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IPCG

INTERNATIONAL POLYMER COLLOIDS GROUP

Newsletter
February 1999

IPCG Website

Bob Fitch has set up the IPCG website, on http://www.newmex.com/IPCCG_Home/ For more information, including input into the site, contact him on bobfitch@newmex.com. This is a most timely and economic way for us to communicate, and will eventually replace this hard-copy Newsletter.

Conferences - 1999

Forth International Symposium on Polymers in Dispersed Media
11 – 15 April 1999 - Lyon (France)
Contact Prof. C. Pichot: christian.pichot@ens-bma.cnrs.fr

Gordon Research Conference on Polymer Colloids
June 27 – July 2 1999. Tilton, New Hampshire.
Contact Françoise Candau, candau@ics.u-strasbg.fr, or http:/www.grc.uri.edu

Sixth Meeting of the UK Polymer Colloids Forum
22 – 23 September, 1999, Loughborough University, UK
Contact Peter Lovell

As previously notified to members by email, because of the growing size of this Newsletter, it is necessary to limit contributions to (extended) abstracts of work in progress or in press, titles and sources of papers which have been published, and news items such as conference details. IPCG members who wish to communicate full text of papers can post them on the IPCG website.

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International Polymer Colloids Group Meeting

Gold Coast, Australia July 16, 1998

Present: Gilbert, Ho, El-Aasser, Tauer, Kawaguchi, Lovell, Kim, Waters, Omi, Napper, Elaissari (for Pichot), van Herk

Future IPCG Meetings

1999

March 21-25	ACS Symposium on Polymer Colloids (Contact: El-Aasser)
April 12-15	Lyon (Contact: Pichot)
June 27 - July 2	Gordon Conference (Contact: Françoise Candau)

2000

June 18-21 74th Colloid and Surface Science at Lehigh University (includes Polymer Colloids). Contact El-Aasser

July 23-29 IACIS Meeting, at Bristol; contact Vincent.

2001

Gordon Conference - Convenor: Do Ik Lee

2002

July 14 – 19. Engineering Foundation (similar format to Gordon for collaboration), tentative name *Polymer Colloids and Heterophase Polymerization.* Organizers: Tauer/El-Aasser.

Agenda Items for next meeting at Gordon Conference:

- possible Chinese members of the IPCG
- electronic version of newsletter

First circular and call for papers

Sixth Meeting
of the
UK Polymer Colloids Forum

22-23 September 1999, Loughborough University

The UK Polymer Colloids Forum was set up under MacroGroupUK in the Autumn of 1993 with expansion of UK academic activity in the field as one objective. Another aim was to bring the UK polymer colloids community together for discussions of topics and issues of both academic and industrial importance, the principal vehicle for which has been the regular meetings of the Forum. Following on from the previous five meetings, the sixth meeting of the Forum is now arranged for September 1999, with the following invited speakers having agreed to give plenary papers:

Professor Doug Hourston (Loughborough University, UK)
"The Application of Modulated-Temperature Differential Scanning Calorimetry and Related Techniques to Film Formation"

Dr. Alex van Herk (Eindhoven University of Technology, The Netherlands)
"Alternative Methods of Initiation Applied to the Preparation of Polymer Colloids"

Professor Gerard Riess (Mulhouse University, France)
"Use of Polymeric Surfactants in Emulsion Polymerizations"

Call for Papers and Further Information

Position papers, technological papers, and experimental and theoretical research papers on any topic relevant to the field of Polymer Colloids are invited for presentation. Papers from UK academics and industrial scientists will be particularly welcome.

If you wish to offer a paper for inclusion in the meeting and/or receive the second circular giving details of the programme and registration, please return the form below by 16 April 1999.

✂ -

Sixth Meeting of the UK Polymer Colloids Forum
Loughborough University, United Kingdom, 22-23 September 1999

☐ I wish to receive the second circular giving programme details and registration information.

☐ I wish to offer the following paper(s) for inclusion in the programme and <u>enclose 200-300 word abstract(s)</u> of the paper(s).

Paper title(s) ....
....
....

Preferred method of presentation ☐ oral ☐ poster

Please complete in CAPITAL LETTERS:

Surname .... Initials .... Prof/Dr/Mr/Mrs/Miss

Address for correspondence ....
....
....

Tel .... Fax ....

Name(s) of accompanying person(s) ....

Return by 16 April 1999 to: Dr. P.A. Lovell, Manchester Materials Science Centre, University of Manchester & UMIST, Grosvenor Street, Manchester, M1 7HS, UK

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ON THE EFFECT OF POLYMERIC HYDROPHILICITY ON STABILITY OF EMULSIFIER-FREE ACRYLATE LATEXES UNDER THEIR FREEZING-THAWING

T.Aclamazova

Institute of Physical Chemistry, Russian Academy of Sciences, Moscow

The investigation on stability of emulsifier-free acrylate latexes has been developed in view of the effect of polymeric nature and surface forces of particles on their interaction. In this work the effect of polymeric hydrophilicity on latex stability under its freezing-thawing is studied. The study is based on the correlation of polymeric hydrophiliSity to monomeric solubility of in water. The variation of hydrophilicity of latex polymer is achieved by using three monomers significantly differed in water solubility (polybutylacryle pBA, polyethylacrylate pEA and polymethylmethacrylate pMMA). The hydrophilicity is also changed by adding water soluble methacrylic acid (MAA).

The freeze-resistancy of latexes is studied by carrying their 3-fold freezing at -9 grad C during an hour with the following thawing. The concentration of latex coagulum and radius of latex particles (R) were determined after every cycle of their freezing. Zeta-potential of particles surface was also measured.

The coagulum formation is observed after freezing the all three latexes studied.The most concentration of coagulum is formed after third cycle of latex freezing-thawing. The latexes can be arranged according to ascending their freeze-resistancy as pBA<pEA<pMMA. The carboxyl-containing latexes of these polymers are characterized by the greater freeze-resistancy as it was expected. As followed from these data, the latex freeze-resistancy increases in accordance to increasing the polymeric hydrophilicity and respectively monomeric solubility in water : BA (0.2%)<EA (1.4%) <MMA (1.5%). The increase of hydrophilicity and zeta-potential of polymer by adding water-soluble MAA is also accompanied by increasing latex freeze-resistancy.

The variation of radius of noncarboxyl- and carboxylcontaining polymer particles was measured after every cycle of latex freezing-thawing. The size of noncarboxylcontaining particles of pBA and pEA already increases after first cycle. The size of particles of carboxylcontaining pBA- and pEA-latexes is constant in the course of two cycles of freezing-thawing. Their size increases after third cycle of freezing-thawing.

In case of the more hydrophilic polymer - pMMA, the size of particles formed in the absence of MAA is constant after two cycles and increase after third cycle of latex freezing-thawing. In case of carboxyl containing pMMA, the particles size stays constant in the course of all three cycles of freezing-thawing.

The effect of low temperature on particles size can be also connected with elastic properties of polymer. The film-forming properties of polymers studied significantly differed: glass temperature (Tg) of pMMA is rather higher than 0 and -9 grad whereas Tg of pBA and pEA is lower than them. In this connection the change in particles radius under freezing-thawing effect can be explained the film-forming properties of polymers. The particles of more elastic polymers as pBA and pEA can coalesce greater than pMMA.The addition of MAA in copolymeric content is also accompanied by increasing surface zeta-potential, from one side, and from the other, by decreasing the elastic properties of polymer molecules.

Taking into account the observed correlation of polymeric hydrophilicity and zeta-potential of particles surface to the coagulum formation in the course of latex freezing-thawing, the analysis of surface forces of particles interaction has been carried out at present. The estimation on role of surface forces in particles coagulation under low temperature effect is based on considering their interaction in view of the modern theory of DLVO. The result of estimating electrostatic, structural and molecular components of potential energy of particles interaction will be submitted in the following report.

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

February 1999

FUNCTIONALIZED MONODISPERSE PARTICLES WITH CLOROMETHYL GROUPS FOR THE COVALENT COUPLING OF PROTEINS

J. Sarobe, J.A. Molina, J. Forcada, F. Galisteo, R. Hidalgo

The functionalizaced core-shell monodisperse latex particles with surface chloromethyl groups were synthesized by means of a two-step emulsion polymerization process in a batch reactor at two reaction temperatures. In a first step, the core was synthesized by means of a batch emulsion polymerization of styrene (St), and in the second step, the shell was formed by batch emulsion copolymerization of St and (chloromethyl) styrene (CMS) using the seed obtained previously. The latexes were characterized by TEM and conductopotentiometric titrations in order to obtain the particle size distribution and the amount of the different surface groups, respectively. Covalent binding of protein to chloromethyl groups was studied using lysozyme at two pHs, 7 and 11. Two different methods were used to determine the amount of protein covalently bound or physically adsorbed: desorption with surfactants, and chloride ions release upon chemical binding.

MODELING OF MWD IN EMULSION POLYMERIZATION: PARTIAL DISTINCTION APPROACH

G. Arzamendi, C. Sayer, N. Zoco, J.M. Asua

A mathematical model for the calculation of the MWD in emulsion polymers is presented. The model is based on an intermediate level of description of the system, and hence is computationally more efficient that the existing detailed models, while its predictions are as accurate as those of the detailed models. The importance of the compartmentalization was assessed to determine the conditions in which there is a need to account for the compartmentalization. It was found that under many practical conditions, the predictions of models even simpler than that developed in this work are accurate enough. Only for highly compartmentalized systems, under conditions in which $0.5<\bar{n}<0.7$, with a strict control of the operation variables and very good GPC analysis, the differences between the models would be greater than the experimental variability. The feasibility of the on-line estimation of the MWD in seeded systems was studied. It was found that an accurate, robust and quick prediction of the MWD in seeded systems using available on-line measurements (calorimetry, gas chromatography) seems to be possible.

REACTIVE SURFACTANTS IN HETEROPHASE POLYMERIZATION. XXIV. EMULSION POLYMERIZATION OF STYRENE WITH MALEATE- AND SUCCINATE-CONTAINING CATIONIC SURFACTANTS

A. Montoya-Goñi, D.C. Sherrington, H.A.S. Schoonbrood, J.M. Asua

A series of alkyl pyridinium bromide maleate and succinate diester surfactants has been used as stabilizers in the free radical emulsion polymerization of styrene. High conversions of styrene were achieved readily with the maleate surfactants, but the succinates gave rise to varying levels of retardation. In two of the latter cases, use of the surfactant at a concentration below its critical micelle concentration appears to be a key factor, but the other retardations are difficult to account for. Little difference in reactivity and latex properties was found with the maleate surfactants despite the position of the maleate group being very different in the series of molecules examined. Chemical incorporation of the maleate surfmers into the polymer particles appears to occur early on in the polymerizations, but a sufficiently high proportion of groups is on the surface to yield stable latex emulsions. The surface tensions of the final latices produced with both the maleate and succcinate surfactants are high, suggesting a large proportion of succinate species are also surface adsorbed. However, the surface tensions of these latices are a little lower than those of latices produced with the maleates, suggesting the proportion of solubilized succinate surfactant is a little higher. This seems to be important in terms of the robustness of the stability of the latices to the addition of electrolytes, the succinate-stabilized species being consistently more tolerant. This suggests that while chemically bound surfactants can improve some of the properties of latices, e.g. the hydrophobicity of films, this might be at the expense of latex stability.

MODELING INVERSE MICROEMULSION POLYMERIZATION

A. Sáenz de Buruaga, J.C. de la Cal, J.M. Asua

A mathematical model for inverse microemulsion polymerization has been developed. The model has been used to fit experimental results of the effect of initiator concentration, light intensity, emulsifier concentration, and dispersed phase weight fraction on the monomer conversion evolution, particle size and polymer molecular weight in the inverse microemulsion polymerization of 2-methacryloyl oxyethyl trimethyl ammonium chloride (MADQUAT) initiated by UV light in the presence of AIBN. A good fitting of the experimental data was achieved.

COMPARISON BETWEEN CONVENTIONAL EMULSION AND MINIEMULSION POLYMERIZATION OF VINYL ACETATE IN A CONTINUOUS STIRRED TANK REACTOR

I. Aizpurua, M.J. Barandiaran

The conventional emulsion and miniemulsion polymerization of vinyl acetate in a continuous stirred tank reactor (CSTR) were studied in an attempt to demonstrate the feasibility of miniemulsion polymerization as a strategy to eliminate the oscillatory behaviour of CSTR reactors, even in very unfavourable conditions. Reactions were carried out under a wide range of operating conditions. No oscillations in the time evolution of the conversion and particle number were observed in any of the miniemulsion polymerizations, while the opposite was found in most of the conventional emulsion polymerizations. Different dependencies of the emulsifier and initiator concentrations on the reaction rate and particle number were obtained for both emulsion and miniemulsion polymerizations, as a consequence of the different nucleation mechanisms. Furthermore, almost the same average molecular weight was obtained for the emulsions and miniemulsions carried out under similar experimental conditions.

CONTINUOUS INVERSE MICROEMULSION POLYMERIZATION

A. Sáenz de Buruaga, J.C. de la Cal, J.M. Asua

The inverse microemulsion polymerization of MADQUAT in a continuous stirred tank reactor is investigated. The effect of removing the oxygen from the feed tank, initiator concentration, aqueous phase volume/emulsifier volume ratio, and residence time on the monomer conversion, particle size and molecular weight was investigated. The removal of the oxygen allowed to obtain high conversions with moderate amounts of initiator. In general, the process did not present oscillations.

EMULSION POLYMERIZATION IN A LOOP REACTOR: EFFECT OF THE OPERATION CONDITIONS

P.H. Araujo, C. Abad, J.C. de la Cal, C. Pinto, J.M. Asua

The effect of several operation conditions (temperature, residence time, recycle ratio, initiator concentration and emulsifier concentration) on the performance of a continuous loop reactor during the redox initiated emulsion copolymerization of vinyl acetate and Veova 10 was investigated. The study was carried out under industrial-like conditions, namely, high solids content latexes (55wt%) and high conversions (~90%). Both polymerization mechanisms and practical issues such as production rate and product quality are discussed.

Contribution from the Department of Polymerization Reactions,
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Reported by **Jaro Barton**

Preparation of partly hydrophobized, crosslinked polyacrylamide particles by terpolymerization of acrylamide/N,N-methylenebisacrylamide/ styrene in inverse microemulsion.

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Abstract :

Free-radical polymerization of termonomer system acrylamide, AAm, N,N'-methylenebisacrylamide, MBAAm , and styrene, S, initiated by water-soluble ammonium peroxodisulfate, APS, or by toluene-soluble dibenzoyl peroxide, DBP, in inverse microemulsion toluene/S/AOT//water/AAm/MBAAm, leads to the formation of partly hydrophobized crosslinked polymer particles of tailored chemical composition, degree of crosslinking and polymer particle size.The polymerization kinetics measurements pointed at the important role of exiting water soluble AAm and MBAAm monomer radicals generated by thermal decomposition of APS in water pools of inverse micelles for initiation of polymerization reactions of sparingly water-soluble S monomer in the oil-phase of the inverse microemulsion. It was shown that the polymerization and copolymerization reactions of S in the presence of AAm and/or MBAAm are effectively initiated by wa-ter-soluble APS as well as by oil-soluble DBP initiators. In the absence of radicals ca-pable to escape the water pools of inverse micelles such as monomer, solvent or emul-sifier radicals only very low polymerization rate of the monomer in the oil phase should be expected .The extent of the above-mentioned mechanism of initiation depends on the concentration of monomer present in the water pools or entering the water pools of inverse micelles, rate of initiation in the water pools and exit rate of monomer,solvent or emulsifier radicals escaping from the inverse micelles. Thus for monomers only sparingly soluble in water pools of inverse micelles the observed rates for polymerization initiated by APS initiator, generally should be be very low. Increasing of the mass ratio of S/Toluene in inverse microemulsion led to an increase of polymer particle diameter

from ca. 20nm to ca. 50 nm .This was attributed to toluene swelling of the styrene-rich structural moieties of AAm/S copolymer located on the surface of polymer particles. During dialysis the polymerized single-phase w/o Winsor IV inverse microemulsion gradually converts itself into a two-phase o/w Winsor I dispersion system with volume fraction of aqueous phase, Φ_{aw} ~ 0.950 .Water phase contains water swelled, crosslinked polymer particles of diameters lying around 80 nm . After evaporation of water from the dialyzed inverse microemulsion, solid, dried, crosslinked polymer particles in the form of a transparent film, practically not contaminated by AOT surfactant, were obtained.

(Full paper should appear in Polymer International).

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Single Chain Characterization of Hydrophobically Modified Polyelectrolytes Using Cyclodextrin \ Hydrophobe Complexion

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Determining the molecular weight of hydrophobically modified alkali soluble emulsions (HASE) using conventional techniques such as gel permeation chromatography or static light scattering is difficult because of hydrophobic associations in solution. Several approaches can be contemplated to prevent this hydrophobic association. For example, one can use a suitable water miscible organic solvent or to reduce the hydrophobic association in aqueous solution. However, organic solvent does not destroy association completely and therefore interpreting light scattering data can become complicated. Another approach is to cut off the hydrophobes by hydrolyzing the polymers. However, hydrolysis of the polymer can sometimes modify the polymer chains by truncating any branching or grafting that can occur during synthesis. A third approach is to use surfactant molecules to shield the hydrophobes from associating. However, at low concentration, the surfactant molecules can promote polymer association and, at high concentration, the surfactant molecules themselves can form aggregates. A fourth option is to use cyclodextrin, a molecule with hydrophobic cavity and hydrophilic outer shell, to shield the hydrophobes. The advantage of using cyclodextrin in our studies is that it does not change the characteristics of the solution other than just preventing the hydrophobic association.

The HASE polymers studied here were synthesized by emulsion copolymerization of a carboxylic acid monomer, an acrylate monomer, and an associative "macromonomer" that provides the alkali-soluble polymer with the major portion of its associative functionality. The macromonomer carries hydrophobic groups of either C8, C12, or C20 linear alkyl groups that are spaced away from the backbone of the polymer by a poly(oxyethylene) chain. For comparison, a control polymer that contained no macromonomer was also synthesized. Details of the synthesis procedure and characterization of all the HASE polymers have been reported previously [1]. The current study is relevant because it provides fundamental characterization of model HASE polymers whose rheological properties have been reported in the literature previously [2-5].

To determine the single chain molecular weight (M_w), two different approaches were used to prevent the hydrophobic association of HASE polymers in solution. In one approach, the polymer was hydrolyzed at a very high pH and at a high temperature to cleave the hydrophobic constituents. Aqueous gel permeation chromatography, dynamic (DLS) and static (SLS) light scattering measurements were then performed on these hydrolyzed polymers to determine M_w, hydrodynamic radius (R_h) and radius of gyration (R_g). In the second approach, methyl , -cyclodextrin was used to shield the hydrophobes. The molecular weight, R_h and R_g of a single chain were measured using DLS and SLS. The molecular weight of the control polymer without macromonomer was ~7.0×10^5 g/mole using both the techniques. The molecular weight of HASE polymers with the C8, C16, or C20 hydrophobic groups was ~2.0×10^5 g/mole. Thus, some chain transfer occurred from the macromonomer. To the best of our knowledge, this is the first application of methyl , -cyclodextrin to determine the molecular weight of a single polymer chain.

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POLYMER COLLOID GROUP NEWSLETTER

Contribution from the Institut Charles Sadron (CRM)
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reported by **Françoise CANDAU**

Summaries of progress in several research areas of our group are presented below

Hydrophobically-modified polyacrylamides prepared by micellar polymerization: scaling behavior of the zero-shear viscosity.

(F. Candau, E. Jimenez-Regalado, J. Selb) [Ref. 5]

We have recently reviewed (see Ref. 9) the major advances achieved in the field of hydrophobically modified polyacrylamides (HMPAM) prepared by micellar polymerization since this process was introduced in the early eighties. A characteristic feature of this technique is the production of copolymers with a multiblock structure, where the number and length of the hydrophobic blocks vary with the initial number of hydrophobes per micelle. However, a major problem, which has been long underestimated by most authors is the compositional heterogeneity of the samples arising from a more rapid incorporation of the hydrophobe in the copolymer with conversion. A decisive step was recently brought about in our group with the use of *N,N*-disubstituted acrylamides as the hydrophobes [E. Volpert, J. Selb, F. Candau, *Macromolecules* 1996, 29, 1452-1463]. In the latter case, the particular microenvironment inherent to the micellar process and the difference in polarity between bulk and micelles are capitalized upon to produce highly homogeneous samples. Having in hand these model samples, we were able to correlate molecular structure and macroscopic properties by undertaking a thorough study of the main parameters affecting the rheological behavior of HMPAM.

