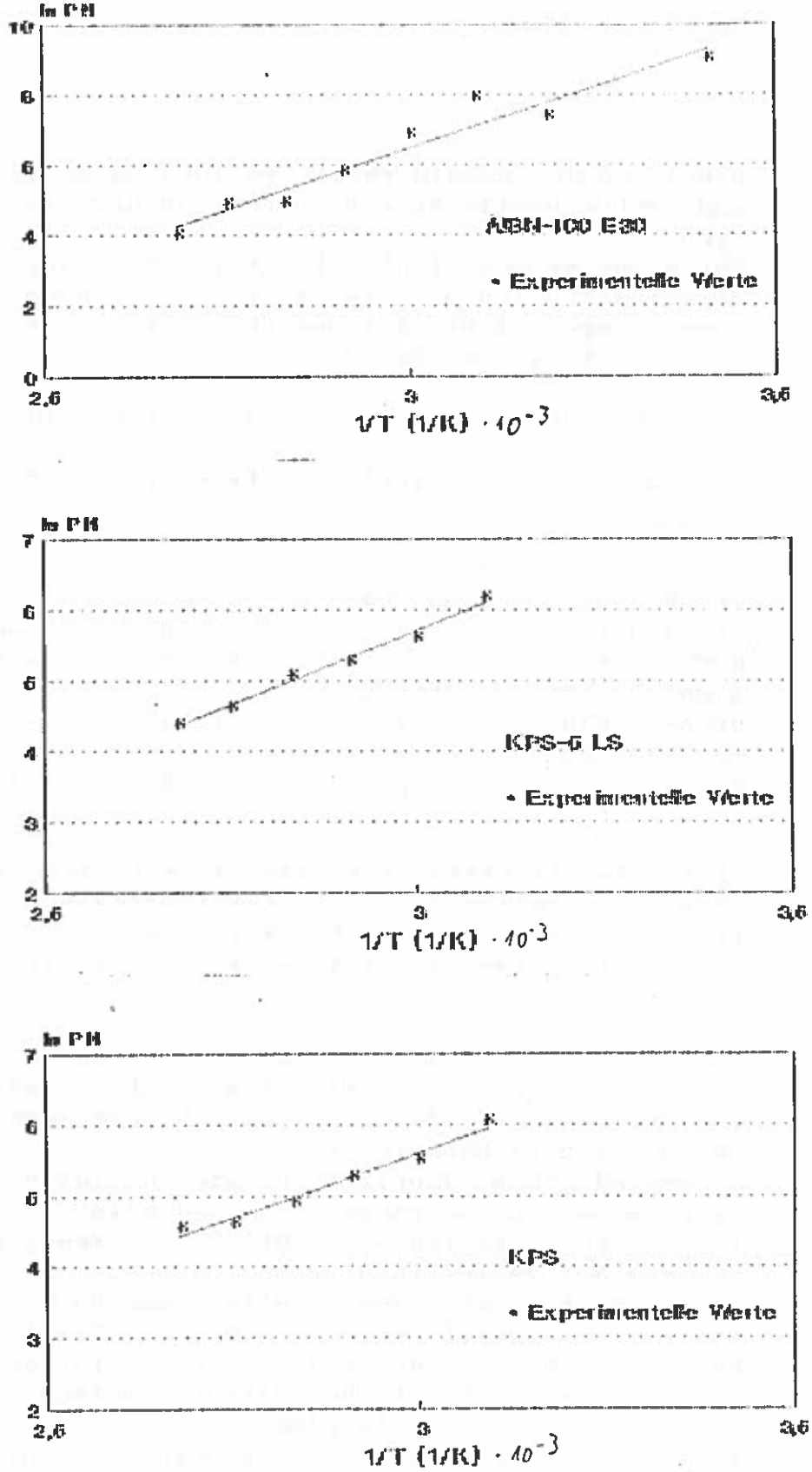


Figure 3: ARRHENIUS-plots for the mean degree of polymerization IES: AIBN-100 E30, KPS-5 LS and KPS

tion) could considerably be lowered up by micellar catalysis and subsequently $E_{A,P}$ becomes less negative according to equation (1).
For a comparison of all IES it is therefore necessary to consider for the IES with two $E_{A,P}$-values those of the low temperature range. Table 2 shows the differences in the $E_{A,P}$-values for all IES investigated.