Measurements of the zero shear viscosity were performed for series of polyacrylamides containing hydrophobic blocks of *N-N*-dihexylacrylamide (DiHexAM). The number of hydrophobic stickers per chain was tuned by adjusting either the molecular weight of the polymer or the total hydrophobe content. The length of the hydrophobic block, that is expected to control the lifetime of the associations was also varied, owing to the specificity of the free radical micellar copolymerization technique. The major result of this study is that the zero-shear viscosity of samples with the same hydrophobic block length follows, over 6 decades, a unique scaling law of both hydrophobic block density and molecular weight with an exponent close to 4 (see Figure) [Ref. 5]. It can be remarked that the molecular weight dependence of the zero-shear viscosity is quite close to the prediction of the reptation model meant for entangled unmodified samples. This suggests that once a tie between two hydrophobic sequences breaks up, this is followed by a motion involving the whole polymer, resulting in an hindered reptation. Another interesting result is the large increase in the zero-shear viscosity with the average block length of the hydrophobe (see Figure) and this is likely correlated to the increase in the life-time of the junctions.

The above features are in qualitative agreement with the trends expressed in the sticky reptation model of Leibler et al. [*Macromolecules* 1991, 24, 4701], even though the latter was derived for systems with a large number of entanglements per chain, which is not the case here.

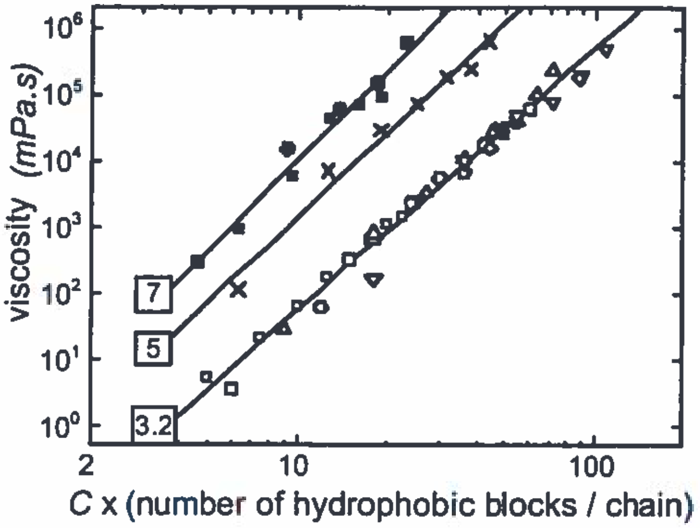

Figure: Log-log plot of the zero-shear viscosity as a function of the reduced variable (polymer concentration × number of hydrophobic blocks per chain) ≡ (M_w × hydrophobic block density), for various AM / DiHexAM copolymers with different molecular weights, hydrophobe contents and microstructures. The labels on the graph refer to the length of the hydrophobic blocks

Fluorocarbon polymerizable surfactants: viscometric behavior, micellar polymerization and interactions with associating polymers.

(K. Stähler, J. Selb, F. Candau) [Ref. 7]

The micellar aggregation of two fluorocarbon surfactants bearing a polymerizable acrylamido group and differing only in the degree of amido substitution (CONH or $CONC_2H_5$) has been investigated by viscometry. The two surfactants exhibit distinct solution properties with a micellar growth occuring at a much lower concentration for the *N*-monosubstituted sample which shows in addition a shear thickening and rheopectic behavior. The ability of the latter surfactant to form hydrogen bonding is responsible for this difference in behavior. Micellar copolymerization of acrylamide with these surfactants or with an hydrocarbon analogue gives copolymers with a polysoap-like behavior. The copolymers in aqueous solution show a pronounced intramolecular hydrophobic aggregation expressed by relatively low viscosity values when compared with those of other hydrophobically modified water-soluble polymers reported in the literature. Surfactant-polymer mixed systems do not show a strong incompatibility between fluorocarbon and hydrocarbon moieties.

Interactions between polyampholytes and ionic surfactants.

(I. M. Harrison, F. Candau, R. Zana, *Colloid Polym. Sci.*, in press).

The interactions of two partially charged ampholytic terpolymers, consisting of acrylamide, sodium 2-acrylamido-2-methylpropanesulphonate (AMPSNa) and 2-(methacryloyloxyethyl)trimethyl ammonium chloride (MADQUAT) with molar compositions 80/12/08 and 80/08/12, and two fully charged ampholytic copolymers containing only the two latter comonomers and molar compositions of 80/20 and 50/50, with cationic surfactants, tetradecyl-trimethylammonium bromide (TTAB) and cetyl-trimethylammonium bromide (CTAB), and the anionic surfactant sodium dodecylsulphate (SDS), are investigated. The studies include phase behaviour (swelling, solubilisation, precipitation), viscometry, electrical conductivity, and potentiometry (bromide ion and surfactant ion-specific electrodes). The 80/08/12 and 80/12/08 polyampholytes swell in water, and are solubilised in the presence of cationic or anionic surfactants above a particular surfactant concentration that is proportional to the polymer concentration. 80/20 is soluble in water but precipitates in the presence of TTAB, whereas 50/50 is insoluble in water and in the presence of TTAB but is solubilised upon addition of SDS. The results indicate that TTAB binds to 80/12/08 with little or no cooperativity. Solubilisation appears to be the result of an increasing polyelectrolyte character of the polyampholyte upon neutralisation of its charged sites by the bound surfactant ions of opposite charge. The binding of TTAB by the 50/50 polyampholyte is very weak and non-cooperative. In contrast, 80/20 binds TTAB cooperatively, much like a true polyelectrolyte-surfactant system of opposing charge. In particular, the binding is characterised by the existence of a critical aggregation concentration. A partial phase diagram of this system has been determined from the TTA^+-electrode potential data. The behaviour of true polyelectrolytes and polyampholytes with respect to their interaction with surfactants is discussed.

RECENT PUBLICATIONS

1. *The influence of salicylate counterions on the aggregation behavior of a polymerizable cationic surfactant.*
   G. Tuin, F. Candau, R. Zana, Colloids Surfaces, Part A (1998)

2. *Dynamics of a high molecular weight polyelectrolyte.*
   M. Pabon, J. Selb, F. Candau, Langmuir 14, 735-737 (1998)

3. *Associating behavior of polyacrylamides hydrophobically modified with dihexylacrylamide.*
   E. Volpert, J. Selb, F. Candau, Polymer 39, 1025-1033 (1998)

4. *Adsorption of hydrophobically associating polyacrylamides on clay.*
   E. Volpert, J. Selb, F. Candau, N. Green, J.F. Argillier, A. Audibert, Langmuir 14, 1870-1879 (1998)

5. *Scaling Behavior of the Zero Shear Viscosity of Hydrophobically Modified Polyacrylamides.*
   F. Candau, E. Jimenez Regalado, J. Selb, Macromolecules 31, 5550-5552 (1998)

6. *Synthesis and characterization of new hydrocarbon and fluorocarbon polymerizable surfactants.*
   K. Stähler, J. Selb, P. Barthelemy, B. Pucci, F. Candau, Langmuir 14, 4765-4775 (1998)

7. *Fluorocarbon polymerizable surfactants: viscometric behavior, micellar polymerization and interactions with associating polymers.*
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   F. Candau, J. Y. Anquetil, in "Micelles, Microemulsions and Monolayers: Science and Technology" D. O. Shah ed., Dekker , New York (1998), Chapter 8, pp 193-213

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Contribution from M Cohen-Stuart:

Langmuir **14**, 6846-9, 1998

"Formation of micelles with complex coacervate cores"

M A Cohen Stuart, N A M Besseling, R G Fokkink.

Modeling Morphology Development in Seeded Emulsion Homopolymerization

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We are interested in furthering the understanding of factors that may produce heterogeneous particles. Of particular interest are copolymerizations or terpolymerizations where differences in monomer solubility and reactivity could yield significant composition gradients across the radius. The initial stage of this study examines the development of particle morphology in the seeded emulsion polymerization of styrene. It is the first stage in the development of a model capable of predicting composition gradients in emulsion copolymerizations where the two monomers have widely differing water solubilities.

The starting point for this investigation into morphology development was the determination of the relevant reaction kinetics, thermodynamic factors and mass transfer phenomena. Phase partitioning and diffusivities of all species are important considerations since it is the coupling of the reaction kinetics with transport phenomena and thermodynamics that can produce non-uniform latex particles. Development of an accurate expression for monomer diffusivity is important because the diffusivities of radicals in this model are directly dependent on the diffusivity of monomer. Using the same data as previous authors (Adams et al., 1990a) a new expression was determined that fit the experimental diffusivity data well, yet also gave reasonable agreement to the limiting conversion phenomenon seen in experimental polymerizations. The dependency of radical diffusivities on monomer diffusivity results from the fact that radicals diffuse in two ways: 1) center-of-mass diffusion, whereby the entire radical moves throughout the polymer particle; 2) reaction-diffusion, whereby the radical adds monomer units to its growing end and thus the reacting end gradually moves throughout the polymer particle. Center-of-mass diffusion is calculated as a function of the diffusivity of monomer and is inversely proportional to the length of the reacting radical. Reaction diffusion is calculated as a function of the rate of reaction. Using a modification of the approach developed by Mills et al. (1991), the radicals in this model are classified based on their ability to diffuse. The approach developed by Mills et al. divided radicals on the basis of whether or not the radical underwent center-of-mass diffusion. Those radicals that undergo center-mass-diffusion are classified as "short" radicals, and those that are too long to undergo center-of-mass diffusion, thus migrating only by reaction diffusion, are classified as "long" radicals. The current approach developed in this work uses those same two classifications with the introduction of a third radical classification known as "tiny" radicals. "Tiny" radicals are those radicals which are small enough to have center-of-mass diffusion and are also capable of desorption from the polymer particles. (This classification is designed to provide a flexible framework for future work involving other monomer systems.) Radicals were also classified on the basis of whether or not they were surface anchored. Surface-anchored radicals were also classified based on their lengths with the classifications discussed previously.

The modeling of phase partitioning during Interval II was achieved using constant partition coefficients between the polymer, aqueous and monomer droplet phases. During Interval III, a modification of the 0.6 power law (Gilbert, 1995) was used to determine partitioning between the aqueous and polymer phases. The modification allowed the calculation a dynamic partitioning coefficient based on the concentration of monomer in the polymer particles.

A complete set of chain-length-dependent kinetics was used to describe the propagation, chain transfer and termination reactions. All kinetic rate coefficients, including the entry and desorption rate coefficients, were based on the approach outlined by Gilbert (1995) with the exception of the termination rate coefficients. Simulations showed better agreement with experimental results when the chain-length-dependent termination coefficients as determined by Adams et al. (1990b) were used. A slight modification was also made on the expression for radical desorption such that it was assumed that a radical could undergo a specified number of propagation steps before exit was deemed impossible.

The model was set up as a set of ordinary differential equations to account for generation, consumption and diffusion of species such as monomer, polymer and radicals in a single polymer particle that was divided into concentric shells. The initial state of the model is a monomer swollen seed particle that is divided into a predetermined number of initially equal volume shells. Each shell has a balance for all species located within that shell, as well as a volume balance to account for shell shrinkage or expansion. The single polymer particle was deemed to be representative of all the events occurring in all polymer particles within the system.

The investigation into non-uniform latex morphologies was conducted by examining the radial profiles of new polymer formed in the polymer particles. For the investigation into the effect of seed diameters on the resultant morphology, seed diameters of 50, 200, 400 and 800 nm were used at constant seed loadings such that the rate of polymerization within the system was nearly constant in every case simulated. In agreement with the earlier findings of Mills et al. (1990), it was found that the size of the seed particle had a pronounced effect on the resultant morphology, with large size seeds having very heterogeneous morphologies. With the 50 nm seed it was found that the new polymer formed was distributed very evenly throughout the particle with no gradient between shells. However for the 400 and 800 nm seeds it was found that there were severe gradients between the inner and outer regions of the particle, with essentially all of the new polymer formed being located in the outer area adjacent to the polymer-water interface (Figure 1). The results showed that the larger the particle diameter, the more inhomogeneous the resultant morphology becomes, and the smaller the particle diameter, the more homogeneous the particle becomes. Results indicate that morphologies become non-uniform in the 300 nm range.

Previous investigators into latex morphology examined both monomer gradients and radical gradients as being the potential cause of non-uniform latex morphologies. Our simulations showed that no significant monomer gradients were present when inhomogeneous morphologies existed. This is attributed to the relatively quick rate of diffusion of the monomer molecules. However, in all cases where significant inhomogeneities were found, a significant radical gradient was present. In simulations where there were extreme radial gradients in new polymer formed, as in the 400 nm case, the radial radical gradient was also quite large (Figure 2). These results are in agreement with the findings of Mills et al. (1990) and Chern and Poehlein (1987).

Figure 3 shows a plot of normalized concentration of surface-anchored radicals versus dimensionless radius. When the particles are small, the concentration of surface-anchored radicals is essentially uniform, or possibly there is a small gradient. However at larger particle sizes, the concentration of surface-anchored long radicals drops off rapidly as one moves inward towards the center of the particle. Therefore there is a significantly greater amount of polymerization in the outer areas of the particle due to the fact that, in large size particles, surface-anchored radicals are not able to penetrate the inner regions of the particle. In a large particle a surface-anchored radical is more likely to terminate before reaching the inner parts of the particle, and thus the majority of the polymerization occurs near the polymer-water interface. In a simulation in which all entering radicals were not surface anchored radicals, it was found the morphology was nearly uniform, even at large particle sizes.

In scenarios in which the rate of entry was varied to determine the effect on morphology, it was found that increased entry rates increased the heterogeneity of the particle morphology. This was attributed to the surface-anchored radicals terminating with entering radicals before being able to transfer and penetrate the inner regions of the particle. While the effect of increased entry rate did have a significant effect on particle morphology, it was not as profound as the effect of seed diameter over reasonable values.

The model developed to date agrees with findings of previous studies. We are now prepared to expand the model to account for morphology development in copolymer systems.

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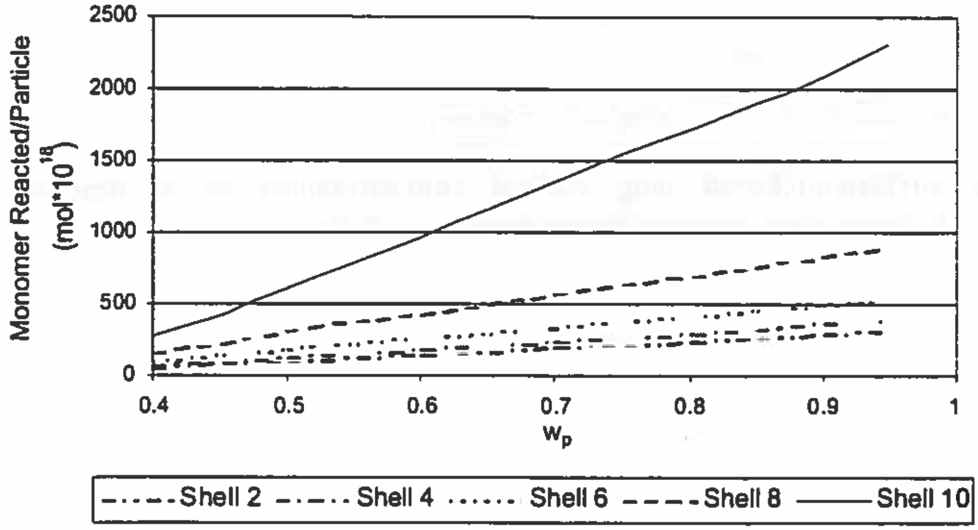

Figure 1. Monomer converted to polymer in each shell as a function of weight fraction polymer for 400 nm diameter seed.

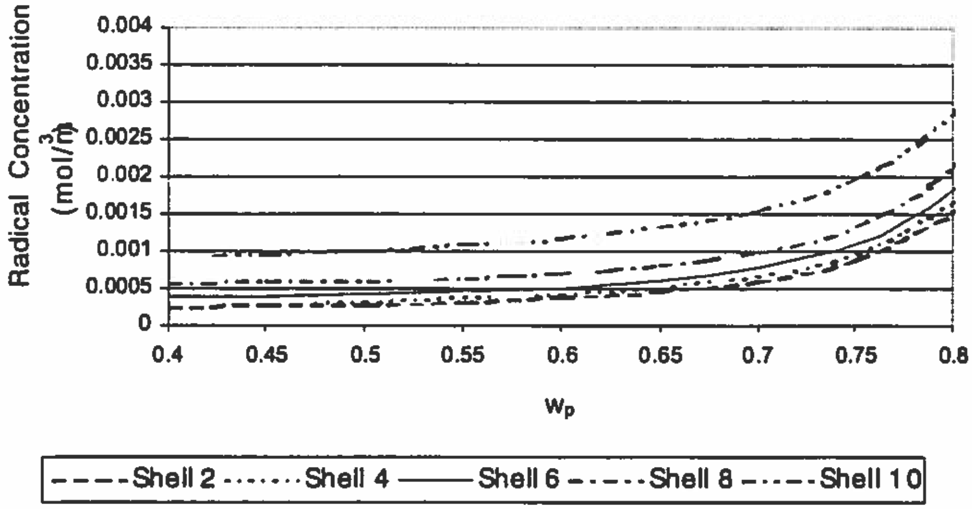

Figure 2. Total radical concentrations in each shell as a function of weight fraction polymer for 400 nm diameter seeds.

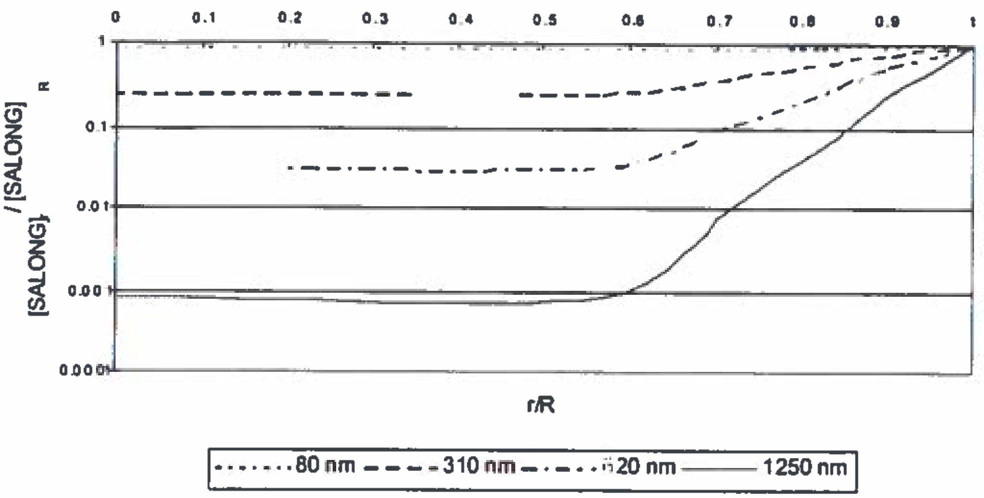

Figure 3. Normalized surface-anchored long radical concentrations as a function of dimensionless radius for different sized particle diameters at $w_p = 0.39$.

Predicting the Effectiveness of Chain Transfer Agents in Emulsion Polymerization

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Introduction

Chain transfer agents (CTAs) are widely used to regulate molecular weight in emulsion polymerizations. In a homogeneous polymerization (e.g. solution or bulk), it is a straightforward procedure to estimate the molecular weight distribution being produced at any instant during a polymerization if the concentrations of chain transfer agent and monomer are known. Typically the CTA and monomer are consumed at different rates, resulting in either upward or downward drift in the average molecular weight. (If the transfer constant C_{tr} (k_{tr}/k_p)>1, CTA is consumed faster than monomer, while if C_{tr}<1, monomer is consumed faster than the CTA.) The concentrations of CTA and monomer can usually be determined by on-line measurements such as GC (CTA) and densitometry (monomer). However in an emulsion polymerization, the CTA and monomer are partitioned between three phases: monomer droplets, aqueous phase, and particles. It is the concentrations in the particles that determines the molecular weight produced at any instant, but it is often very difficult or impossible to determine the CTA concentration inside the particles ([Tp]) during a process. (The monomer concentration inside the particles ([Mp]) can be calculated from thermodynamic relationships.) If it can be assumed that the CTA is in equilibrium between all phases, then [Tp] can be calculated. In many cases, however, the CTA is not in equilibrium and thus [Tp] cannot be readily determined. Failure to achieve equilibrium is due to very low water solubilities (large partition coefficients) and/or high transfer constants, which result in the CTA being consumed by reaction faster than it can diffuse from the monomer droplets to the polymer particles. The particles are often therefore "starved" with respect to CTA. Without an accurate method to determine [Tp] during reaction, it is not possible to predict the molecular weight being produced. It is the objective of this work to study the CTA concentration within the particles during reaction and its effect on the cumulative and instantaneous molecular weight distributions. Seeded styrene emulsion polymerization with n-dodecanethiol was the chosen system.

Experimental

Seeded styrene emulsion polymerizations were conducted using monodisperse seed particles with a radius of 65 nm. Potassium persulphate was used as initiator and sodium dodecyl sulphate as surfactant. All reactions were run at 50°C in a thermostatted bath. Experiments were run in conditions corresponding to either zero-one or pseudo-bulk kinetics. In order to explore a wide range of conditions, n-dodecanethiol (n-DDT) concentrations of 0, 1.0 and 5.0 wt% (based on monomer) were used. Samples were taken during the runs and quenched with a hydroquinone solution. Gas chromatography (GC) was used to measure n-DDT in the samples, while monomer conversion was determined gravimetrically. Molecular weight distributions (MWDs) were measured using GPC (Waters 2690 Separation Module with Millenium 2010 software).

Results

Using the cumulative MWDs obtained from GPC, pseudo-instantaneous MWDs (i.e. the MWD of polymer produced during a specified conversion interval) were obtained by subtracting successive MWDs that had been normalized with respect to conversion (1,2). Using these pseudo-instantaneous MWDs and the GC data, it is possible to infer the ratio of CTA to monomer in the particles using the following procedure. Knowing the overall monomer concentration, the monomer concentration in the particles can be calculated by applying thermodynamic relationships and assuming the monomer is in equilibrium among all phases. The pseudo-instantaneous number molecular weight distribution is then used in conjunction with MWD models describing either zero-one or pseudo-bulk conditions to calculate the ratio [Tp]/[Mp] for each conversion interval. The value of [Tp] can then be determined since [Mp] has been calculated. The equilibrium value of the CTA concentration in the particles ($[Tp]_e$)can be calculated by assuming equilibrium exists among the three phases.

From the experimental data, values of [Tp] and $[Tp]/[Tp]_e$ were determined for both zero-one and pseudo-bulk conditions as a function of conversion. Values typically range from $\sim 10^{-1} - 10^{-3}$, depending on the type of kinetics and the conversion. Zero-one conditions showed [Tp] values closer to equilibrium values than pseudo-bulk systems.

The feasibility of using GC measurements of n-DDT to infer the instantaneous MWD was also investigated. The approach appears promising but there are difficulties associated with it that need further study.

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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. 51, January, 1999, which can be found at the end of this report. Abstracts of several reports are given below.

1. Miniemulsion Copolymerization of Styrene and *n*-Butyl Acrylate

Christopher D. Anderson & Fido N. Willybiro

Miniemulsion copolymerizations of styrene and *n*-butyl acrylate were first performed in order to study the effects of using Triton X-405 as surfactant. It was observed that miniemulsion polymerizations at a higher temperature (70°C) resulted in the coalescence of droplets and hence reduced the extent of droplet nucleation. Miniemulsion polymerizations were also performed using a reduction/oxidation initiator system at a lower temperature (35°C) to minimize the effect of droplet coalescence. Lower temperature, redox-initiated miniemulsion polymerizations had a greater number of droplets nucleated than the higher temperature polymerizations. SLS was used along with Triton X-405 to form mixed surfactant miniemulsions. The mixed surfactant miniemulsions had a kinetic profile which was intermediate between that of Triton X-405 alone and SLS alone. The temperature-dependent partitioning characteristics of Triton X-405 play an important role in the nucleation mechanism of the present monomer/surfactant system.

Miniemulsion homopolymerizations and copolymerizations of styrene and *n*-butyl acrylate were also performed where polystyrene and poly(*n*-butyl acrylate) were predissolved in various combinations in the monomers to explore the phenomenon of 'enhanced droplet nucleation'. The rates of reaction and number of particles profiles were obtained and compared. 'Enhanced droplet nucleation' was observed in styrene homopolymerizations, Sty/BA copolymerizations, and BA homopolymerizations. Different types of predissolved polymers produced the same reaction kinetics. Homopolymerizations of *n*-butyl acrylate appear to be limited to a maximum number of particles.

2. NMR Characterization of Copolymer Latexes Based on Polystyrene and MMA/MAA-Macromonomer

Dingying Xu

Copolymer latex particles based on 90% (w/w) styrene and 10% (w/w) MMA/MAA-macromonomer were prepared at 70°C by batch miniemulsion polymerization using sodium persulfate as initiator. Previously synthesized copolymer latexes based on styrene (80% w/w) and macromonomer (20% w/w) were shown to contain macromonomer-rich small particles, which are believed to be formed from the extra amount of the macromonomer that is immiscible with the styrene in the system. The investigation of the 90/10 styrene/macromonomer latex with different techniques has shown that a microphase separation process is occurring in the latex. The extent of this phase separation is found to be dependent on the aging time and the aging conditions, such as temperature. ^{1}H spin-diffusion solid-state NMR, a serum replacement technique, and transmission electron microscopy are the major methods used to characterize the latex particles. As a consequence of the results gathered so far on the styrene/macromonomer copolymer system, the use of this macromonomer as a compatibilizing agent to improve the mechanical properties of the heterogeneous composite particles does not seem to be an achievable goal, since the microphase separation process is a dynamic phenomenon in this particular copolymer latex system.

Another copolymer latex based on 85% (w/w) 4-vinyl pyridine and 15% (w/w) MMA/MAA-macromonomer was prepared using the same recipe as in the styrene/macromonomer system. Preliminary kinetic results indicate that these two monomers copolymerize very well. This observation can be justified by the literature values of the reactivity ratios between MMA and 4-vinyl pyridine, which are $r_1 = 0.574 \pm 0.004$ and $r_2 = 0.790 \pm 0.009$, respectively. The ^{1}H spin-diffusion measurements on the latex indicate a homogenous (one-phase) composition of the latex particles.

3. Film Formation from Latex Blends

Jason Tang

Latex blending is a strategy commonly used to reduce volatile organic components (VOCs). Therefore, a deep understanding of the parameters governing film formation from latex blends is necessary. This program focuses on the investigation of the influence of the particle/particle interface on particle packing in latex blend films after drying, and the morphology and properties of the resulting films. Model hard/soft latex blends consisting of polystyrene (PS) (hard) and poly(*n*-butyl methacrylate-co-*n*-butyl acrylate) [P(BMA/BA)] (soft) latex particles have been used in this project. Carboxyl groups were incorporated to alter the surface properties of the latex particles.

To investigate each specific parameter influencing film formation in latex blends, well-defined particles with monodisperse size, homogeneous composition, and independent control of particle size and carboxyl group surface density were synthesized by well-designed semi-continuous emulsion polymerization processes. With the well-defined particles that were obtained, model latex blends were prepared. Following the previous study of the influence of carboxyl groups on the latex particles on the drying kinetics for these model latex blends, the drying kinetics study was extended to investigate the effect of the degree of neutralization of the carboxyl groups with different bases. It was found that for the latex blends with low carboxyl group coverage on the PS latex particles (i.e., 10%), the drying rate increased as the extent of neutralization using a strong base increased; for the latex blends prepared with high carboxyl group coverage on the PS latex particles (i.e., 77.2%), the drying rate first decreased and then increased as the extent of neutralization with a strong base increased. If the carboxyl groups were neutralized by NH_4OH, the drying rate increased as the ratio of $[NH_4OH]/[COOH]$ increased for the latex blends with both low and high carboxyl group coverage on the latex particles.

The surface morphology and properties of polymer films prepared from the model latex blend were also investigated in terms of neutralization of the carboxyl groups. Gloss and surface smoothness increased substantially as the extent of neutralization increased. Among all the bases used for the neutralization, NH_4OH showed the smallest improvement of the surface gloss and smoothness. The surface smoothness also increased as the radius of the counterions of the specific base increased, although the improvement was less than that obtained by variations in the extent of neutralization.

Models were proposed to explain these phenomena. It seems that the PS latex particles with high carboxyl group coverage might form clusters by the formation of interparticle hydrogen bonds. Neutralization of the carboxyl groups might disrupt the clusters and result in the particles becoming more uniformly distributed on the surface of the films. Also, a low extent of neutralization of the carboxyl groups on the latex particles would disrupt the clusters and allow most of the carboxyl groups to be freely hydrated via hydrogen bonding with water.

4. Hybrid Composite Latexes

Pilmoon Jeong

A direct miniemulsification process has been used to prepare artificial latexes. Recently, a seeded polymerization study was performed to prepare core-shell latex particles using the artificial latex as a seed after stripping off solvent. This solvent can be replaced with a vinyl monomer such as styrene, which would be subsequently polymerized to form hybrid composite latexes. Direct miniemulsification of Kraton polymer solution in styrene was performed with SLS surfactant and HD cosurfactant as in conventional miniemulsions. Experiments in this system have shown that hexadecane still operates as a cosurfactant, but its effect is not as great as in a conventional miniemulsion system due to the presence of the Kraton rubber. It was found that the use of cetyl alcohol as cosurfactant is more effective in reducing the amount of large droplets (over 500 nm) by lowering the interfacial tension between the water and the oil phase (Kraton rubber and monomer). Higher homogenization pressure and a lower number of homogenization cycles were preferred to reduce the numbers of both very small droplets and large miniemulsion droplets. The use of a membrane filtration method demonstrated a noticeable effect in reducing the amount of large miniemulsion droplets over 500 nm. The sonification time for the membrane filtration process still needs to be optimized. The density gradient centrifugation results showed that the latex obtained by polymerizing the membrane-filtered emulsion contains relatively more homogeneous hybrid particles than that generated from a homogenized emulsion (using sonification and Manton-Gaulin homogenization).

Emulsion droplets were examined by TEM after solution or vapor staining with OsO_4. During the solution staining process, coalescence of droplets was not observed. However, the vapor staining method produced aggregates of droplets and droplets with irregular shapes.

From the kinetic studies carried out using different initiators, it was observed that the KPS-initiated latex system produced two times more particles than the AMBN-initiation system possibly due to a secondary nucleation of particles in the KPS system. An observed induction time could be shortened for the system utilizing oil-soluble initiators by purifying the Kraton rubber three times. This continued induction period indicates that the Kraton rubber contains some other material which is not easily removed by a purification process using toluene as a solvent and methanol as a nonsolvent and consumes a fraction of radicals generated in the monomer droplets.

5. Towards an Understanding of Steric Stabilization when using PEO-PS-PEO Triblock Copolymer as the Stabilizer in Non-Aqueous Emulsion Polymerization Systems

Xiaorong You

In order to understand the different kinetic behaviors of PEO-PS-PEO triblock copolymers in a model non-aqueous emulsion polymerization system consisting of ethyl methacrylate (EMA) and lauryl methacrylate (LMA) comonomers, a method was developed to measure the adsorption of PEO-PS-PEO triblock copolymer on latex particles. The PEO-PS-PEO triblock copolymer could be found in 4 different locations in the latex system: (1) entrapped inside the copolymer particles; (2) anchored to the surface of the copolymer particles; (3) physically adsorbed onto the particles; and (4) as "free" triblock copolymer in the propylene glycol continuous phase. The locations of the triblock copolymers were determined via I_2 titration of the serum (obtained from a serum replacement cell), the clean latex and a supernatant (obtained by centrifugation of the latex).

A transition was observed in the amount of PEO-PS-PEO triblock copolymer that was physically adsorbed on the latex particles for a PS block length of about 30 units. When the PS block size is less than 30 units, adsorption is decreased due to the rearrangement of mixed PEO brush and adsorbed PS block. When the PS block length is greater than 30 units, adsorption is increased since the PS swollen core prefers to remain on the particle surface as opposed to desorbing into the propylene glycol medium. Also, the lower limit for the PS unit length is controlled by the binding energy between the PS block and the latex surface. The upper limit of the PS block length is governed by the solubility of the PS block in propylene glycol.

The amount of PEO-PS-PEO, which is anchored onto the latex particle surface, increases monotonically with the PS block length by virtue of a greater binding energy for longer PS unit lengths.

Due to the high solubility of ethyl methacrylate and lauryl methacrylate in propylene glycol (5wt%), homogeneous nucleation is predominant during the entire emulsion polymerization process. The final particle size is governed by the limited surface coverage by the triblock copolymer on the particle surface.

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Enhanced Droplet Nucleation in Miniemulsion Polymerization— A Kinetic and Mechanistic Study
(P.J. Blythe)

Miniemulsion Copolymerization of Vinyl Acetate and Vinyl 2-Ethylhexanoate Monomers
(E.L. Kitzmiller)

Miniemulsion Copolymerization of Styrene and n-Butyl Acrylate Using Triton X-405 as a Surfactant
(C.D. Anderson)

Enhanced Particle Nucleation in Miniemulsion Copolymerizations
(F.N. Willybiro and C.D. Anderson)

NMR Characterization of Copolymer Latexes Based on Polystyrene and MMA/MAA-Macromonomer
(D. Xu)

Living Free-Radical Miniemulsion Polymerization of Styrene
(T. Prodpran)

Living Free-Radical Miniemulsion Polymerization of Styene
(G. Pan)

Encapsulation of Inorganic Particles via Miniemulsion Polymerization
(B. Erdem)

The Role of Mixed Anionic-Nonionic Systems of Surfactants in the Emulsion Polymerization of Styrene
(D. Colombié)

The Effect of Chain Transfer to Triton X-405 on the Kinetics of the Emulsion Polymerization of Styrene
(K. Antoine and D. Colombié)

Emulsion Polymerization of Styrene Using a Reactive Surfactant
(X. Wang)

The Role of the Polymerizable Surfactant Sodium Dodecyl Allyl Sulfosuccinate in the Emulsion Copolymerization of Vinyl Acetate/Butyl Acrylate
(P.C. Hohl)

Grafting Reactions Occurring in the Emulsion Polymerization of Vinyl Acetate Using Poly(Vinyl Alcohol) as Emulsifier
(B.M. Budhlall)

Morphology and Film Properties of Carboxylated Poly(n-Butyl Acrylate)/Poly(Methyl Methacrylate) Composite Latexes
(M. _andor)

Film Formation from Latex Blends
(J. Tang)

The Effect of Crosslinking on Latex Film Formation
(H. Mohd. Ghazaly)

Hybrid Composite Latexes
(P. Jeong)

Effect of Agitation on Scale-Up of Emulsion Polymerization Reactors
(S. Krishnan)

Effects of Dissolved Polymers on the Transport of Colloidal Particles in a Microcapillary
(S. Amnauypanich)

Kinetics and Morphology of Particle Aggregates
(S. Phattanarudee)

Towards an Understanding of Steric Stabilization when using PEO-PS-PEO Triblock Copolymer as the Stabilizer in Non-Aqueous Emulsion Polymerization Systems
(X. You)

DISSERTATION AND THESIS TITLES

RECENT PUBLICATIONS

Contribution to the International Polymer Colloids Group Newsletter

Alice P. Gast
Department of Chemical Engineering, Stanford University, Stanford, CA 94305-5025

The Gast research group consists of seven Ph.D. students and two post-doctorial researchers. Eric Furst, Dean Wang, Albert Lee, and Poe Ratanabanangkoon, along with John Pople, a post-doctoral researcher, are advised by Alice P. Gast. Szu Wang, Giusuppe Trigiante and Sammy Farah are jointly advised by Alice P. Gast and Channing R. Robertson. Joe Hur is jointly advised by Alice P. Gast and Eric S. G. Shaqfeh. We also have three visiting post-doctorial researchers: Tamara Coussaert from Belgium, Wolfgang Feneberg from Germany, and Pan MingXiang from China. We are interested in studying the physical and chemical processes governing the behavior of complex and macromolecular fluid. In our research, we aim to understand these processes and their influence on bulk properties through a combination of colloid science, polymer physics, and statistical mechanics. The following are representative abstracts from the research projects of different members of the group.

Characterizing the Structure of Various pH Dependent Block Copolymer Micelles

Albert S. Lee, Vural Butun+, Steven P. Armes+, Alice P. Gast

+School of Chemistry, Physics and Environmental Science
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Abstract

We use light and neutron scattering techniques to characterize the structure of various novel pH dependent diblock copolymer micelles suspended in water. The molecular weights of these copolymers range from 10,000 to 30,000, and the copolymers are studied in dilute aqueous solution, at concentrations between 0.1 and 1 wt %. Each copolymer contains a 2-(diethylamino) ethyl methacrylate (DEAEMA) or 2-(dipropylamino) ethyl methacrylate (DPAEMA) block and a water soluble block consisting of 2-(dimethylamino) ethyl methacrylate (DMAEMA), betainized DMAEMA, or polyethylene oxide. Under neutral to basic conditions the DEAEMA or DPAEMA blocks are insoluble in water and aggregate to form the micelle core. Protonation of the amine groups along the side chains of DEAEMA or DPAEMA under acidic conditions causes the copolymers to be soluble in water. We measure scattered light intensity as a function of pH or added salt to find critical pH's or salt concentrations where the transition from single chains to micelles occurs. Dynamic light scattering (DLS) experiments provide micelle hydrodynamic radius distributions, and we use small angle neutron scattering (SANS) to measure other structural properties including the micelle radius of gyration and the degree of swelling in the micelle corona. The DLS results show micelle radii ranging from 15 to 80 nm. Under certain conditions these copolymers behave as polyelectrolytes which cause for interesting inter and intra molecular interactions. The light and neutron scattering experiments are performed under varying pH and salt

concentrations and provide insight into how the intermolecular forces and interactions govern the micelle aggregation and structural behavior. A star-like micelle model is also used to provide additional insight into the micelle structural properties.

Phase Diagram of the Yukawa System

Dean C. Wang and Alice P. Gast

Abstract

First-order phase transitions, such as freezing, are important processes which occur in many widely-varying systems, from the basic elements to colloidal suspensions to plasmas. A complete microscopic theory of crystallization, however, has yet to be formulated. Such a theory could help elucidate such phenomenon as the order-disorder transition found in colloidal systems. One approach that has been used in recent years to study this problem is density functional theory (DFT), which attempts to utilize information from liquid state theory to locate the equilibrium solid and hence the freezing transition. We have formulated a revised version of Denton and Ashcroft's Modified Weighted Density Approximation (MWDA) formalism of DFT that takes into account the static solid lattice in addition to the uniform liquid. Using this new model, we are able to obtain thermodynamic properties and generate phase diagrams of hard and soft spheres, including power law and Yukawa fluids.

Microscopic Mechanics using Laser Tweezers

Eric M. Furst, Alice P. Gast

Abstract

Optical gradient force trapping techniques, or laser tweezers, have become increasingly useful and important tools for studying the microscopic structure, mechanics, and interactions in biological, colloidal, and macromolecular materials. In our present work, we use optical trapping to study the micromechanical properties of dipolar chains and chain aggregates in a magnetorheological (MR) suspension. The tunable anisotropic particle interaction of these materials is interesting for the macroscopic liquid-solid rheological transition they exhibit in an applied field and for investigating the fundamental role of interactions on the structure and dynamics of colloidal suspensions. Using dual-trap optical tweezers, we are able to directly measure the deformation of dipolar chains parallel and perpendicular to the applied magnetic field. We observe the field-dependence of the mechanical properties of the chains, such as tensile strain, chain reorganization, and rupturing. These forms of energy dissipation are important for understanding and tuning the yield stress of an MR suspension.