Table 2: Comparison of $E_{A,P}$-values (in kJ/mole) for all IES

IES	$E_{A,P}$ 1)	$E_{A,P,NT}$ 2)	$E_{A,P,HT}$ 3)	T_G (°C) 4)
KPS	-30,55	/	/	/
KPS-5 LS	-35,04	/	/	/
KPS-100 LS	/	-32,15	-8,48	80
KPS-100 E30	/	-36,22	-14,63	80
AIBN-100 E30	-55,25	/	/	/
PEGA-10 E30	/	-51,78	-11,36	90
PEGA-100 E30	/	-53,74	-8,64	80
PEGAS	/	-78,29	-35,61	70

1) Activation energy over the whole temperature range
2) Activation energy in the low temperature range
3) Activation energy in the high temperature range
4) Boundary temperature between the high and low temperature range

It is possible to distinguish between three different groups of initiators. All polymerizations with persulfate lead to values in the range of -35 kJ/mole which correspond well to the estimated value by equation (1).
A second group comprises the azo-initiators AIBN and PEGA with $E_{A,P}$-values in the range of -50 kJ/mole.
The highest negative value of -78,3 kJ/mole is observed for the surface active initiator PEGAS.
An explanation of these results seems to be possible if we consider the locus of radical formation. The locus of radical formation is mainly determined by the solution properties and interfacial activity of the initiator molecules.
Table 3 summarizes this idea.
It seems to be clear that regarding the initiator the locus of radical formation determines the overall activation energy of the mean degree of polymerization in emulsion polymerization systems. The more the radical formation occurs at the particle water interface or in a region of the particles near the particle water interface the higher negative is $E_{A,P}$.

Table 3: Relation between locus of radical formation and overall avtivation energy of P_N compared to the estimated value by equation (1) $E_{A,PI}$ (kJ/mole)

Initiator	Locus of radical formation	Comparison $E_{A,PI}$ to $E_{A,P}$
KPS	Water	$E_{A,P} \approx E_{A,PI}$
AIBN PEGA	Monomer/(interfacial region) Water/(monomer/interface)	$E_{A,P} \approx E_{A,PI} - 20$
PEGAS	Interface	$E_{A,P} \approx E_{A,PI} - 40$

The difference to the estimated value by equation (1) is in the range up to 40 kJ/mole for the surface active initiator PEGAS and it correspondes well to typical energies of a physical adsorption. In the case of adsorbed radicals or radicals in a surface region this additional energy is required to the desorption of the radicals.
As I see it, investigations regarding the temperature dependence of emulsion polymerization kinetics , of latex properties and unconditional also of polymer properties (P_N, molecular weight distribution, copolymer composition ...) give new insights into mechanism and possibilities of emulsion polymerization techniques.

[1] - K. Tauer, K.-H. Goebel, S. Kosmella, K. Stähler, J. Neelsen
Makromol. Chem., Macromol. Symp. 31 (1990) 107-121

Emulsion Polymerization with Surface-active Azo-initiators. Variable Equipment of Latex Particles for Applications in Biology and Medicine

B.-R.Paulke, K.Tauer, S.Kosmella

Emulsion polymerization and co-polymerization are convenient methods for fitting the properties of polymer particles, like size, density, molecular weight of the polymeric material etc. The latex particle can be seen as a building block system. The building blocks (see scheme) can be put together nearly at choice either by the polymerization alone or by the combination of polymerization and following reaction steps.

```
(para-)magnetic        ---------------            coloured

      I    (un) charged    --  cross-linked (or not) I
      I                                              I
      I                    narrow                    I
      I hydrophobic  --    size      --  hydrophilic I
      I                 distribution                 I
      I                                              I
      I    (un) porous    ----     > < 1 um          I
      I                                              I

 functionalized        ---------------        fluorescent
```