Two-dimensional Enzymatic Reactions

Giuseppe Trigiante, Channing R. Robertson, Alice P. Gast

Abstract

The reaction between Clostridium Histolyticum collagenase, a proteolytic enzyme, and its model substrate FALGPA has been investigated under two-dimensional conditions, i.e. with both enzyme and substrate confined on quartz surfaces. In the setup FALGPA was covalently attached to the surface of quartz while collagenase was non-covalently adsorbed. The enzyme was shown to be free to move across the surface with a characteristic diffusion constant, while it did not measurably desorb from the surface, i.e. adsorption was irreversible. It could effectively react with its substrate, and the observed kinetics was very different from the one displayed in solution.

Investigation of Two-Dimensional Streptavidin Crystallization

Szu-Wen Wang, Alice P. Gast, and Channing R. Robertson

Abstract

Many applications motivate the study of the fundamental physical factors that govern ordered protein assembly on surfaces. These include two-dimensional (2D) protein crystallization for complex structural analyses, biosensors, and biocompatible materials. We have used the growth of 2D streptavidin crystals to study molecular interactions in protein arrays. Streptavidin molecules bound to biotinylated lipid self-assemble in an ordered monolayer on a Langmuir trough, creating 2D crystals with distinct macroscopic morphologies. These morphologies are observed with fluorescence microscopy, while the lattice arrangement is determined using transmission electron microscopy and electron diffraction techniques.

Changes in protein-protein interactions are accomplished by pH alterations and genetic manipulation. Under conditions of pH > 7.0, dendritic X-shaped morphologies are formed and show C222 symmetry. Needle-like domains observed at acidic conditions (pH < 4) correspond to reported crystals with P1 symmetry. Near pH 5.7, we find a new crystal phase with P2 symmetry. While only three crystal phases exist over the pH range of 4-9, we observe several unique and intermediate domain shapes between pH 4.5-6.5. This observation is explained by solid-phase coexistence, and the different morphologies are composed of various coexisting crystal ratios. These observations suggest that it is possible to control 2D protein self-assembly by directed manipulation of protein interactions, resulting in protein arrays with desired properties. Indeed, our experiments have shown that specific amino acids at crystal contact regions can be replaced to modify the attraction or repulsion between contact regions. Interaction alterations in the P1 crystal form give interesting morphological, crystallographic, and thermodynamic changes in both P1 and P2 crystals. Our results confirm that macroscopic and microscopic changes in 2D crystalline properties can be elicited by selectively altering specific intermolecular interactions.

Contribution from the group of Ton German at Eindhoven University of Technology to the IPCG Newsletter (H.M.A.van.der.Heijden@tue.nl, http://www.chem.tue.nl/spc/)

I. Post-Crosslinking of Functional Polymers Using Photo Acid Generators[#]

John M.G. Verstegen[§] *and Anton L. German*[*]
Eindhoven University of Technology, PO Box 513, 5600 MB Eindhoven, The Netherlands

[#] This is a brief summary of the Ph.D. thesis of John M.G. Verstegen "Post-Crosslinking of Functional Polymers Using Photo Acid Generators. Synthesis of Hydroxy-Functional Monomers and Their Application in Emulsion Polymerization", Eindhoven University of Technology, 1998.

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[*] Author of Correspondence

This thesis aims at investigating the preparation of latexes and latex films containing functional monomers, and the crosslinking of these latex films by means of UV irradiation. In principle, three components are essential in the system, *i.e.*, a polymer containing reactive groups, a crosslinker and a photoinitiator. The latter, a so-called Photo Acid Generator (PAG), generates protons after irradiation by UV light. These protons serve as a readily diffusing catalyst for the reaction between polymer and crosslinker.

In this research, the following aspects have been investigated: monomer synthesis, emulsion polymerization of these functional monomers, crosslinking and the effect pigmentation.

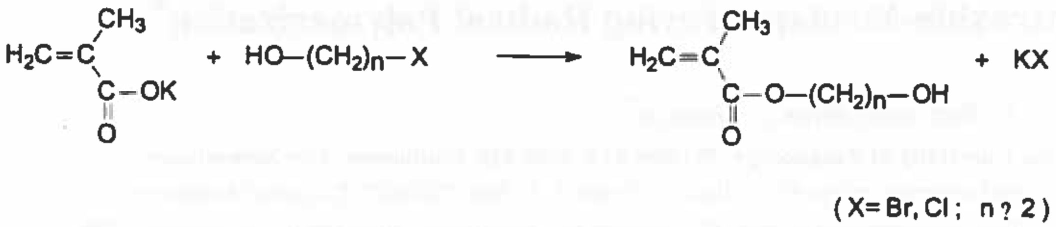
The first part of the thesis is focused on hydroxy-functional (meth)acrylate monomers. These monomers were used to synthesize copolymers bearing functional groups, which can be crosslinked using an external crosslinker. However, the commercially available hydroxy-functional (meth)acrylates have a high water solubility, which will lead to chemically heterogeneous polymers in batch emulsion copolymerization processes. In order to avoid this problem, two complementary strategies have been developed. The first one is the synthesis of a series of ω-hydroxy-1-alkyl methacrylates having a longer alkyl chain. The reaction of methacryloyl chloride with an α,ω-diol proved to be the best route for practical reasons. A decreasing water solubility was indeed determined in the series 3-hydroxy-1-propyl- (HPMA), 4-hydroxy-1-butyl- (HBMA), 6-hydroxy-1-hexyl- (HHMA) and 8-hydroxy-1-octyl- (HOMA) methacrylate.

The second strategy involves drastically decreasing the initiator concentration during the batch emulsion polymerization process. In this way, the probability of oligomers terminating in the aqueous phase decreases, which results in a more efficient incorporation of the hydroxy-functional monomers. This was indeed observed in batch emulsion polymerizations of STY-HPMA and STY-HEMA.

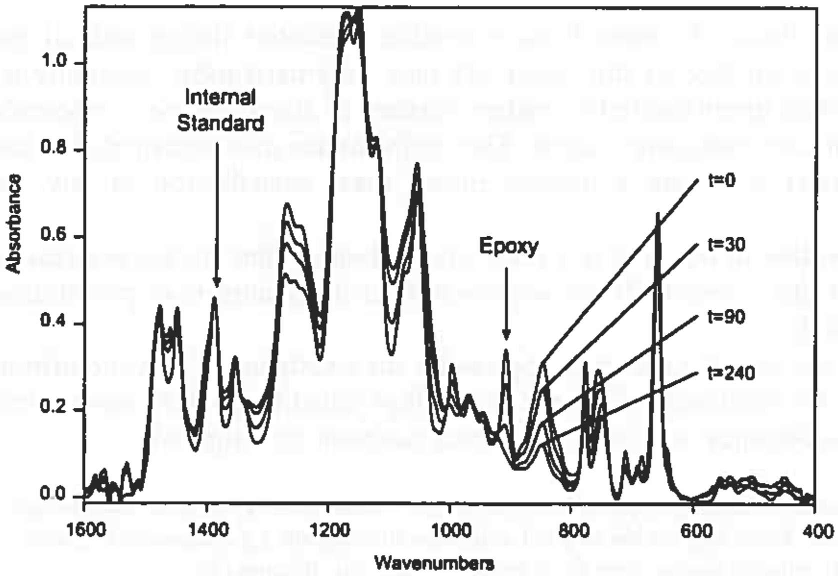
The use of the newly synthesized functional monomers was investigated in batch emulsion copolymerization with comonomers having a low water solubility, such as STY and BMA. For the systems STY-HPMA and STY-HBMA, emulsion copolymerizations as well as computer simulations with TRISEPS were carried out.
First, it was necessary to determine the bulk reactivity ratios. Experiment and prediction were in good agreement for the azeotropic composition. On the basis of these experiments it was concluded that an ω-hydroxy-1-alkyl methacrylate monomer having an alkyl chain length of four, already gives a sufficiently low water solubility to allow the preparation of homogeneous hydroxy-functional copolymers with styrene in batch emulsion polymerization.
Subsequently, emulsion copolymerizations were carried out of the ω-hydroxy-1-alkyl methacrylates HPMA, HHMA and HOMA with BMA. No composition drift was observed in the systems HHMA-BMA and HOMA-BMA. Only the HHMA-BMA copolymers were used for further crosslinking experiments.

The second part of the thesis describes the crosslinking reactions, which were examined for two different systems. First, the trans-etherification of hydroxy-functional monomer and polymer with a complementary crosslinker, *i.e.*, hexa(methoxymethyl)melamine (HMMM), was investigated. In model experiments with HEMA and HMMM, two acid catalysts were used, *i.e.*, pTsOH and a Photo Acid Generator. The latter one generates an acid after UV irradiation. The system appeared to perform satisfactorily, despite the fact that the efficiency of the PAG was 2 to 3 times lower as compared to pTsOH. Next, it was tried to crosslink HHMA-BMA latexes with HMMM using pTsOH as catalyst, but this was not (yet) successful.
In addition, an epoxy-functional system was investigated for which no external crosslinker was needed. Epoxy-functional co- and terpolymers were prepared by copolymerization of glycidyl methacrylate (GMA) in solution and solution cast films were successfully crosslinked by UV light in the presence of a PAG. The main parameters in this process are the concentration of epoxy-functional groups, the glass transition temperature of the polymer and the curing temperature.
Epoxy-functional latexes were also prepared via a mini-emulsion polymerization process in the presence of a hydrophobic PAG. In this manner it was possible to form polymer particles which contain PAG. Crosslinking of films derived from these latexes by UV light has not yet been accomplished.

In the final part the catalytic function of the H^+-ions, generated by a PAG after exposure to UV-light, was investigated for an epoxy-functional model system. The efficiency of the PAG and the penetration depth of the H^+-ions were investigated, in the presence as well as in the absence of a white pigment (TiO_2). The principle appeared to work well for the non-pigmented system; in the presence of pigment the polymerization reaction also proceeded, but more slowly.



Reaction of the potassium methacrylate salt with a ω-halo-1-alkanol.



FTIR spectra of the cationic curing of solution copolymer BG_S1.

II. Nitroxide-Mediated Living Radical Polymerization[#]

Stefan A. F. Bon[§] *and Anton L. German*[•]

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[#] This is a brief summary of the Ph.D. thesis of Stefan A. F. Bon "DEBUT: Collected Studies on Nitroxide-Mediated Controlled Radical Polymerization", Eindhoven University of Technology, 1998.

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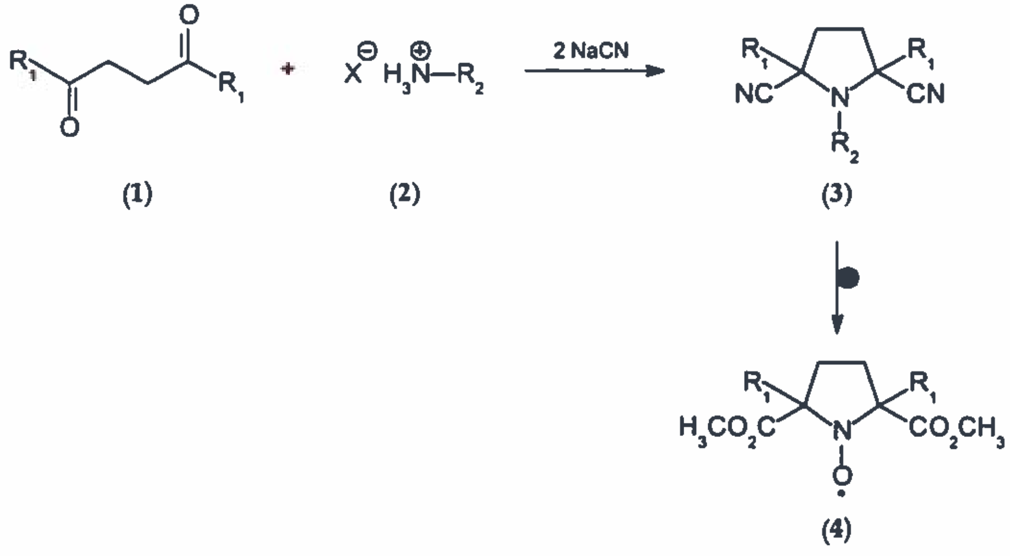
Three different lines of research on nitroxide-mediated living radical polymerization are presented. The advantage of this relatively new polymerization technique is that a controlled chain-growth of an approximately constant number of alkoxyamine compounds is possible when proper reaction conditions are chosen. The performance of a homopolymerization then yields a polymer material featuring a narrow molar mass distribution at any stage of monomer conversion.

The first line of research is a study on synthetic routes for the preparation of a wide range of cyclic nitroxides. Three different approaches for the synthesis of pyrrolidine-based nitroxides were investigated.

Beside the use of a common approach - the treatment of a cyclic nitrone with a Grignard reagent – for the synthesis of simple tetra-alkyl substituted derivatives, the double Strecker reaction of 1,4-diketones with primary amines has been investigated.

Scheme 1 Double Strecker reaction of a symmetrical 1,4-diketone (1) with an *N*-protonated amine compound (2) and two equivalents of cyanide to yield a mixture of different 2,5-dicyano-2,5-disubstituted-*N*-substituted pyrrolidines (3), suitable as precursor for nitroxides of general structure (4).



It was concluded that both product yield and stability of the synthesized 2,5-dicyanopyrrolidines, as well as the rate of reaction and the stereochemical outcome were influenced by steric factors. The applicability of this method is as yet restricted by the limited success of the conversion of both nitrile groups to esters, so that in the end only the synthesis of *cis*-2,5-dimethoxycarbonyl-2,5-dimethylpyrrolidin-*N*-oxyl had been accomplished.

The third synthesis route is a newly developed method based on the 1,3-dipolar cycloaddition of azomethine ylides, carrying four carbon substituents, to activated olefins. The preliminary results showed that this method has great potentials for the stereo-controlled synthesis of pyrrolidine compounds with a variety of substituents at the C(2) and C(5) positions. Reactions carried out using an imine-enamine mixture, derived from *L*-alanine methyl ester and methyl pyruvate, and dimethyl fumarate, fumaronitrile, methyl acrylate and methyl methacrylate all proceeded under mild conditions.

Moreover, a proper choice of the reaction conditions showed that the stereochemical outcome of the cycloaddition could be controlled.

Within the scope of the research on synthesis routes towards nitroxides, efficient methods to prepare alkoxyamines were investigated. Beside a brief literature survey on different synthetic approaches, an efficient method for the synthesis of alkoxyamine species, in which the alkoxyamine C-O bond was formed via coupling of a carbon-centered radical species with a nitroxide, is reported. Di-*tert*-butyl peroxalate was used as a radical source, which produces *tert*-butoxy radicals (half-life *ca.* 13.7 h at 298 K). The required carbon-centered radicals were formed by secondary processes, particularly addition to and hydrogen-atom abstraction from the solvent by the *tert*-butoxy radicals.

The second line of research is a kinetic study on the mechanism of nitroxide-mediated CRP. Two of the most important aspects to be considered were the reversible and non-reversible homolysis of the alkoxyamine C-O bond. Principally, the individual rate coefficients and Arrhenius parameters for the related kinetic events have been investigated. The processes of trapping a carbon-centered radical with a nitroxide via coupling or disproportionation have been thoroughly discussed. A correlation between the Arrhenius equations for the overall decomposition of an alkoxyamine and the alkoxyamine C-O bond homolysis was derived, which yielded the difference in activation energy and the ratio of the pre-exponential factors for trapping via coupling or via disproportionation. Literature data revealed that the latter process had a higher barrier for activation of *ca.* 17-34 $kJ \cdot mol^{-1}$ and was marked by a lower value of the pre-exponential factor.

Two methods to determine the rate coefficient for alkoxyamine C-O bond homolysis were presented. Both methods were based on dissociating the alkoxyamine in the presence of a scavenger, *i.e.*, a different nitroxide or molecular oxygen, under pseudo-first order conditions.

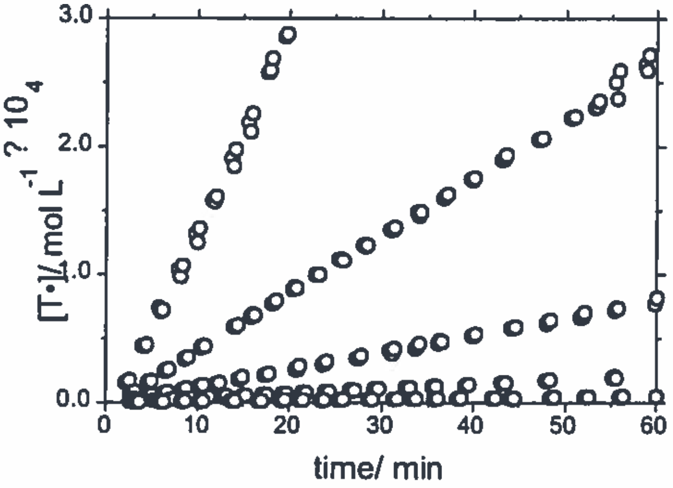


Figure 1 [TEMPO] *vs.* time measured by quantitative ESR for a 0.01 mol·L^{-1} solution of *N-(2-tert*-butoxy-1-phenylethoxy)-2,2,6,6-tetramethylpyridine in toluene at 333 K, 343 K, 353 K, 363 K and 373 K. Note that the concentrations are based on the volume at room temperature.

Solvent effects and the influence of the alkoxyamine chemical structure on the rate coefficient for homolysis were studies. One of the important results was the higher rate coefficient for homolysis of alkoxyamines with longer chain-lengths, which was primarily reflected in an increase in the pre-exponential factor.

The mechanism of the TEMPO-mediated CRP of styrene has been investigated. From these results it became clear that the polymerization proceeded via ordinary free-radical kinetics, extended with the novel kinetic events, such as the reversible alkoxyamine homolysis.

Among other things, this conclusion was drawn from the observation that the initial overall rate of polymerization was independent of the amount of alkoxyamines and, thus, solely determined by the additional radical flux, *i.e.*, the thermal self-initiation of styrene, and the rate of bimolecular termination. The latter process did not show a pronounced chain-length dependence in the area of low conversion.

Other aspects discussed included the suppression of the Trommsdorff effect in nitroxide-mediated CRP systems, the conditions needed to control chain-growth and the influence of permanent chain-stopping reactions, such as chain-transfer to monomer. It was shown from simple model calculations that the number of alkoxyamine molecules in the nitroxide-mediated CRP of styrene in bulk should be in the order of at least 10^{-2} mol·L^{-1} to limit the fraction of "dead" polymer chains.

Finally, the third line of research is to apply the nitroxide-mediated CRP technique in an emulsion polymerization system. Seeded emulsion polymerization of styrene mediated by TEMPO showed that proper control of chain-growth was possible.

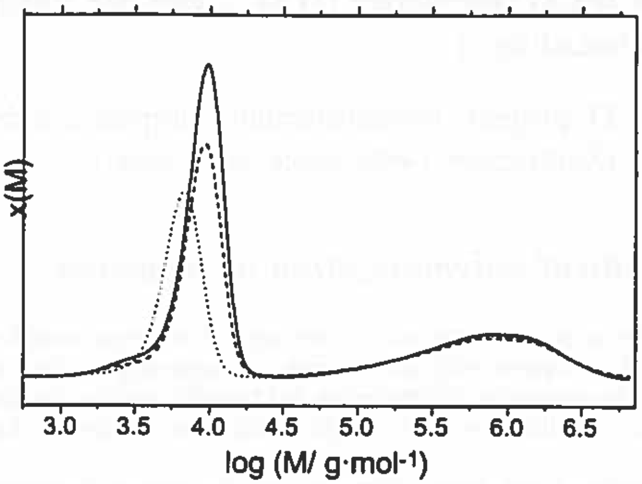


Figure 2 The differential log MMDs obtained from the refractometric GPC spectra of latexes from a seeded emulsion CRP experiments without sodium hydrogen carbonate after 12 h, 24 h, and 36 h of reaction at 398 K. Chain-extension experiments, performed by addition of a second batch of monomer and followed by analysis of the final MMD of the obtained polymer material, indicated that *ca.* 16% of the chains were deactivated permanently after the first step. This was primarily ascribed to trapping via disproportionation.

Contribution from the group of Ton German at Eindhoven University of Technology to the IPCG Newsletter (H.M.A.van.der.Heijden@tue.nl, http://www.chem.tue.nl/spc/)

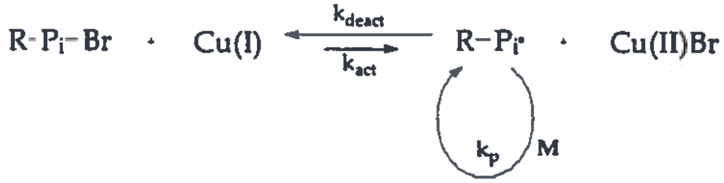
Summary of the Ph.D. project 'Intramolecular composition drift', Gregory Chambard (September 1996-September 2000)

Atom transfer radical polymerization in emulsion

Free radical polymerization in general is the most widely applied technique used for the commercial production of polymers and plastics, since it requires only mild reaction conditions and it is not very sensitive towards impurities such as water. However, the occurrence of termination and transfer reactions disables the controlled fine-tuning of polymer properties, such as the molecular-weight distribution, endgroup functionality, composition and microstructure.

Only recently systems enabling a high degree of control over the cause of the reaction became accessible in radical polymerization. These controlled radical polymerization mechanisms involve the reversible transformation of the polymer into a dormant species. Atom transfer radical polymerization (ATRP) is the most versatile and robust system and makes use of a copper complex to catalyse the reaction. The application of ATRP in emulsion offers great possibilities to produce well-defined polymers at a large scale. The general reaction scheme is depicted below.

Since the copper complex is of primary importance in ATRP, the first step was to create a high partitioning for the complex between monomer and aqueous phase. By using the large hydrophobic diphenylpropyl carbaldehyde imine as ligand, the existing copper/imine complex was adapted in order to create low water solubility. Since electronic interactions between the copper complex and the surfactant have to be avoided, non-ionic surfactants were applied. Application of the developed system in seeded and *ab initio* emulsion polymerization resulted in stable latices, but polymerization showed only partly the characteristics of a controlled reaction. Instead of linear growth, the molecular weight increased extremely fast at low molecular weight (see figure 1), after which a steady growth set in. Within 5% conversion molecular weights up to 10^5 g/mol were obtained, indicating polymerization according to the free radical mechanism. In addition, both molecular weight data and kinetics show that the polymerization was controlled up to 60-70% conversion, after which molecular weights did not increase anymore. Control over polymerization was probably lost, because of transfer to monomer, caused by a low monomer concentration in the particles.



To investigate the influence of ligand, the imine was replaced by di-heptylbiyridine (dHbpy). The reaction showed more control and molecular weights increased nicely with conversion (see figure 2).

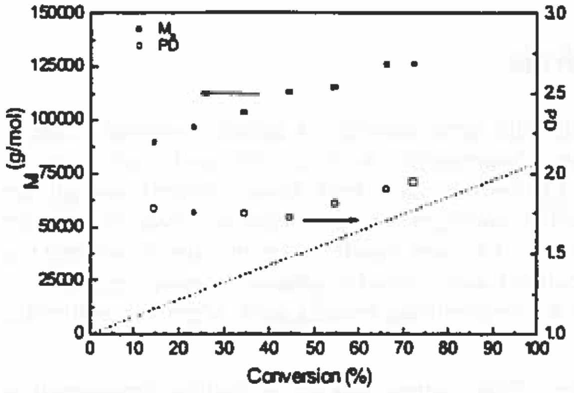


Figure 1.

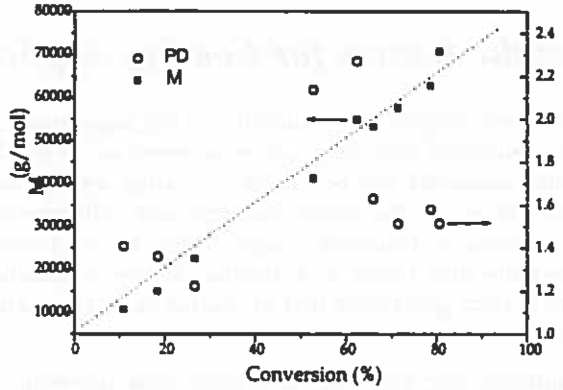


Figure 2.

It is known that the resulting copper complex has a different equilibrium constant and tends to stabilize the Cu^{2+} more than the copper/imine complex. Furthermore, the copper/dHbpy complex is much less hydrophobic than the copper/imine complex. We suspect that the difference in water solubility plays the keyrole in this case, and we are currently investigating the effect of partitioning of the copper complex.

Comments and suggestions are welcome: G.Chambard@tue.nl

Summary of the Ph.D. project 'Telechelic polymer latex for UV crosslinkable coating', Hans de Brouwer (September 1996-September 2000)

Telechelic Latices for Coating Applications

This project investigates the possibilities of the preparation of telechelic latex materials. A system is desired in which such end-functional polymers can be prepared in an emulsion polymerization without additional reaction steps. These latex materials can be useful in coating applications. Latices that have been functionalized through the copolymerization of a functional monomer have a distribution of functional groups both within and over the polymer chains. Lowering the molecular weight of such a system with the use of a chain transfer agent in order to improve the film formation may result in a fraction of non-functional material and a poorly defined network structure. A telechelic system guarantees that all chains can participate in the crosslinking process even when the molecular weight is low.

Allylic sulfides have been used to prepare these telechelic latices. These compounds act as addition fragmentation chain transfer agents in radical polymerizations according to the depicted mechanism.[i,ii,iii] They allow a high degree of tailoring to make them suitable for specific systems. An allylic sulfide has been designed with a water solubility, functionality and reactivity suitable for the emulsion polymerization of both styrene and (meth)acrylates.
Combined use of this type of CTA with a functional initiator will result in a completely telechelic product. This has been confirmed with Gradient Polymer Elution Chromatography (GPEC).[iv] Standards with a varying number of hydroxyl groups could be separated in fractions with none, one, two, three and more than three hydroxyl groups per polystyrene chain. A amine-functionalized column was used together with a gradient from dichloromethane to tetrahydrofuran. In solution polymerizations, the CTAs proved very effective in producing hydroxyl-telechelic polystyrene even with a non-functional initiator, provided that the radical flux was low.

Chain transfer agents with different chain lengths (n = 2, 6, 11) have been prepared. Their reactivities in the styrene polymerization were of the same order of magnitude; transfer constants (C_T) slightly above unity. Only a slight dependence on n was observed. Their transfer constants were determined using the ln-number distribution method.[v,vi] We are currently investigating whether quantumchemical calculations can provide insight in the dependence of C_T on n.

n	C_T
2	1.8
6	1.5
11	1.6

CTA2 was expected to be too water-soluble. This results in a hindrance of radical entry by making it more difficult for waterphase radicals to reach their critical degree of polymerization for entering the polymer particles. Both CTA6 and CTA11 had a water solubility, 7_10^{-2} and 4_10^{-4} mol_dm^{-3} at 50°C, comparable to common emulsion monomers like styrene and methyl methacrylate and these two CTAs therefore have been evaluated in emulsion polymerizations.

CTA11 allowed the successful preparation of a telechelic latex while CTA6 acted as an efficient inhibitor for both *ab initio* and seeded systems. The system with CTA11 is currently being optimized through the application of an addition profile for the monomer and chain transfer agent.
Some other fields of research we are working on in the scope of this project are pointed out below:

A different allylic sulfide has been designed to equip acrylates with natural-oil end-groups. This type of hybrid system may be beneficial for the properties of traditional alkyd paints. We are studying the morphology of these systems as a function of acrylate chain-length, comparing them with other hybrid systems.

A recently patented system called reversible addition fragmentation chain transfer (RAFT)[vii] is being investigated as an alternative to the allylic sulfides. Dithioesters generally exhibit this reversible behaviour which means that the compound remains active as a CTA after it has reacted with a propagating polymer chain. This polymeric CTA releases the previously terminated propagating chain upon a succesive transfer reaction. Besides the incorporation of functional groups, similar to the allylic sulfides, this semi-living system allows control over the molecular weight distribution and copolymer structure as well. Details can be found in the corresponding reference.

The effect of molar mass on the film formation is being examined. The rate of deformation of individual latex particles and monolayers is being monitored with atomic force microscopy, the mechanical properties of latex films are measured and together with glass transition temperatures and minimum film formation temperatures correlated to the molar mass in order to find optimum values for coating applications.

Comments and suggestions are welcome: J.A.M.de.Brouwer@tue.nl

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[i] G.F. Meijs, T.C. Morton, E. Rizzardo, S.H. Thang, *Macromolecules*, **24**, 3689 (1991)

[ii] E. Rizzardo, G. F. Meijs,S.H. Thang, *Macromol. Symp.* **98**, 101 (1995)

[iii] D. Colombani,P. Chaumont, *Prog. Polym. Sci.* **21** (3), 440 (1996)

[iv] W. J. Staal, P. J. C. H. Cools, A. J. M. van Herk, A.L. German, *J. Liq. Chromatography*, **17**, 3191 (1994)

[v] P.A. Clay, R.G. Gilbert, *Macromolecules*, **28**, 552 (1995)

[vi] G. Moad, C.L. Moad, *Macromolecules*, **29**, 7727 (1996)

[vii] J. C. Chiefari, Y. K. Chong, F. Ercole, J. Krstina, J. Jeffery, T. P. T. Le, R. T. A. Mayadunne, G. F. Meijs, C. L. Moad, G. Moad, E Rizzardo, S H. Thang, *Macromolecules*, **31**, 5559 (1998)

Contribution to the IPCG Newsletter from the Australian Key Centre for Polymer Colloids

Reporter: Bob Gilbert
Chemistry School, Sydney University, NSW 2006, Australia.

Chemical-fixing ultramicrotomy technique for imaging rubber latex particles. N Subramaniam, A Simpson Gomes, MJ Monteiro, RG Gilbert .

A new chemical fixation method is described for imaging the morphology of rubbery latex particles, such as modified natural rubber latex. Glutaraldehyde is added to the latex, followed by OsO_4. The sample is then dehydrated in ethanol, epoxy resin then added, and the sample cured in an oven, followed by ultramicrotoming with a glass knife and imaging with transmission electron microscopy. Applied to natural rubber latex samples in which methyl methacrylate has been polymerized, a "fruit-cake" (inclusion) morphology is clearly seen, in accord with the morphology seen with alternative, but much more laborious, techniques.

How γ radiolysis gives unique information in emulsion polymerizations. RG Gilbert. Proc. AINSE 40th Anniversary Symposium, in press.

γ radiolysis as an initiation medium for free-radical polymerization can give unique mechanistic information: it can penetrate opaque media yet can be switched off instantly, enabling radical loss mechanisms to be investigated. It also gives a steady radical flux at any temperature, which is convenient for looking at reactions at low temperatures, thereby giving the means of obviating complications that can occur at elevated temperatures. Being able to penetrate opaque media is especially useful for emulsion polymerizations. Methods have been presented in the past to show how the rate coefficients for radical loss (exit and termination) can be obtained from such relaxation experiments, along with comparison of theories for these quantities. Means have recently been developed that enable termination rate coefficients to be obtained by two completely independent means, thereby verifying the results from both, as well as showing the correctness and limitations of theories for this process. By combining a knowledge of the exit rate coefficient with the steady-state rate using a chemical initiator, it is now possible to obtain reliable and accurate values of the rate coefficient for entry, i.e., for initiator efficiency. Because the important information from the γ system comes from relaxation (i.e., after removal from the source), the complexities of the radical initiation process involving γ radiation usually do not need to be considered. However, care must be taken for systems such as vinyl esters, where evidence has been obtained that unusual species are formed which undergo slow subsequent polymerization but rapid termination. Limiting the applications of the technique. This evidence is that, while many experiments have shown that the exit rate coefficients so obtained are in accord with those predicted form a measurement of the rate coefficient for transfer to monomer, in the case of vinyl esters qualitatively different behaviour is obtained.

Cryo-sectioning technique for imaging rubber latex particle morphology. N. Subramaniam, A. Simpson Gomes, MJ Monteiro, O. Shaffer and RG Gilbert.

A method is described for imaging the morphology of rubbery latex particles, such as modified natural rubber latex. A drop of latex is placed on a pin-head and cooled in liquid nitrogen, sliced with a diamond knife and vapour-stained with OsO4, then viewed by transmission electron microscopy; extreme care is required in the slicing and sample manipulation. When applied to latexes made by emulsion polymerization of methyl methacrylate in a natural rubber latex seed, inclusions are clearly visible, as also seen in an alternative imaging technique (extrusion in a polystyrene matrix). This verifies that cryoultramicrotomy gives an adequate representation of the true morphology.

Novel graft copolymers from mechanistically-designed seeded emulsion polymerization. N. Subramaniam, M.J. Monteiro, J.R Taylor, A. Simpson-Gomes, R. G Gilbert. Macromol. Symp., in press.

While natural rubber and natural rubber latex (NRL) have technical and environmental advantages, there are limitations in applications, which could be extended by creating a graft copolymer in the latex with artificial monomer(s) through the double bond on the *cis*-polyisoprene. Previous attempts to create such grafting through second-stage polymerization with the NRL as seed did not give uniform morphology of the resulting polymer, presumably because of insufficient grafting. This is overcome by combining two strategies: (a) the second-stage monomer system includes one or more components that are extremely water-insoluble, thereby avoiding secondary particle formation and subsequent imbibement, and (b) the second-stage monomer is chosen to have free-radical chemistry that can readily form graft sites with polyisoprene which undergo further propagation. One monomer that satisfies these criteria is lauryl acrylate, and indeed uniform morphology is observed in using this monomer polymerized with NRL as seed under appropriate conditions.

Polymerization of acrylamide in solution and inverse emulsion : number molecular weight distribution with chain transfer agent. M. Pabon, J. Selb, F. Candau, RG Gilbert. Polymer, in press.

The molecular weight distributions of the free-radical polymerization of acrylamide in solution and in inverse emulsion are examined as a function of concentrations of initiator and of amount of added chain transfer agent (sodium formate). When these distributions are displayed as ln(number molecular weight distribution), readily obtained from the GPC trace (essentially by dividing by the square of molecular weight), the results can be semi-quantitatively interpreted in terms of the amounts of chain stoppage by transfer and by termination.

Spontaneous ("thermal") initiation in emulsion polymerization. R.G. Gilbert, D.I. Christie, J.P. Congalidis, J.R. Richards. Polymer Preprints (presented at ACS National Convention, Anaheim, 1999)

A study of rates and molecular weight distributions in the seeded emulsion polymerizations of styrene and of chloroprene under zero-one conditions, including initiation by gamma radiolysis, showed the extent of spontaneous polymerization in particles and droplets. For chloroprene, the dominant chain-stopping events in both phases are found to be transfer to monomer and termination with spontaneously-generated radicals.

The following publications have appeared since the previous Newsletter:

A theoretical study of propagation rate coefficients for methacrylonitrile and acrylonitrile. DM Huang, MJ Monteiro, RG Gilbert, Macromolecules, **31**, 5175-87 (1998).

Measurement of diffusion coefficients of oligomeric penetrants in rubbery polymer matrices. MC Griffiths, J Strauch, MJ Monteiro and RG Gilbert. Macromolecules, **31**, 7835-7844 (1998).

Measurement of transfer constant for butyl acrylate free-radical polymerization. S. Maeder and R.G. Gilbert. *Macromolecules*, **31**, 4410-8, 1998.

Adsorption of amino-functional polymer particles onto keratin fibres. L. Pille, J.S. Church, R.G. Gilbert, J. Coll. Interfacial Sci., **198**, 368-377, 1998.

Modelling particle size distributions and secondary particle formation in emulsion polymerisation. E.M. Coen, R.G. Gilbert, S. Peach, B.R. Morrison and H. Leube, *Polymer*, **39**, 7099-7112 (1998).

Contribution to the IPCG newsletter of Dr Alex M. van Herk, Technical University Eindhoven

Radical polym. Basic kinetics and mechanisms Polym. in ordered media Emulsion polym.

Amaia Montoya-Goñi
Surfactants, organic synthesis

Sean Wilkinson
Addition fragmentation polym./ reactive surfactants

On-line Raman spectroscopy

Semi-continuous em. Pol./Raman
Vacancy **SEP**

Continuous em. copolymerization
Scholtens **TUE**

Coagulation phenomena in em. polym.

Reaction calorimetry
Vacancy **SEP**

Incorp. of acrylic acid in em. pol.
Slawinski **Rhodia/TUE**

In-situ blends preprd. in em.
Peerlings **NWO-PPM**

Joseph Park
Film formation/AFM

Impact mod. of glassy polymers
Vacancy **DPI**

Vegetable oils in waterborne paints
v. Hamersveld **IOP-**

Alkoxysilane functional latices
Molenaar **IOP/TNO**

Special particle architectures
Hubert **ICI**

Polym. kinetics in ordered media
Jung **SON**

Organic/Inorganic hybrid latices
Vacancy

Mark Rees
Kinetics/CLDT/PLP//PEBP

Chain-length dependent termination

Chain-length dependent termination

Improved copolymerization models
Seegers **SON**

Intramolecular composition drift
Chambard **TUE**

Modulated initiation, control of MW

Gilles Olive
Nitroxide synthesis

Vacancy
Living Radical Polymerizations/Block copolymers

Telechelics prepared in emulsion
de Brouwer **SEP**

CRP of vinylesters
Bussels **TUE**

Living radical in emulsion
Smulders **Brite-Euram**

Gradient copolymers/GPEC
Beyers **DPI**

Nikhil Singha
Organometallics/ATRP

Vacancy
Organometallics, Cu and Co-complexes

New catalytic CTA in em. polym.
Pierik **TUE/Akzo-Nobel**

Mechanism of ATRP in em. pol.
Vacancy **Applied for, SON**

☐ Post-doc

APPLICATION OF RAMAN SPECTROSCOPY TO INVESTIGATE POLYMER LATEXES AND EMULSION POLYMERIZATIONS

Mark van den Brink, Alex M. van Herk and Anton L. German,
Department of Polymer Chemistry (SPC), Eindhoven University of Technology,
P.O. box 513,5600 MB, The Netherlands

Recent developments in lasers, optics and detectors are responsible for an enormous increase in sensitivity of Raman spectrometers[1]. The technique is most sensitive to symmetric bonds such as vinyl bonds, while water only gives a weak Raman spectrum. Furthermore, the application of fiber optics is possible, since light in the visible part of the spectrum is used. All this makes Raman spectroscopy a very suitable candidate for the remote on-line monitoring of emulsion polymerization processes[2].

The present paper focuses on the differences between measurements in homogeneous and heterogeneous polymerization systems. The main difference between these two systems is that in homogeneous systems light can travel virtually unhindered, whereas in heterogeneous systems the path length of the light is in the order of tenths of millimeters.

We have used Raman spectroscopy to study polymer latexes and polymerization processes. It turned out to be possible to monitor emulsion polymerizations on-line, using a set up as shown in Figure 1.

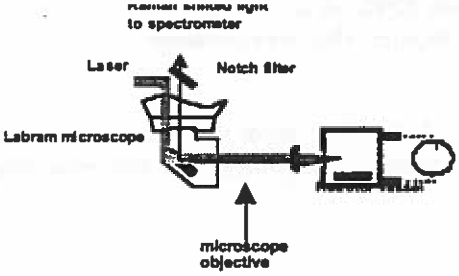

Figure 1: schematic set-up of the process

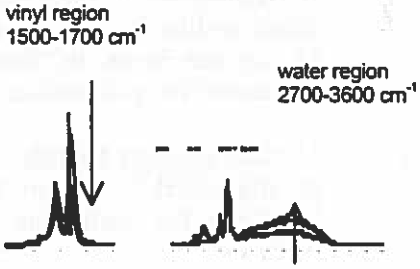

Figure 2: selected regions of the Raman spectra obtained from an emulsion polymerization of styrene

Figure 2 shows some of the normalized spectra obtained from the emulsion polymerization of styrene. From these results it proved to be possible to obtain monomer concentrations. Surprisingly, the contribution of the water peak between 3200-3500 $\mathrm{cm^{-1}}$ increases with increasing conversion, while the amount of water is supposed to be constant during the process. Additional measurements on polymer latexes showed that this effect may be attributed to light scattering, and that the effect correlates with particle size. Thus, besides information on monomer conversion, Raman spectroscopy may yield additional information on particle size or particle number.