The inner part of this scheme contains necessary latex parameters whereas the outer shell represents supplementary particle equipment. Especially this equipment makes polymer particles interesting for medical applications, like cell labelling, immunological tests in diagnostics, magnetic cell, protein or DNA separation and enrichment etc.
We used surface-active azo-initiators as tools in our efforts to achieve a variable equipment of polystyrene and polymethacrylate latex particles. Synthesis and structure of the initiators, derived from 2,2'-azoisobutyronitrile (AIBN), were described by TAUER et al. /1/. We preferred "PEGA 600"

from the series of two-sided poly-(ethylene glycol) modified AIBN derivatives with a nominal molecular weight of the poly-(ethylene glycol) of about 600.

The two terminal hydroxyl groups were used for

* covalent coupling of reactive dyes *(Nylosol/Sandoz)*,
  fluorescent dyes *(RITC, TRITC ..)*

and

* the introduction of ammonium groups into the polymer, resp.

The dye coupling reactions to the initiator were performed in absolute acetone at temperatures between 298 and 313 K. Then the solutions were used to start styrene emulsion polymerization. The result was an excellent colour and fluorescence intensity of the latex particles. The amount of free dye in the latex serum was neglectable and could easily be separated by ultrafiltration.
The introduction of ammonium groups for cationic particle stabilization was realized via the reaction between PEGA 600 and 3-chloro-2-hydroxypropyl ammonium chloride either in dimethyl formamide or "in situ" during styrene emulsion polymerization with cationic emulsifier. In each case a base was added to activate the ammonium compound. We obtained stable cationic modified latexes. They remained stable after remove of the emulsifier and showed an electrophoretic mobility between +0.3 and +0.8 $um s^{-1}/Vcm^{-1}$. Emulsifier-free polymerization was not possible in this way.
The combination of surface-active initiator with cationic emulsifier was also applied in the stabilization of freshly precipitated magnetite Fe_3O_4 and the following styrene emulsion polymerization. The products were paramagnetic latexes in the size range between 100 and 150 nm with nearly 10 per cent magnetite by weight. There was no hysteresis in the magetization curves.

/1/ K.Tauer, K.-H.Goebel, S.Kosmella, K.Stähler, J.Neelsen, Makromol.Chem., Macromol.Symp. 31, 107-121 (1990)

J. Chem. Phys., in press 1991

PARTIAL STRUCTURE FACTORS IN COLLOIDAL SILICA MIXTURES DETERMINED WITH SANS CONTRASTVARIATION

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Small-angle neutron scattering experiments at various contrasts were performed on concentrated mixtures of colloidal spheres, differing in size. Both colloidal components consisted of fairly monodisperse silica cores, coated with a layer of octadecyl-chains. Cyclohexane was used as dispersing medium; variation of the contrast was achieved by using mixtures of ^{1}H-cyclohexane and ^{2}H-cyclohexane. Scattered intensities were measured at 3 volume fractions up to 0.4, at equal partial volume fractions.

The different contrast dependence of the scattering amplitudes of both colloids allowed us to calculate partial structure factors. This was done using a method which has not been reported previously. Describing the intra-particle structures with layered-sphere models, and using a decoupling approximation, 3 partials were obtained from a system of linear equations.

The scattering curves at the various contrasts constitute a consistent data set, at all volume fractions. Although the *separate* components interact like hard spheres, the partial structure factors in the mixture reflect marked deviations from hard-sphere behavior. Their nature can be qualitatively explained with an attractive interaction between unequal particles. This is confirmed with simple model-calculations.