1) B. Chase, *Appl. Spectrosc.*, 48, 14A (1994)
2) C. Wang, T.J. Vickers, J.B. Schlenoff and C.K. Mann, *Appl. Spectrosc.*, 46, 1729 (1992)

Publications and submitted publications 1998

1 A linear Accelerator as a tool for investigations in free radical polymerization kinetics and mechanisms by means of pulsed electron beam polymerization
J.L.M. Botman, A.T.A.M. Derksen, A.M. van Herk, M. Jung, F.-D. Kuchta, L.G. Manders, C.J. Timmermans, M.J.A. de Voigt,.,
Nuclear Inst. And Methods in Physics Research, **B 139**, 490-494 (1998)

2 Pulsed-Laser polymerization of methyl methacylate in liquid and supercritical carbon dioxide,
M.A. Quadir, J.M. DeSimone, A.M. van Herk, A.L. German,
Macromolecules **31**, 6481-6485 (1998)

3 Modeling of emulsion co- and terpolymerizations. Will it ever be possible ?
A.M. van Herk, A.L. German,
Macromol. Theory Simul. **7**, 557-565 (1998)

4 Non-linear regression by visualization of the sum of residual space applied to the integrated copolymerization equation with errors in all variables.
I Introduction of the model, simulations and design of experiments
M. van den Brink, A.M. van Herk, A.L. German
Submitted for publication in *Journal of Applied Polymer Science*

5 Non-linear regression by visualization of the sum of residual space applied to the integrated copolymerization equation with errors in all variables.
II Application to the system methyl methacrylate--α-methylene-γ-butyrolactone using on-line Raman spectroscopy
M. van den Brink, W. Smulders, A.M. van Herk, A.L. German
Submitted for publication in *Journal of Applied Polymer Science*

6 Vesicle-polymer hybrids
M. Jung, D.H.W. Hubert, P.M. Frederik, H. Fischer, A.M. van Herk, A.L. German
Submitted for publication in "*Recent Research Developments in Macromolecules research*"

7 Emulsion polymerization
A. Aerdts-Vermeylen, A.L.. German, A.M. van Herk, B. Klumperman, J. Kurja
Materials Science and Technology, *A Comprehensive Treatment, Polymer Synthesis*, VCH-verlagsgesellschaft mbH p 269-319 (1998)

8 Encapsulation of Aluminium hydroxide,
F. Geurts, A.M. van Herk, A.L. German
To be submitted to Journal of Microencapsulation

9 Photooxidative Degradation of Poly(alkyl methacrylate)s
H. Kaczmarek, A. Kamiñska, A. van Herk.
Submitted to European Polymer Journal

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International Polymer Colloids Group Newsletter

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The abstracts of our papers published in 1998 are compiled in the following.

(1)Single Crystal of Colloidal Silica Particles in a Dilute Aqueous Dispersions Studied by a Two-Dimensional Ultrasmall-Angle X-ray Scattering. T. Konish and N. Ise, *Phys. Rev. B* 57, 2655-2658 (1998).

A two-dimensional ultrasmall-angle X-ray-scattering apparatus was constructed with a full width at the half maximum of the intensity profile of the incident X-ray beam being about 17 s of arc. This apparatus enabled us to obtain the scattering intensity as a function of the scattering vector. The scattering profile of a colloidal crystal of silica particles in an aqueous dispersion was studied and analyzed with the aid of a method of Busing and Levy. The diffraction planes corresponding to 22 scattering peaks observed were uniquely identified; The lattice system was determined to be bcc with a lattice constant of 0.38μm and its $[1\bar{1}1]$ was parallel to the capillary axis.

(2)Novel Crystallization Process in Dilute Ionic Colloids. H. Yoshida, J. Yamanaka, T. Koga, N. Ise and T. Hashimoto, *Langmuir* **14**, 569-574 (1998).

The crystallization process in an electrostatically stabilized dilute silica colloid dispersion was studied in an order-disorder coexistence regime by confocal laser scanning microscopy and ultra-small-angle X-ray scattering. In shear-melted homogeneous disordered dispersions, space-filling grains of bcc lattice were first formed by a conventional nucleation and growth process, which was followed by a lattice contraction resulting in a "cheese-with-holes-like" structure of coexisting ordered and disordered regions. The process was accounted for in terms of the long-range interparticle attraction.

(3)Monte-Carlo Study of Structural Ordering in Charged Colloids Using a Long-Range Attractive Interaction. B. V. R. Tata* and N. Ise,. *Phys. Rev. E* **58**, 2237-2246 (1998).

Monte-Carlo simulations have been carried out for aqueous charged colloidal suspensions interacting via an effective pair potential $U_s(r)$, the Sogami potential, which has the long-range attractive term in addition to the usual screened Coulomb repulsion. Simulations are performed over four orders of magnitude of particle volume fractions (ϕ) under salt free as well as added salt conditions. The computed pair correlation function $g(r)$ at high values of ϕ show a fcc crystalline order, which is found to transform to a bcc crystalline order upon lowering of ϕ. The crystalline order is found to melt into a liquidlike order upon the addition of salt. A purely repulsive potential based on DLVO theory was earlier claimed to be responsible for the formation of bcc and fcc phases and the associated order-disorder transitions. It is clearly shown here that $U_s(r)$ also explains equally well such phenomena and the results are shown to be in close agreement with experimental observations. Simulations in the dilute regime show a vapor-liquid transition upon variation of ϕ and the coexistence of ordered and disordered regions with voids upon variation of the charge on the particles. These results explain the reported experimental observations, which suggested the existence of a long-range attraction in the interparticle interaction. For very low volume fractions calculated pair correlation functions show only a single peak and are found to be independent of ϕ. The reported results on the direct measurement of the pair potential are critically discussed in the light of the present results. (*Present address: Indira Gandhi Centre for Atomic Research, Kalpakkam, TN 603102, India)

(4)Reentrant Solid-Liquid Transition in Ionic Colloidal Dispersions by Varying Particle Charge Density. J. Yamanaka, H. Yoshida, T. Koga, N. Ise, and T. Hashimoto, *Phys. Rev. Lett.* **80**, 5806-5809 (1998).

The influence of the particle surface charge density on the solid-liquid phase transition in electrostatically stabilized colloidal silica and polymer latex dispersions is examined. Both systems show a reentrant transition with increasing charge density. This is not explainable in terms of the Yukawa potential and the charge-renormalization model.

(5)On the Solution Viscosity of Ionic Polymers and their Conformation in Solutions. N. Ise, *Proc. Japan Academy*, **B74**, 192- 200 (1998).

The viscosity behavior of linear, flexible ionic polymers in solutions and its accepted interpretation were discussed. Experimental viscosity data by Yamanaka et al. (*J. Am. Chem. Soc.* **112**, 587-592 (1990)) were pointed out to show the α value of the Houwink-Mark-Sakurada equation being smaller than two, a value expected for rod-like conformation. The viscosity of latex dispersions, telechelic polymer solutions, and microgel dispersions showed that the intra-molecular interaction does not play a role as important as was supposed to be in the previous argument. The Booth theory of primary electroviscous effect of charged particles (distortion of ion cloud under flow) was found to be satisfactory in explaining dependencies of viscosity of colloidal particles on charge number (Q), size, and salt concentration, particularly for large κa ($1/\kappa$: Debye's radius, a: the particle radius) and at small Q. Taking into consideration that the macroion domain corresponds to extremely high concentrations of ionic groups, the formation of multiple ions by a counterion-mediated attraction, which was not considered so far, was tentatively suggested. Further, the contribution of localized ordered domains of macroions that were recently unveiled was suggested to be presumably influential in viscosity properties.

(6) Recent Study of Counterion-Mediated Attraction between Colloidal Particles and between Particles and Interface Studied by the Ultra-Small-Angle X-Ray Scattering. N. Ise and T. Konishi, *Special Issue in Honor of Professor Egon Matijevic, Croatica Chemica Acta* **71**, 1005-1017 (1998).

The application of the 1D- and 2D-ultra-small-angle X-ray scattering (USAXS) methods to the structural study of dilute colloidal silica particle dispersions is reviewed. A single colloidal crystal showed 22 sharp diffraction peaks, which allowed us to uniquely determine the lattice symmetry (bcc), lattice constant (around 0.3 – 0.4 μm) and crystal orientation. In dilute dispersions, the closest interparticle spacing was confirmed to be smaller that the average spacing, pointing to the important role of a counterion-mediated attraction between the particles. The scattering profile had six-fold and four-fold symmetries with $[1\bar{1}1]$ and [001] directions being parallel to the axis of the capillary (dispersion container), respectively. In both cases, the (110) planes, the most densely packed planes of bcc, were in contact with and parallel to the capillary surface, confirming the presence of a possibly counterion-mediated attractive interaction between negatively charged interface and particles. After the capillary was shaken, only the six-fold symmetry was found, which is reasonable in the light of larger contact between the capillary surface and the (110) planes (and hence greater stabilization of the system) than for the four-fold symmetry.

Contribution to IPCG Newsletter

Haruma Kawaguchi, Dept. of Applied Chemistry, Keio University, Yokohama, JAPAN

The abstracts of two among the latest Master's Theses in my group are given below.

1 "Development of genetic diagnosis system by means of DNA-carrying latex particles and S1 nuclease" by Kyoko Nakamura, K.Fujimoto, and H.Kawaguchi

Mutations of K-ras genes are frequently found in primary pancreatic, colorectal and lug carcinomas. Therefore it is very useful to detect such a genetic abnormality for the early detection of cancers.

We developed DNA-carrying latex particles to separate mutant DNA from normal DNA by means of bioseparation for diagnosis. In this system, it was also found that non-complementary DNA (point-mutational DNA) was loosely hybridized with single-strand DNA immobilized on latex particles. Therefore, in this study, we tried to distinguish loosely hybridized DNA from completely hybridized one by using the feature of S1 nuclease, which is an enzyme to cleave the single-stranded site in DNAs.

Soap-free emulsion polymerization of styrene and glycidyl methacrylate was carried out to prepare the core-shell type particles. Its diameter was about 200nm.

Point-mutational and wild-type DNAs were hybridized with biotin-labeled DNA immobilized onto the latex particles. After S1 nuclease was added, biotin-labeled DNAs remaining on the latex were detected.

Although complementary wild-type DNAs were partially cleaved by S1 nuclease at high concentrations of S1 nuclease or high temperatures, we could distinguish point-mutational DNAs from wild-type DNAs.

Detection of wild type DNA in the mixture of wild-type and point-mutational DNAs was made by this method. When excess amount of point-mutational DNA was added, S1 nuclease didn't cleave point-mutational DNA. Therefore, we examined the effect of the position of point mutation on cleavability of S1 nuclease. As a result, it was proved that cleavability was decided by the stability of double strand DNA, which was strongly related with the presence of mutation and its position.

2 "Development of polymeric Microspheres exhibiting Discontinuous Transition" by Hiroshi Matsuoka, K.Fujimoto and H.Kawaguchi

Poly (n-isopropylacrylamide) (NIPAM) gels in water undergo volume-phase transition caused by hydrophobic interaction at a given temperature (the so-called lowest critical solubility temperature; LCST). Therefore, monodisperse microspheres having PNIPAM gel layers on the surface exhibit large variation of their colloidal properties (their hydrodynamic size, electrophoretic mobility, colloidal stability, etc.). Hence, they had been offered to many applications, especially in the biological field. However, the response of these properties to temperature was continuous, which limits the applications of thermosensitive microspheres. The aim of this study is to develop PNIPAM microspheres exhibiting discontinuous transition in several properties.

In order to perform this objective, the effect of crosslinking density in the shell layers on the thermosensitivity of microspheres was investigated. The changes of the properties of microspheres around LCST became more conspicuous with decreasing degree of crosslinking. This fact forced us to prepare the ultimate architecture of less crosslinked shell, that is, the PNIPAM hairy layers. They were prepared by grafting NIPAM on core microspheres, but their properties changed continuously with temperature because of the entanglement of hair polymers. Moreover, there is a significant decrease in the hydrodynamic size below LCST. This can be interpreted as the formation of n-clusters. To avoid them, ionic groups were incorporated into the PNIPAM hair grafted on nicrospheres. Incorporation of acrylic acid into the PNIPAM hair gave electrorepulsive force to grafted polymer chains to suppress the entanglement and n-clustering, and the resulting microspheres changed their properties discontinuously at the transition temperature. Only 0.02% acrylic acid in PNIPAM was enough to make the response sharp.

Theoretically, it is well known that changing temperature is equivalent to changing solvent composition, and PNIPAM shell-carrying microspheres undergo volume-phase transitions in response to changes in solvent composition. Microspheres bearing PNIPAM gels or PNIPAM hairs which contain no ionic groups did not changed their properties sharply. On the contrary, microspheres whose shells were composed of PNIPAM hair containing ionic groups exhibited discontinuous transition.
It was concluded that our objective "development of polymeric microspheres exhibiting discontinuous transition" was realized.

Publications in 1998
107 V. Juranicova, S. Kawamoto, K. Fujimoto, H. Kawaguchi, J.Barton,
Inverse microemulsion polymerization of acrylamide in the presence of N,N-dimethylacrylamide. Angew. Makromol., 258, 27-31 (1998)

106 M. Hatakeyama, K. Nakamura, S. Iwato, K. Fujimoto, H. Handa, H. Kawaguchi,
DNA-carrying latex particles for DNA diagnosis. 2. Distinction of normal and point mutant DNA using S1 nuclease, Colloids and Surfaces B: Biointerfaces, 10, 171-178 (1998)

105 M. Hatakeyama, S. Iwato, K. Fujimoto, H. Handa, H.Kawaguchi,
DNA-carrying latex particles for DNA diagnosis. 1. Separation of normal and point mutant DNAs according to the difference in hybridization efficiency, Colloids and Surfaces B: Biointerfaces, 10, 161-169 (1998)

104 M. Hatakeyama, Y. Ogura, J. Sawada, K. Fujimoto, H. Kawaguchi,
Preparation of dimerized polypeptide-carring microspheres and purification of specific proteins bound to these microspheres. Colloids and Surfaces B: Biointerfaces, 10, 41-49 (1998)

Contribution from S. C. Johnson Polymer, 8310 16th Street, P.O. Box 902, Sturtevant, WI 53177 – 0902

Reporter: D. Sunil Jayasuriya

Presented at the XXIV FATIPEC Congress, Interlaken, Switzerland , June 08,1998 and published in
European Coatings Journal, Oct 1998.

Contribution 1: Waterbased Crosslinkable Surface Coatings.

Richard J. Esser [a] James E. Devona [b], Dave E. Setzke [b] and Loek Wagemans [a]

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[b] S.C. Johnson Polymer, P. O. Box 902, Sturtevant, WI 53177-0902, U.S.A.

ABSTRACT

Novel waterborne one-pack and storage stable polymers for coatings are described which form cross-linked films upon drying at ambient temperatures. The coatings are based on proprietary acetoacetoxy-functional polymers which can be conveniently made via multi-stage emulsion polymerization. They are especially useful in high quality furniture applications, where they offer fast dry combined with hardness, early stackability, high film clarity, luster, and superior chemical resistance. Key properties of the coatings are discussed and compared with other water borne furniture coatings.

Contribution 2:

Presented at the 24th Annual InternationalConference on Organic Coatings, Athens,
Greece (July 6 –10th,1998)

A STUDY ON THE CHEMISTRY OF ALKYLCARBODIIMIDE ETHYLMETHACRYLATES AS REACTIVE MONOMERS FOR ACRYLIC AND VINYL ESTER-BASED LATEXES

J. W. Taylor[1], M. J. Collins[2], and D. R. Bassett[3]

[1] Technology Development Department, SC Johnson Polymer, P.O. Box 902, Sturtevant, WI 53177
[2] **Waterborne Research Laboratory, Eastman Chemical Company, P.O. Box 1955, Kingsport, TN 37662**
[3] UCAR Emulsion Systems, Union Carbide Corporation, 410 Gregson Dr., Cary, NC 27511

ABSTRACT

The preparation of carbodiimide methacrylates from their corresponding urea methacrylate is described. Carbodiimide methacrylates were reacted with waterborne carboxylic acid-containing acrylic polymers to produce waterborne polymers with methacrylate functionality. Nuclear magnetic resonance showed that more than 80% of the theoretical level of methacrylate functionality survived the modification process. Using a similar modification process, the level of methacrylate survival for a variety of epoxy methacrylates and 1-(2-aziridinyl)ethyl methacrylate was compared to carbodiimide methacrylates. Waterborne polymers modified with epoxy

methacrylates gave polymers with less methacrylate functionality than carbodiimide methacrylates. The reaction of 1-(2-aziridinyl)ethyl methacrylate with waterborne carboxylic acid-containing polymers produced waterborne polymers that contained up to 98% of the theoretical level of methacrylate functionality. The gel fraction of cured films was measured to demonstrate the crosslinking potential of polymers with methacrylate functionality.

Contribution 3:

Presented at the 28th Great Lakes ACS Conference, Milwaukee, WI (June 1 – 3,1998)

Kinetic Studies of the Copolymerization of 2-Ethylhexylacrylate

S. Mohammed, S. A., Blechinger, K. E. Sorenson and R. J. warner
S. C. Johnson Polymer, Sturtevant, WI 53177.

Copolymerizations of 2-ethyl hexyl acrylate (2-EHA) with butyl acrylate (BA) and methyl methacrylate (MMA) were carried out in a reaction calorimeter (RC1, Mettler Toledo). The polymerizations were run at 30% solids level at 80 ⊕C. Toluene and lauryl peroxide were used as the solvent and initiator respectively. The polymerization kinetics were followed by monitoring the heat of polymerization. An IR probe (ReactIR, ASI Applied Systems) was introduced into the reactor in order to follow the consumption of the two monomers individually as a function of time. The copolymerizations were carried out at several comonomer compositions. The reactivity ratios for the monomers could be determined from the data obtained by the combination of calorimetry and infrared spectroscopy. The effect of comonomer composition on the copolymerization kinetics was also investigated.

Contribution 4:

Presented at the 28th Great Lakes ACS Conference, Milwaukee, WI (June 1 – 3,1998)

Reaction Calorimetry and Infrared Techniques in Seeded Emulsion Polymerization of Styrene

R. J. Warner, P. E. Gloor, D. D. Schatz, L. P. rector, D. S. Jayasuriya, C. M. Geise, W. Lee, S. Mohammed, S. A. Blechinger
S.C. Johnson Polymer, Sturtevant, WI 53177 – 0902

Seeded emulsion polymerization is generally employed to maintain the number of particles during the course of the reaction. The number of particles is one factor that determines the rate of emulsion polymerization. In this work, varying proportions of seed latex and monomer were allowed to interact and the monomer, subsequently, was allowed to polymerize. The proportions were designed such that some systems held more monomer than the seed latex could imbibe, resulting in a system where monomer droplets were present, and some systems had sufficient seed latex to imbibe all the monomer resulting in no monomer droplets present in the system. The batch polymerization process usually proceeds from a system of swollen particles and monomer droplets to swollen particles as a critical step. Our goal was to investigate the effect of particle number on the polymerization of styrene by following the reaction with infrared detection as well as by calorimetry (de la Rosa, Lehigh). The reactions were followed calorimetrically using Mettler-Toledo RC1 calorimeter and ASI ReactIR 1000. Absorbance frequencies for styrene monomer and poly(styrene) were identified making the task of following these moieties by IR possible. The combination of IR and calorimetry techniques showed that, for our systems, the number of particles increased during the polymerization of styrene that contained monomer droplets. Droplet containing systems were those that had the seed latex content less than 45% of the total solids.

Contribution to IPCG newsletter from the

Leiden Colloid and Interface Science Group

Towards a quantitative description of ionization properties of linear and branched polyelectrolytes
M Borkovec and GJM Koper

Ionization properties of various polymeric amines are shown to be explained in terms of a simple Ising model with short range interactions. This model is commonly used in statistical mechanics to describe magnetic systems. The basic parameters of the model are microscopic dissociation constants of each ionizable site and a small number of interaction parameters. For a system with a finite number of ionizable sites, this model reduces to the classical description of polyprotic acids and bases in terms successive equilibria. However, the model is equally well applicable to systems with a large number of ionizable sites and thus the protonation behavior of polyelectrolytes can be studied within the same framework. We shall demonstrate that one can model the macroscopic dissociation constants of a number of low molecular weight polyprotic amines, as well as the titration behavior of linear and branched poly(ethylene imine) and dendritic poly(propylene imine) with a single set of model parameters. The Ising model further provides a rationalization of the differences in ionization properties of linear and branched polyelectrolytes.

Appeared in Progr Coll Polym Sci **109** (1998) 142-152..

Dissociation behavior of poly(maleic acid): potentiometric titrations, viscometry, pulsed field gradient NMR, and model calculations
J de Groot, GJM. Koper, M Borkovec, and J de Bleijser

Potentiometric titrations, pulsed field gradient NMR, and viscometry of poly(maleic acid) have been carried out in different salt solutions of varying ionic strength. The shape of the titration curve depends strongly on the type of cation used, especially beyond $\alpha = 0.5$. Above 5 times excess salt concentration, the potentiometric titration curves can be fit satisfactorily to an equation derived on the basis of a random Ising model, using three free parameters: the intrinsic dissociation constant K_0 and two excess free energies ε_r and ε_m, describing the nearest-neighbor interaction across a racemic and mesomeric bond, respectively. The stereochemistry of PNIA is modeled using an additional parameter P_r, which is the probability of racemic propagation during synthesis. This parameter was determined by ^{13}C NMR The results compare favorably with those obtained for other poly(carboxylic acid)s. Except for a gradual expansion of the polymer coil upon charging, no conformational changes are observed by PFG-NMR and viscometry. Rather, attractive intermolecular interactions appear to play a role at high degrees of dissociation.

Appeared in Macromolecules **31** (1998) 4182-4188..

Odd-even shell ionization of AstraMol™ dendrimers
RC van Duijvenbode, M Borkovec, and GJM Koper

Potentiometric titrations of like structure where all odd shells of five generations of poly(propylene imine) dendrimers were performed at 0.1, 0.5, and 1.0 M KCl and NaCl. The titration curves reveal two-step protonation behavior similar to linear polyelectrolytes. The difference to linear polyelectrolytes is that the position of the intermediate plateau lies at 2/3 of the total ionizable groups. The intermediate plateau results from the stability of an onionlike structure where all odd shells of the dendrimer are protonated, while the even shells remain deprotonated.
The titration curve features two distinct steps around pH 6 and 10. The Ising model permits a quantitative analysis of this protonation behavior.

Appeared in Progr Coll Polym Sci **110** (1998) 125-128.i

Poly(propylene imine) dendrimers as retention aid for the deposition of calcium carbonate on pulp fibres
GJM Koper, A Vanerek, and TGM Van de Ven

The kinetics of deposition of calcium carbonate particles of about 2,um diameter has been studied with poly(propylene imine) dendrimers as retention agent. The adsorption process is shown to follow Langmuir kinetics. The measured kinetic parameters are of a similar magnitude to those found for poly(ethylene imine as retention aid. Since larger particles were used in this study, the expected increase in detachment rate was cancelled by a larger bond strength, caused by a higher charge density of the dendrimers. It is concluded that dendrimers are a somewhat better retention aid than poly(ethylene imine) for the retention of calcium carbonate.

To appear in J Pulp Paper Sci **25** (1999)

Contribution to IPCG Newsletter from

Department of Chemistry, University of Malaya, 50603 Kuala Lumpur, Malaysia

Reporter : C.C. Ho

Joint contributor : J.H. Kim : Yonsei University, Seoul, Korea

Atomic force microscopy study of PBMA latex film formation: effects of carboxylated random copolymer

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Joint contributor : J.H. Kim, Yonsei University, Seoul, Korea

Y.-J. Park
M.C. Khew
C.C. Ho
J.-H. Kim

Kinetics of latex formation of PBMA latex in the presence of alkali soluble resin using atomic force microscopy

Joint contributor : J.H. Kim, Yonsei University, Seoul, Korea

Effects of Alkali-Soluble Resin on Latex Film Morphology of Poly(*n*-butyl methacrylate) Studied by Atomic Force Microscopy

Young-Jun Park,[†] Doug-Youn Lee,[†] Mei-Ching Khew,[‡] Chee-Cheong Ho,[*,‡] and Jung-Hyun Kim[*,†]

Department of Chemical Engineering, Yonsei University, 134 Shinchon-dong, Sudaemoon-ku, Seoul 120-749, Korea, and Department of Chemistry, University of Malaya, 50603 Kuala Lumpur, Malaysia

Joint contributor : R.H. Ottewill, University of Bristol, UK

Investigation of the charge distribution of ellipsoidal particles[1]

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INTERNATIONAL POLYMER COLLOIDS GROUP NEWSLETTER

Contribution from the Department of Chemical Engineering,
Yonsei University, 134, Shinchon-Dong, Seodaemoon-Ku, Seoul 120-749, Korea

Reported by Jung-Hyun(Jay) Kim

Role of Alkali-Soluble Random Copolymer in Emulsion Polymerization

- DY Lee, JH Kim, and TI Min

Alkali-soluble random copolymer (ASR), poly(styrene/alpha-methylstyrene/acrylic acid) was used as a polymeric emulsifier in the emulsion polymerization of styrene and methyl methacrylate, respectively. ASR could form aggregates like micelles and the solubilization ability of the aggregates was dependent on the neutralization degree of ASR. The rate of polymerization of styrene decreased as the neutralization degree of ASR was increased with little change in particle size. This result can be explained by the solubilization ability of ASR aggregate and the entry rate of radicals into the particle. As the degree of neutralization of ASR increased, the ASR aggregate was less efficient in solubilizing the monomer, and it was more difficult for radicals to enter the particle through the extended ASR layer on the particle surface, which lead to decrease in rate of polymerization. The polystyrene (PS) latexes prepared using ASR showed the monodispersed particle size distribution. On the other hand, the particle size distribution of poly(methyl methacrylate) (PMMA) latexes became broader as the neutralization of ASR increased. This could be explained by the effects of the water solubility of the monomer and the neutralization degree of ASR on particle formation.

- Accepted, Colloid and Surfaces A.(1998)

Film Formation from Reactive Latex Particles: Influence of Intraparticle Crosslinking on the Mechanical Properties - YJ Park and JH Kim

The effects of functional group density of reactive latexes on the relative rates of interdiffusion and crosslinking reaction during film formation and annealing process were investigated. The average diffusion coefficient *D* of the polymer chain was evaluated from dynamic mechanical analysis and was correlated with the diffusion of polymer chains through particle-particle interfaces. In the film of the reactive particles, the magnitude of D was lower than that of the homopolymer film. These results consistently showed the dependence of chain mobility on tensile strength development of the film of the reactive latexes, in which the mobility of the chains was restricted, leading to the prevention of mechanical strength development.

- Accepted, Colloid & Surfaces A. (1998)

Investigation of Seeded Emulsion Polymerization Using Calorimetric Method: Effects of the Surface Charge Density on Polymerization Rate and Average Number of Radicals per Particle - IW Cheong and JH Kim

A reaction calorimeter was applied to study emulsion kinetics in a seeded emulsion polymerization. Several batches of emulsifier-free seeded emulsion polymerization of styrene were carried out to investigate the electrostatic and steric effects of highly sulfonated seed particles on the average number of radicals per particle and the polymerization rate in Interval II. The radicals entry and exit coefficients were calculated by using "Slope and Intercept method" introduced by Gilbert et al.

- Accepted, Colloid and Surfaces A.(1998)

Selected Recent Journal Publications

1. Synthesis of Resorcinol/Formaldehyde Gel Particles by the Sol-Emulsion-Del Technique – HJ Lee, JH Song and JH Kim, *Mater. Lett.*, 37, 197 (1998).
2. Large and Monodispersed Polymeric Microspheres with High Butadiene Rubber Content via Membrane Emulsification – YK Ha, HJ Lee, and JH KIM, *Colloids and Surfaces A*, **145**, 281 (1998).
3. Emulsion Polymerization of Styrene Using Alkali-Soluble Random Copolymer as Polymeric Emulsifier – DY Lee and JH Kim, *J. Polym. Sci., Polym. Chem.*, **36**, 2865-2872 (1998).

Current Research Projects

1. Study on Dynamic Mechanical and Film Properties of Reactive Latexes.
2. Kinetic Study on Alkali-Soluble Random Copolymer in Emulsion Polymerization.
3. Synthesis and Characterization of Organic Aerogel Using Supercritical CO_2.

Contribution to the International Polymer Colloids Group Newsletter

Do Ik Lee
Emulsion Polymers R&D
The Dow Chemical Company

Porous Latex Composite Membranes: Fabrication and Properties

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Abstract

A new class of microfiltration[MF] and ultrafiltration[UF] membranes has been developed. By placing latex particles onto the surface of a microporous substrate and stabilizing the porous array, voids are formed between the particles which provide narrowly distributed pores that serve as separation channels. The size of the interstitial voids in the array is governed by the diameter of the latex particle. This aqueous based technology has advantages relative to other membrane fabrication processes in terms of the high assymetry of the membranes, the facile adjustment of pore sizes, and the ability to easily modify pore surfaces during the synthesis of particles.

A number of approaches were examined for placement of particles and stabilization of latex composite membranes [LCMs]. Filtration of particles with reactive surface groups that provide covalent linkages at the contact points in the particle array proved most effective in obtaining stable membranes. These membranes had narrow size distributions in both the UF and MF range and were capable of being cleaned and backflushed. The membranes were characterized in terms of gas permeabilities, pure water permeabilities and electron microscopy. The rejection properties of LCMs were also examined during filtration of monodispersed latex particles and a broadly dispersed dextran mixture.

Keywords: Microporous and Porous Membranes, Membrane Preparation and Structure, Ultrafiltration, Microfiltration, Composite Membranes

- To whom correspondence should be addressed.

To be published in 1999 in the Journal of Membrane Science.

THE CRITICAL PIGMENT VOLUME CONCENTRATION CONCEPT FOR PAPER COATINGS: II. CLAY, GROUND CALCIUM CARBONATE, AND CLAY-GROUND CALCIUM CARBONATE MIXTURE / LATEX BINDER COATING SYSTEMS*

Do Ik Lee
Emulsion Polymers R&D

ABSTRACT

A previous study on the model coatings of plastic pigments and latex binders has been extended to No. 1 clay, ultra-fine ground calcium carbonate (UFGCC), and No. 1 clay-UFGCC blend / latex binder coating systems, which are being widely used in the paper industry. The latex binder used was a good film-forming, monodisperse S/B latex of 0.15 μm. No. 1 clay was representative of plate-like pigment particles, whereas UFGCC was of somewhat rounded rhombohedral pigment particles. Both of them had negatively skewed triangular particle size distributions having the mean particle sizes of 0.7 μm and 0.6 μm, respectively. Their packing volumes were found to be 62.5% and 65.7%, respectively, while their CPVC's were determined to be 54.3% and 52.5% by coating opacity, 54.3% and 51.4% by coating brightness, 65% and 63.6% by coating gloss, and 52.7% and 50.5% (an average of 45% and 55.9%) by coating porosity, respectively. Each pigment / latex coating system has shown its unique relationships between coating properties and pigment concentrations, especially above its CPVC. Notably, the clay / latex system has shown higher coating porosity than the UFGCC / latex system at high pigment concentrations above their respective CPVC's. It was found that coating porosity and gloss were related to each other above the CPVC's. More interestingly, the blends of these two pigments have shown unique rheological and coating properties which may explain why such pigment blends are widely used in the industry. These findings have suggested that the unique structure of clay coatings and the unique high-shear rheology of ground calcium carbonate coatings can be judicially combined to achieve superior coatings. Importantly, the low-shear viscosity of the blends was indicative of their unique packing and coating structure, whereas their high-shear rheology was represented by a common mixing rule, i.e., a viscosity-averaging. Transmission and scanning electron and atomic force microscopes were used to probe the state of pigment / latex dispersions, coating surfaces, freeze-fractured coating cross-sections, and coating surface topography. These microscopic studies complemented the above observations. In addition, the ratio, **R**, of CPVC / ϕ_p (Pigment Packing Volume) has been proposed as a measure of the binder efficiency for a given pigment or pigment mixtures or as a measure of binder-pigment interactions. Also, a mathematical model has been discussed to calculate the packing volumes of clay and ground calcium carbonate pigments with their respective particle size distributions.

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* To be submitted to the TAPPI Journal.

Studies on the State of Colloidal Dispersions by a Cryo-Transmission Electron Microscopy (TEM) Technique

Joan Marshall, Analytical Sciences
Do Ik Lee, Emulsion Polymer R&D

Abstract

The state of colloidal dispersions such as latexes, paper coating formulations etc. has been extensively studied by a "Cryo-TEM" technique. The technique consists of freezing a sample , ultra-microtoming the frozen sample, and taking transmission electron micrographs. A small drop of the dispersions is applied to an aluminium specimen stub and plunged into liquid propane at -180°C. The frozen samples are cryo-transferred to a ultra-microtome equipped with a cryo-chamber and thin-sectioned at a temperature of -120°C. Sections which are approximately 90 nm thick are placed on a copper TEM grid, and transferred cold to a cryo-transfer stage for examination in a TEM. The cryo-transfer holder enables the sample to be kept cold and condensation-free while being inserted into the microscope. The sample temperature is raised to -90 °C and maintained at that temperature for several minutes to sublime the ice. Then, images are taken.

A monodisperse 200 nm polystyrene latex at 57% solids and a 3-to-1 blend of 200 nm and 300 nm polystyrene latexes at 57% solids were evaluated by the above-mentioned "Cryo-TEM" technique for the state of their dispersions, that is, the arrangements of latex particles in both the monodisperse and bimodal latexes. The monodisperse latex was iridescent, suggesting that the latex was highly ordered, while the bimodal latex was not iridescent. Figure 1 shows the TEM images of the 90 nm-thick cross-section of a 200 nm monodisperse polystyrene latex at 57% solids prepared by the Cryo-TEM technique. . The figure clearly shows that the more uniform particles are more ordered. Figure 2 shows the TEM images of the 90 nm-thick cross-section of a 3-to-1 blend of 200 nm and 300 nm polystyrene latexes at 57% solids. Unlike Figure 1, Figure 2 shows that the arrangements of bimodal particles are random and that different size particles interfere with the formation of ordered structures without defects. The cross-sections of latex particles shown in Figures 1 and 2 were elongated by sectioning in the direction of cutting.

The "Cryo-TEM" technique has been found to be very useful in studying the state of dispersions of colloidal particles and the effect of various additives on the state of dispersions.

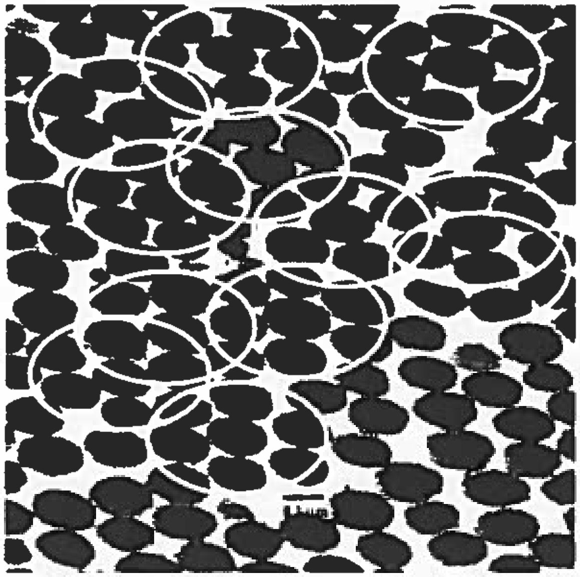

Figure 1. TEM image of the 90 nm-thick cross-section of a 200 nm A polystyrene latex at 57% solids prepared by a "Cryo-TEM" technique: Some ordered particles are circled for illustration in the image.

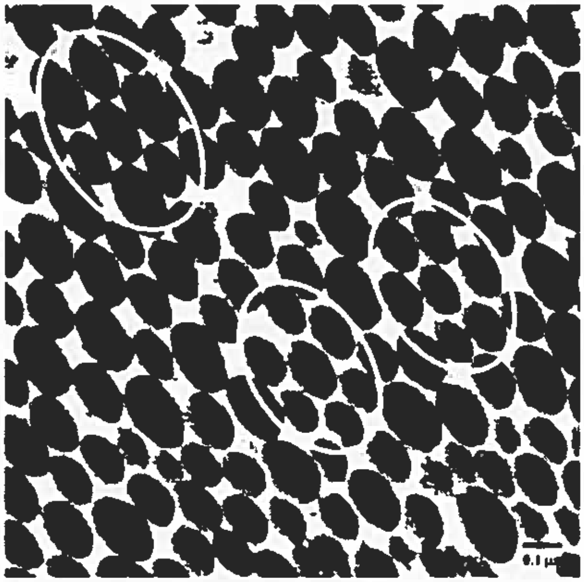

Figure 2. TEM image of the 90 nm-thick cross-section of a 3-to-1 blend of 200 nm and 300 nm polystyrene latexes at 57% solids prepared by a "Cryo-TEM" technique: The structures circled in the image are seemingly ordered, but they are defective due to the difference in particle size.

Dr. Peter A. Lovell

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UK Polymer Colloids Forum

As promised in the last Newsletter, you should all have received from me a copy of the booklet of profiles of all UK academics who are active in the field of Polymer Colloids. If you would like further copies, please let me know.

The most significant change concerning the Forum is that after being Chairman from its inception in 1993, I passed on that role to Professor Brian Brooks of Loughborough University in November 1998. I would like to thank everyone who has helped me in establishing the Forum and wish Brian every success in continuing and expanding its role.

My 'swan song' will be the 6th Meeting of the Forum, which I am organising and will take place on 22-23 September 1999 at Loughborough University. Details of the meeting are given at the front of this issue of the Newsletter.

An Up-Date on the Progress of our Studies into Chain Transfer to Polymer

Research Students: Nasir Ahmad, Ian Gray
Research Associates: David Britton, Tsuyoshi Yamashita, Sylvia Underwood
Collaborator (NMR): Frank Heatley, Chemistry Department, University of Manchester

My collaboration with Frank Heatley on NMR-based studies of chain transfer to polymer continue to be a fruitful area of research. This is just a brief up-date.

Nasir Ahmad has now carried out studies of ethyl acrylate (EA) and methyl acrylate (MA) to complement his earlier work [see IPCG Newsletters 28(1) & 29(1)] on n-butyl acrylate (BA). His experiments have shown that there is no measurable difference between the branching levels resulting from chain transfer to polymer in solution and emulsion homopolymerizations of these acrylates. However, Tsuyoshi Yamashita has been looking at chain transfer to polymer in solution and emulsion polymerizations of 2-ethylhexyl acrylate (EHA) and has found much higher levels of branching than for BA, EA and MA. Interestingly, the additional branching appears to be due entirely to H-abstraction of the backbone tertiary C–H, with no measurable contribution from the side-group C–H. More work is necessary to probe this observation in detail. At present, we are carrying out studies of the effects of comonomers on the extent of chain transfer to polymer in EHA emulsion polymerizations. In another study that extends Nasir's work, Sylvia Underwood has examined the rheological properties of his fully-characterized polyBA samples and found that the data fit to Graessley-Edwards theory. This has enabled us to calculate the interaction density and length of chain contour per unit volume for polyBA, data which have not previously been available.

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

David Britton's work [see IPCG Newsletters 28(1) & 29(1)] on chain transfer to polymer in vinyl acetate (VAc) emulsion polymerizations has been extended to copolymerizations with BA. This has produced some very interesting results, in that there is a synergistic effect. The level of branching is higher than would be predicted by simply adding the 'homopolymerization' branching levels in the corresponding molar proportions. The increase in branching level results from H-abstraction by VAc-ended radicals at the tertiary C–H bonds in BA repeat units. Thus by copolymerizing VAc with relatively small amounts of BA (which is common practice in commercial VAc emulsion polymerizations), the relatively high susceptibility of acrylic tertiary C–H bonds to H-abstraction chain transfer reactions leads to significant increases in the total level of branching in the polymers produced. Additionally, from the perspective of acrylic polymers, the presence of VAc leads to a much higher level of acrylic branch points than would occur in an all-acrylate polymerization due to H-abstraction at BA backbone C–H bonds by highly reactive VAc-ended chain radicals, a reaction that clearly has a higher rate coefficient than the same abstraction by (less reactive) BA-ended chain radicals.

Finally, Ian Gray's work has a slightly different approach. Here we have been investigating the free-radical degradation of hydroxyethylcellulose (HEC) and how HEC chains become attached to particles in emulsion polymerizations, employing gel permeation chromatography and latex particle size measurements as the principal analytical probes. More on this in the future.

Contribution frm J Lyklema:

Appeared in Langmuir **14**, issue 20, 1998:

"Electrokinetics: the properties of the stagnant layer unravelled."