J. Am. Ceram. Soc., 73 [8] 2385–90 (1990)

(1)

Effect of Hydrothermal Conditions on the Morphology of Colloidal Boehmite Particles: Implications for Fibril Formation and Monodispersity

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The synthesis of colloidal boehmite (AlOOH) is studied by heating basic aluminum chloride solutions under constant stirring. The temperature and Al_2O_3:Cl molar ratio influence the product morphology. Synthesis at 140°C generates highly fibrous polycrystalline particles that are on average 360 nm long, 30 nm broad, and 8 nm thick. They contain 0.11 mol of excess H_2O per 1 mol of AlOOH. Synthesis at temperatures between 140° and 190°C produces broader fibrils and less excess H_2O. Preparation at 220°C eventually produces fully crystalline platelike boehmite particles about 260 nm long, 95 nm broad, and 14 nm thick, without excess H_2O. Fibril synthesis requires an Al_2O_3:Cl molar ratio exceeding 1.0 to yield noncoagulated particles. The fibrils are fairly monodisperse with 20% standard deviation in their length for an Al_2O_3:Cl molar ratio about 1.0.

J. Am. Ceram Soc., in press 1991.

(2)

PREPARATION OF COLLOIDAL BOEHMITE NEEDLES BY HYDROTHERMAL TREATMENT OF ALUMINUM ALKOXIDE PRECURSORS

Paul A.Buining , Chellappah Pathmamanoharan , J.Ben H. Jansen and Hendrik N.W. Lekkerkerker

Fairly monodisperse colloidal boehmite fibrils with a high aspect ratio were synthesized by hydrothermal treatment at 150 °C of an acidified aqueous alkoxide solution, prepared by adding an aqueous HCl solution to an aluminum alkoxide precursor. The average particle length could be controlled between about 100 nm and 500 nm by varying the initial amounts of alkoxide and acid. Using two different alkoxides in a 1:1 molar ratio yielded the most needle-like product, having a particle length standard deviation of 40 %. The boehmite particles were polycrystalline and contained 0.14 mole excess H_2O per mole AlOOH, bound to the particle surface.

Abstr.(2):

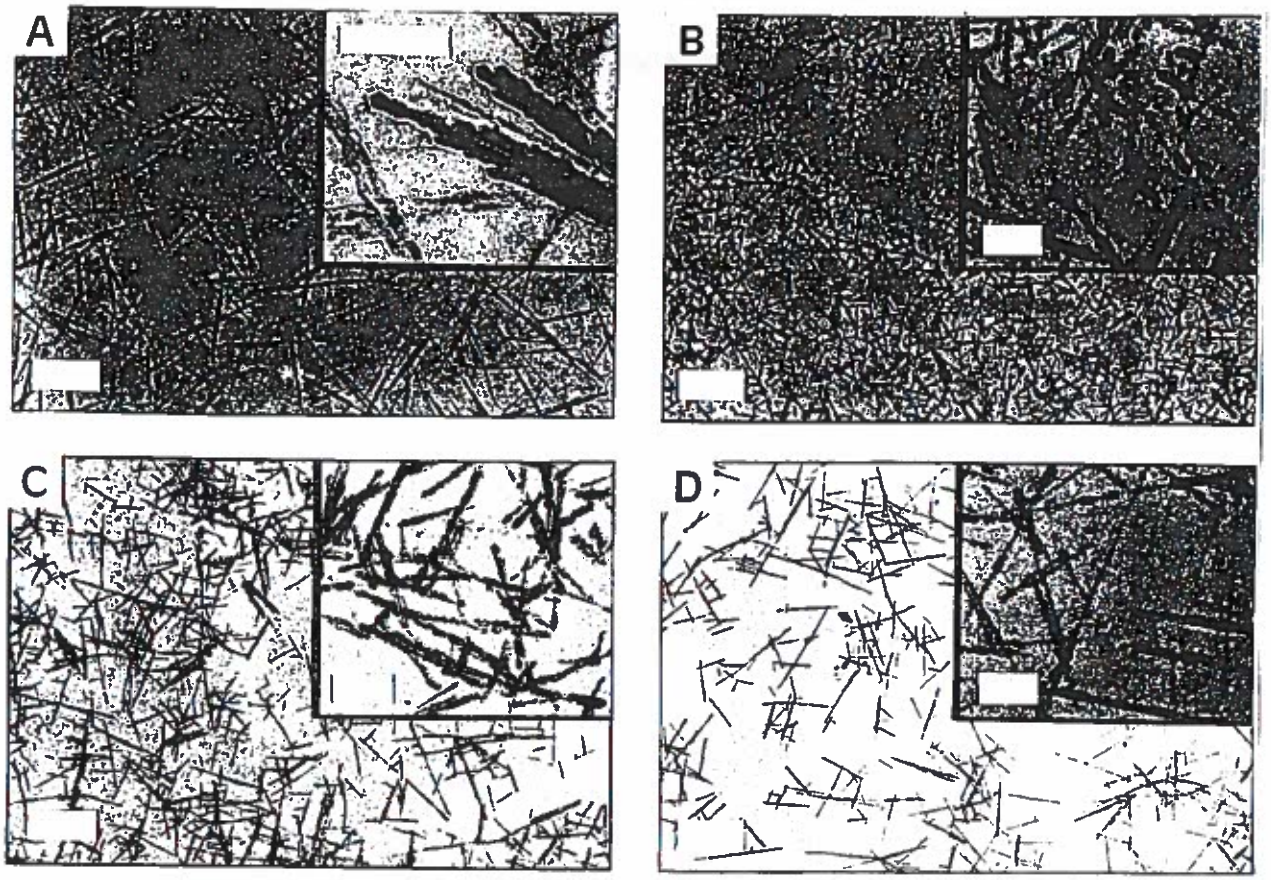
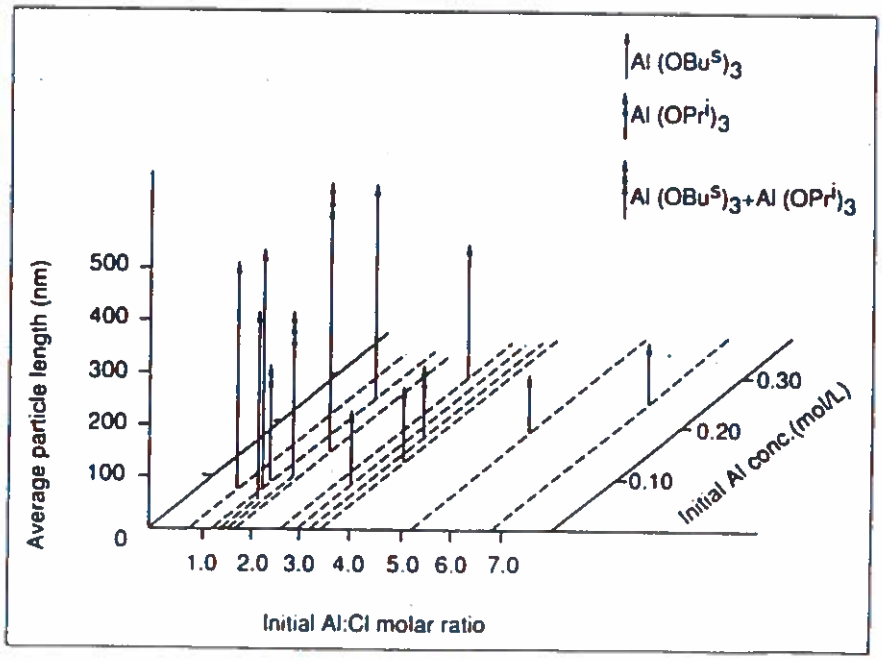


Fig.1. Transmission electron micrographs of boehmite obtained by hydrothermal treatment at 150 °C of solutions prepared with: (A) 0.078 M $Al(OBu^s)_3$, 0.059 M HCl; (B) 0.130 M $Al(OBu^s)_3$, 0.038 M HCl; (C) 0.076 M $Al(OPr^i)_3$, 0.055 M HCl; and (D) 0.048 M $Al(OBu^s)_3$, 0.048 M $Al(OPr^i)_3$, 0.059 M HCl. The lengths of the bars at low magnification represent 0.5 μm, those at high magnification (in the inserts) 0.1 μm.

Fig.2. Average length of boehmite particles, determined with electron microscopy, as a function of initial aluminum concentration and Al:Cl molar ratio (three dimensional plot). Temperature of synthesis 150 °C, duration 20 h. Single arrow: $Al(OBu^s)_3$, double arrow: $Al(OPr^i)_3$, and triple arrow: $Al(OBu^s)_3$: $Al(OPr^i)_3$ = 1.0.



LATEX FILM FORMATION AT THE MOLECULAR LEVEL: THE EFFECT OF COALESCING AIDS ON POLYMER DIFFUSION

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An energy transfer technique is described which allows one to use fluorescence decay measurements to follow the extent of polymer diffusion in annealed latex films. These are poly(butyl methacrylate) [PBMA] films prepared from latex dispersions containing a mixture of 100 nm PBMA particles labeled, respectively, with donor and acceptor fluorescent dyes. From the data analysis, diffusion coefficients for the polymer molecules can be calculated. These diffusion coefficients are enhanced when the latex dispersions are preequilibrated with small amounts of organic solvents commonly used as coalescents. Their effect can be described quantitatively in terms of Williams-Landel-Ferry equation. Some coalescents (e.g. diethyleneglycol butyl ether) shows deviations from simple WLF behavior. These deviations follow the behavior expected for solvent evaporation from the film by a Fickian diffusion process.

* a manuscript on this topic is forthcoming

Contribution To Polymer Colloids Newsletter

Adsorption of Polystyrene-Poly(ethylene oxide) Block Copolymer onto Polystyrene Latex: Fast Adsorption and Slow Rearrangement

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We have observed that in the presence of suitable surfactants, one can elute polystyrene latex particles from an aqueous size exclusion chromatography (SEC) column. The retention times are sensitive to particle size. This offers a new approach to examining the adsorption of block copolymers and other surface-active polymers onto particle surfaces.

The adsorption of polystyrene-poly(ethylene oxide) (PS-PEO) diblock and triblock copolymers onto the surface of a series of PS latex particles of different diameters was studied by SEC and by quasi-elastic light scattering. In the presence of excess block copolymer, the adsorption process is very rapid (seconds). It occurs during the mixing of the latex dispersion and polymer micelles inside the syringe before injection onto the SEC column (Micropak TSK-Gel G5000PW). We observed peaks for the copolymer-stabilized latex, for the block copolymer micelles, and for the unimer. Elution times were on the order of a few minutes. The relative intensities of the peaks was unchanged if the mixture was allowed to stand for 30 minutes before reinjection. The latex peak is sensitive to the particle diameter (d) and exhibits a linear plot of log(d) against retention time. When this plot is extrapolated to the retention time of the micelle, the ordinate value corresponds to the core diameter of the core-

diameter of the core-shell shaped micelle, which was determined independently from scattering experiments. Figure 1 shows a such plot.

Quasi-elastic light scattering measurements, however, revealed that there is a slow rearrangement of the adsorbed chains, i.e., the layer thickness of the adsorbed copolymer chains increases with time by 10 to 20% (see Figure 2). More detailed kinetic studies of the slow rearrangement are underway.

We have preliminary evidence that the corona thickness for the adsorbed chains depends both on the PEO chain length and polymer microstructure (diblock vs triblock). Since PS latex of a variety of particle sizes are available, we should be able also to examine radius of curvature effects on the adsorption process.

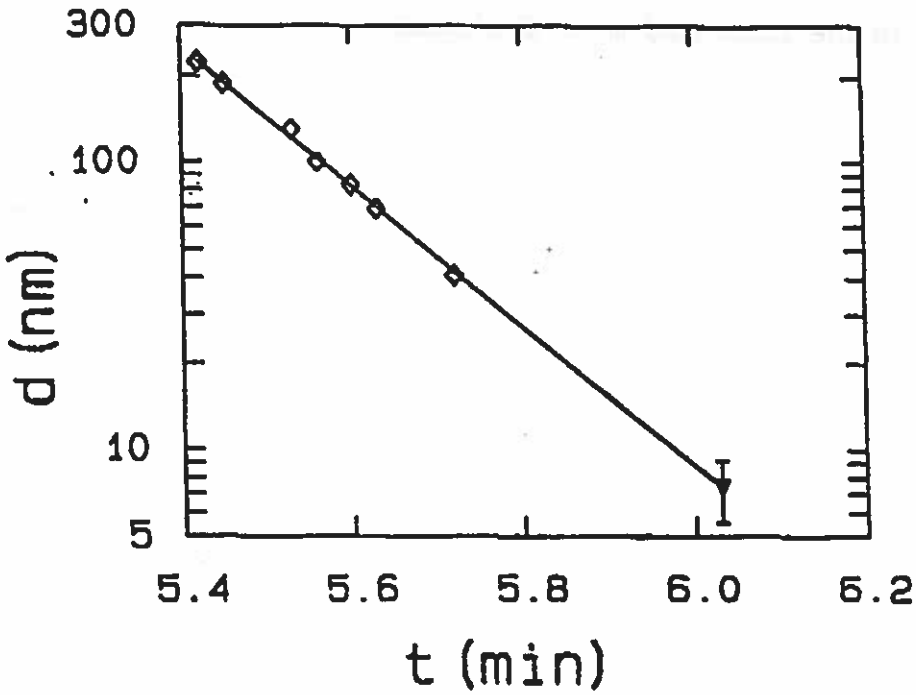

Figure 1. A plot of the core diameter versus the retention time. Diamonds: copolymer-stabilized latices; Triangle: copolymer micelles.

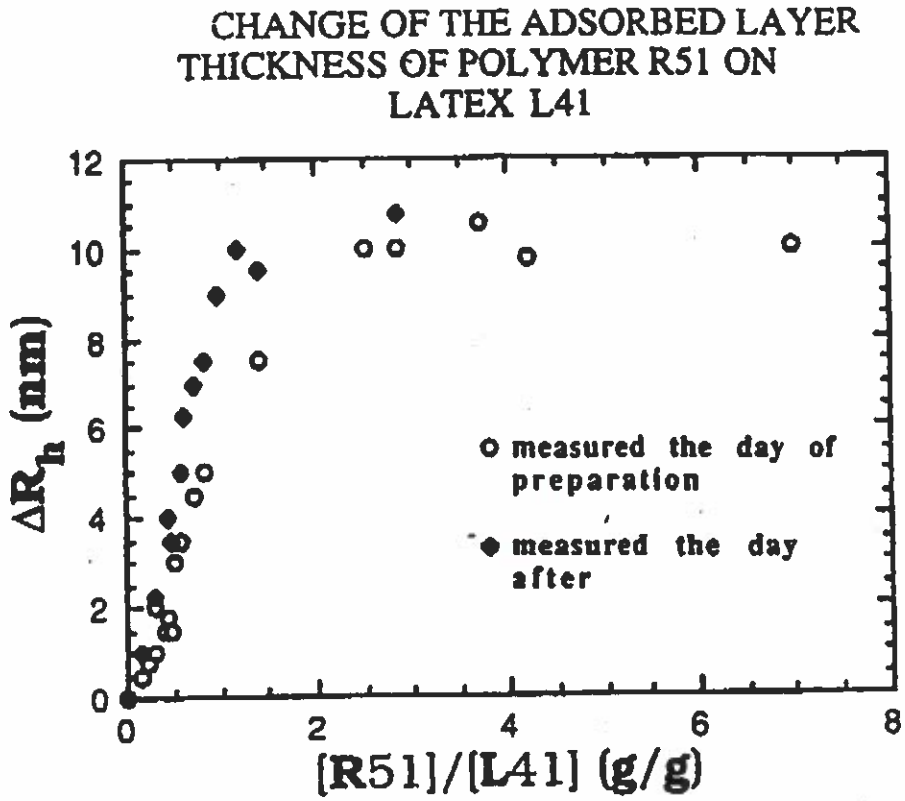

Figure 2. Change of the adsorbed layer thickness.