J Lyklema, S Rovillard, J De Coninck

Contribution to Polymer Colloids Group Newsletter

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News on Polymer Colloids in Japan:

The 10th Polymeric Microsphere Symposium was held in Fukui in November 11-13, 1998 with 65 papers presented and 199 participants. The preprints, although written in Japanese, is available at free of charge by direct request to M. Nomura. The titles of the papers presented are shown below, The 11th Polymeric Microsphere Symposium will be held in 2000.

Recent Research Activity on Polymer Colloids in Fukui University:

(1) Effect of Vinylidene Chloride Content on Film-Formation Property of Vinylidene Chloride-Methyl Acrylate Copolymer Latex

T. Kodani, H.Sakai, T. Okabe, and M. Nomura, *J. Appl. Polym. Sci.*, **69**, 565-572 (1998)

Synopsis: Minimum film-formation temperature (MFFT) of vinylidene chloride (VFC)-methyl acrylate (MA) copolymer latexes prepared by batch emulsion polymerization with various compositions from to 20 97 % of VDC were measured. For latexes with VDC content below 90 wt %, MFFT was similar to polymer T_g . As VDC content increased beyond 90 wt % the MFFT curve plotted against VDC content rose sharply, in contrast with the T_g curve that descended smoothly. Measurements of infrared absorption of latexes in the dispersed state, and X-ray diffraction and infrared absorption of lyophilized polymers were conducted on 40:60,80:20, and 95:5 VDC-MA specimens. These observations indicated that only 95:5 VDC-MA specimens were highly crystalline. It was therefore believed that film-formation property of latex with high VDC content was significantly affected by polymer crystallinity of particles in the dispersed state. Morphology and oxygen gas transmission rate of heat-treated and non-heat-treated coatings of 95:5 VDC-MA latex were investigated. Heat treatment of coatings beyond the temperature at which crystalline polymer began to melt induced effective particle coalescence, resulting in reduced oxygen gas transmission rate. This supported our belief that film-formation property of VDC-MA latex with high VDC content was significantly affected by polymer crystallinity.

(2) Effect of Strage on Film-Formation Property of Vinylidene Chloride-Acrylonitrile-Methyl Acrylate Copolymer Latex

T. Kodani, H.Sakai, T. Okabe, and M. Nomura, *J. Appl. Polym. Sci.*, **69,** 573-579 (1998)

Synopsis: Latex prepared from 91:5:4 wt % vinylidene chloride-acrylonitrile-methyl acrylate monomer mixture by seeded semicontinuous emulsion polymerization was investigated for a change in minimum film-formation temperature (MFFT) during storage, with focus placed on polymer crystallinity in the dispersed rose from 20 oC for 49 weeks. Infrared absorption of fresh and stored latexes in the dispersed state indicated an increase in absorbance at 1048cm^{-1}, which is characteristic of vinylidene chloride polymer, that correlated with the MFFT rise with storage. This suggested that the MFFT rise with storage was caused by increasing crystallinity of the polymer in the dispersed state. X-ray wide-angle diffraction and infrared absorption of powder polymers obtained by lyophilization of fresh and stored latexes also indicated increasing crystallinity with latex storage. Oxygen gas permeabilities of films coated with fresh and stored latexes were measured. Latex is unsuitable as an industrial barrier coating material for films and papers.

(3) Kinetics and Mechanisms of Emulsion Polymerization of Vinylidene Chloride. I. Effects of Operating Variables on the Rate of Polymerization and the Number of Polymer Particles Produced

M. Nomura, T. Kodani, J. Ojima, Y.Kihara, and K. Fujita, *J. Polym. Sci., Part A: Polym. Chem.*, **36**, 1919-1928 (1998)

Synopsis: Emulsion polymerization of vinylidene chloride was carried out at 50°C using sodium lauryl sulfate as emulsifier and potassium persulfate as initiator, respectively. Contrary to the results so far reported, stirring rate did not affect the progress of the polymerization and such an abnormal kinetic behavior as the rate of polymerization suddenly drops in the course of polymerization was not observed. The number of polymer particles produced was proportional to the 0.7 power of the concentration of emulsifier forming micelles and to the 0.3 power of the initial initiator concentration, respectively, and was independent of the initial monomer concentration. The rate of polymerization was in proportion to the 0.3 power of the concentration of emulsifier forming micelles, to the 0.5 power of the initial initiator concentration, to the 0.2 power of the initial monomer concentration and to the 0.45 power of the number of polymer particles, respectively.

The titles of the 10th Polymeric Microsphere Symposium:

1.Effect of Reaction Conditions on Microemulsion Polymerization of styrene. K.Suzuki, M.Takayama, E.Seki, T.Mukose, M.Nomura, Fukui University,

2.Analysis of Particle Nucleation in Emulsion Polymerization of Styrene/SDS by Light Scattering Method. S.Hashiya, M.Nomura, Fukui University, Fukui

3.Determination of Propagation Rate Constant of VDC in Emulsion Polymerization. T.Kodani, H.Saka, Asahi Chemical Industry Co., Ltd., J. Ojima, Y.Kihara, K.Fujita, M.Nomura, Fukui University, Fukui

4.Emulsion Copolymerization of Methyl Methacrylate and Vinylidene Chloride. K.Fujita, Y.Kihara, H.Sakai, M.Nomura, Fukui University, Fukui

5.Kinetic Study of Emulsion Copolymerization of Styrene-MMA in the Absence of Conventional Initiators. Y.-Z.Du, G.-H.Ma, M.Nagai, S.Omi, Tokyo University Agriculture and Technology, Koganei, T.Kimura, Toagousei Co.Ltd., Nagoya

6.Simulation of St-MMA Non-Catalytic Emulsion Copolymerization Reaction. Y.-Z.Du, G.-H.Ma, M.Nagai, S.Omi, Tokyo University, Tokyo, T.Kimura, Toagousei Co.Ltd., Nagoya

7.Variation of Particle Size by Addition of Electrolyte to Hydrolysis and Condensation of Tetraethylorthosilicate(TEOS). Y.Konno, D.Nagao, T.Sato, M.Konno,Tohoku University, Sendai

8.Emulsion Crosslinking Copolymerization of Allyl Methacrylate with Alkyl Methacrylates. A.Matsumoto, K.Inui, T.Shimatani, S.Asai,H.Aota.Kansai University, Osaka, I.Capek, Polymer Institute, Slovak Academy of Sciences, Slovak Republic

9.Crosslinked Polymer Formation in Emulsion Polymerization. H.Tobita, Fukui University, Fukui

10.Preparation of Ethylene-Modified Latexes by Emulsion Polymerization Using Ethylene-Acrylic Acid Resin. J.-S.Shin, D.-Y.Lee, J.-H.Kim, Yonsei University, Seoul, Korea

11.Emulsion Polymerization of Styrene Using Oligomer Type Surfactants. A.Hashimoto, N.Ohama, Chukyo Yushi Co.,Ltd., Nagoya, T.Okaya, The University of Shiga Prefecture, Shiga

12.Emulsion Polymerization of Methyl Methacrylate Using Surface Active Polyelectrolyte. S.Kato, Fukui National College of Technology, Sabae, J.Noguchi, M.Nomura, Fukui University, Fukui

13.Emulsion Polymerization of Styrene Using Butyl Acrylate-Acrylic Acid Polymeric Emulsifier. S.Kato, Fukui National College of Technology, Sabae, M.Matsuzaki, Y.Sanai, Toagouse Co.,Ltd, Nagoya, K.Sudo, M.Nomura, Fukui University, Fukui

14.Application of Functional P(styrene-*co*-acrylic acid) to NAD and Emulsion Polymerizations. N.Fujihashi, H.Onuma, G.-H.Ma, M.Nagai, S.Omi, Tokyo University Agriculture and Technology, Koganei

15.Polymer Emulsions Prepared by Using Poly(vinyl alcohol)s as a Protective Colloid. M.Nakamae, N.Fujiwara, S.Tanimoto, T.Sato, M.Maruyama, Kuraray Co.,Ltd, Kurashiki

16.Effect of Additives on the Elementary Process of Emulsion Polymerization of MMA Using PVA as a Protective Colloid. T.Okaya, ASuzuki, K.Kikuchi,T he University of Shiga Prefecture, Shiga

17.Soap-Free Emulsion Polymerization of Styrene with Poly(ethylene oxide) Macromonomer. K.Tano, S.Kawaguchi, K.Ito, Toyohashi University of Technology, Toyohashi

18.Epoxy Resin-Acrylic Composite Polymer Emulsion Via Mini-Emulsion Polymerization. H.Kawahara, Y.Suzuki, Y.Hasegawa, Y.Okamoto, F.Yoshino, Dainippon Ink & Chemicals Inc., Osaka, H.Kage, Y.Matsuno, Kyushu Institute of Technology, Fukuoka

19.Preparation and Properties of Acryl Silicone/Colloidal Silica Hybrid Emulsion. K.Inokami, Daicel Chemical Industries,Ltd., Himeji

20.Laser-Induced Aerosol Particle Formation from a Gaseous Mixture of Organosilicon Compound and Acrolein. H.Morita, K.Senba, Chiba University, Chiba

21.Aggretion Behavior of Gel Microspheres of Streoregular Poly(methyl methacrylate) from Solution. T.Maegawa, H.Aoyama, T.Takahashi, Fukui University, Fukui

22.Preparation and Characteristic of Micro capsule Containing Proteins by Varorization Method Using (W/O/W)Emulsion.Y.Kawano, K.Shiomori, S.Kiyoyama, Miyazaki University, Miyazaki, Y.Hatate, Kagoshima University, Kagosima

23.Preparation of Microspheres Including Some Photocatalyst. T.Fujuwa, Daicel Chemical Industries,Ltd., Himeji, H.Taoda, T.Nonami, National Industrial Research Institute of Nagoya, Nagoya

24.Preparation and Properties of Cellulose Microspheres. K.Akimoto, H.Saito, N.Ise, Rengo Co.,Ltd., Fukui

25.Preparation of Poly(4-Vinylpyridine/n-Butylacrylate)(4:1) Microsphere and Dumbbell-Like Dipolar Microsphere by Seeded Emulsion Polymerization. H.-M.Ni, G.-H.Ma, M.Nagai, S.Omi, Tokyo University of Agriculture and Technology, Koganei

26.Preparation of Polymeric Particles Containing an Acidic dye by Aqueous Polymerization of a Cationic Surface-Active Monomer. M.Shishido, T.Taniguchi, K.Nagai, Yamagata University, Yonezawa

27.Efficient Particle Growth by Heterocoagulation between Counter-Charged Particles and Subsequent Seed Polymerization. T.Hayakawa, G.-H.Ma, M.Nagai, S.Omi, Tokyo University of Agriculture and Technology, Koganei

28.Synthesis of Monodisperse Micron-Sized Polystyrene Particles with Radical Polymerization in Aqueous Media. T.Mogi, A.Aoyagi, M.Konno, Tohoku University, Sendai

29.Synthesis of Monodisperse Microparticles Including PI Prepolymer. T.Hashimoto, G,-H.Ma, M.Nagai, S.omi, Tokyo University of Agriculture and Technology, Koganei

30.Production of above 10⊃ μm-sized, Monodispersed Polymer Paeticles by One-Step Seeded Polymerization for Monomer-Swollen Polymer Particles Prepard Utilizing the Dynamic Swelling Method. M.Okubo, E.Ise, T.Yamashita, Kobe University, Kobe

31.Production of Micron-sized, Monodispersed Polymer Particles Having "Snow-man" Shape by Seeded Polymerization for Monomer-'adsorbed' Polymer Particles Prepared by Utilizing the Dynamic Swelling Method with Tightly Cross-Linked Seed Particles. M.Okubo, T.Yamashita, E.Ise, Z.Wang, Kobe University, Kobe

32.Formation of Multi-Hollow Structures in Carboxylated Polymer Particles Prepared with Different Monomer Addition Methods by the Alkali/Cooling Method. M.Okubo, A.Sakauchi, M.Nakamura, Kobe University, Kobe

33.NMR Analysis on the Prodution of Multi-Hollow Polymer Particles by the Alkali/Cooling Method(2). M.Okubo, K.Shiba, M.Nakamura, Kobe University, Kobe

34.Effect of the Polymer Composition on the Production of multi-hollow Polymer Particles by the Acid/Alkali Method. M.Okubo, A.Ito, H.Mori, Kobe University, Kobe

35.Behavior of Nonionic Emulsifier Molecules on the Preparation of Polyer Nanoparticles by the Particle Dissolution Method(3). M.Okubo, R.Shinohara, N.Fukami, Kobe University, Kobe

36.Preparation of Uniform Hollow Microspheres by Employing SPG Emulsification Technique. R.Kanda, G.-H.Ma, M.Nagai, S.Omi, Tokyo University of Agriculture and Technology, Koganei

37.Preparation of Magnetite Microcapsules by Employing SPG Emulsification Technique. A.Kanetaka, Y.Shimamori, G.-H.Ma, M.Nagai, S.Omi, Tokyo University of Agrculture and Tecnology, Koganei

38.Preparation of New Magnetic Polymer Particles and its Application for Biomedical Field. K.Kasai, K.Fan, M.Kitajima, M.Hikata, JSR Co.,Ltd., Yokkaichi

39.Distinction Between Complementary DNA and Point-Mutational DNA Using DNA-Carrying Affinity Latex. K.Nakamura, K.Fujimoto, H.Kawaguchi, Keio University, Yokohama

40.Development of Polymeric Microspheres for Protein Renaaturation. H.Shimizu, K.Fujimoto, H.Kawaguchi, Keio University,Yokohama

41.Development of Thermo-Sensitive Microspheres with Sharp Response. H.Matsuoka, K.Fujimoto, H.Kawaguchi, Keio University, Yokohama

42.Preparation of thermosensitive Core-Shell Type Microspheres with a Charged Core and Their Dispersion Stability. M.Sasaki, K.Fujimoto, H.Kawaguchi, Keio University, Yokohama

43.Preparation of Unsymmetrical Microspheres and Their Assembing. K.Nakahama, K.Fujimoto, H.Kawaguchi, Keio University, Yokohama

44.Control of the Morphologies of Micron-sized Monodispersed Composite Polymer Particles by Post-Treament(2). M.Okubo, A.Tanaka, J.Izumi, T.Yamashita, Kobe University, Kobe

45.Analysis of Polymeric Microparticle Morphology Prepared by SPG Membrane Emulsification Technique. T.Senba,G.-H.Ma,M.Nagai,S.Omi,Tokyo University of Agriculture and Technology, Koganei

46.Small Angle X-ray Scattering for Emulsion Particles. K.Saga, S.Fukaya,P.Chen, M.Aoki, T.Kawaguchi,K.Sudoh,M.C.Research Center, Yokohama, F.Hoshino, K.Takano, Mitsui Chemicals, Inc., Yokohama, K.Inoue, T.Fujisawa, RIKEN, Hyogo

47.Rheological Properties of Sterically Stabilized Emulsion. P.Chen, S.Fukaya, K.Saiga. M.Aoki, K.Sudoh, M.C.Research Center, Yokohama, F.Hoshino, K.Takano, Mitsui Chemicals, Inc., Yokohama

48.Application of Electron Microscope and SPM to Morphological Investigation on Emulsion. N.Kuramitsu, K.Saiga,H.Tamura, P.Chen, M.Aoki, K.Sudoh, M.C.Research Center, Yokohama, F.Hoshino, K.Takano, Mitsui Chemicals, Inc., Yokohama

49.Synthesis and Properties of Core-Shell Type Microspheres with Microseparated Surface. R.Saoto, A.Fujita, K.Ishizu, Department of Polymer Chemistry, Tokyo Institute of Technology, Tokyo

50.Estimation of Sulfate Groups at the Particle Surfaces by Isothermal Titration Calorimeter with Extremely Small Amount of Polystyrene Emulsion. M.Okubo, A.Sakauchi, T.Suzuki, Kobe University, Kobe

51.AFM Study on Interaction and Adhesive Force between Surfaces in Alcohol-Water Solutions. Y.Kanda, K.Hogashitani, Kyoto University, Kyoto

52.Dispension Stability of Latices Induced by Polyelectrolytes. 1) Charged Species and Adsorption Properties. S.Satou, J.Shirai, T.Nashima, K.Furusawa, University of Tsukuba, Tsukuba

53.Dispersion Stability of latices Induced by Polyelectrolytes. 2) Structure of Adsorbed Layers and its Effect on Colloid Stability. J.Shirai, T.Nashima, K.Furusawa, University of Tsukuba, Tsukuba

54.Dispersion Stabilization of Carbon Black in Water by Copolymerization Method Using Polymerizable Surfactants. Y.Igarashi, M.Kumagai, T.Taniguchi, K.Nagai, Yamagata University, Yonezawa

55.Dispersion Stabilization of Carbon Black in Water Using Poly(*N*-Alkylamide)s. T.Taniguchi, A.Takeda, K.Nagai, Yamagata University, Yonezawa

56.Cooperrative Adsorption of Macroions on the Colloidal Spheres. T.Okubo, M.Suda, S.Morino, S.Suzuki, Gifu University, Gifu

57.Nucleation and Growth Mechanism of Colloidal Crystallization. T.Okubo, A.Tsuchida, S.Takahashi, K.Taguchi, Gifu University, Gifu

58.Electro-Optic Effects of Colloidal Crystals. A.Tsuchida, T.Tanahashi, M.Kuzawa, T.Okubo, Gifu University, Gifu

59.Reactability of the Particle Containing α-Glycol Group. H.Isaka, H.Harakawa, N.Numa, Kansai Paint Co.,Ltd., Hiratsuka

60.Film Forming Property of Vinylidene Chloride-Methacrylate Terpolymer Latex. T.Kodani*, H.Sakai*, A.Takayama, M.Nomura, *) Asahi Chemcal Industry Co.,Ltd., Miyazaki

61.Film Formation and Moisture Permeability of Hi-Carboxylated Latex. T.Aida, T. Yamamoto, J.Hasegawa, Nippon Zeon Co.,Ltd., Kawasaki

62.Surface Analysis of Dry Film from Acry-Polyurethane Emulsions. S.Takemoto, S.Satoki, S.Yamazaki, Daicel Chemical Industries Ltd., Himeji

63.Preparation and Properties of Sol-Gel Coatings with Dispersed Fluoropolymer Latex. T.Arase, T.Araki, Y.Tanaka, T.Shimizu, Daikin Indutries,Ltd., Osaka

64.The Effect of Polymer Components on The Rheological Behavior of Coating Colors. H.Yamada, A.Ogawa, S.Matsuda, Asahi Chemical Industry co.,Ltd., Osaka

65.Development of a Reaction Calorimeter with Good-Temperature Controllability for High-Exothermic Reactions: Application to Emulsion Polymerization Reactions. N.Ashizawa, T.Kobatashi, S.Hirobe, Todoroki Industrial co., K.Fujita, K.Suzuku, M.Nomura, Fukui University, Fukui

January, 1999

Contribution to the IPCG Newsletter

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Publications 1998-continued

(1) Production of hollow polymer particles by suspension polymerization

M. Okubo, Y. Konishi, H. Minami,
Colloid Polym. Sci., **276**, 638-642 (1998)

Polymer particles having single hollow in the inside were successfully prepared by suspension polymerization for divinylbenzene/toluene droplets dissolving polystyrene (PS) in an aqueous solution of poly(vinyl alcohol). Such a hollow polymer particle was not obtained without PS. The hollow structure was affected by the molecular weight and the concentration of PS.

(2) Formation of micro-heterogeneous film from composite polymer emulsion prepared by the stepwise heterocoagulation method

M.Okubo, Y. Lu
J. Appl. Polym. Sci., **69**, 2221-2228 (1998)

Blend emulsion of two kinds of particles, in which composite polymer particles were prepared by utilizing the stepwise heterocoagulation method proposed by the authors in 1990, was cast to prepare a micro-heterogeneous film. In the film, discontinuous phase consisted of large anionic hard polymer particles and continuous one consisted of small cationic soft polymer particles with the content of 30 wt% as film forming additives. The storage stabilities of the blend emulsions after the stepwise heterocoagulation were examined under various conditions. The morphology of the film prepared was estimated from attenuated total reflectance Fourier transform infrared spectroscopic and dynamic mechanical spectroscopic measurements.

(3) Synthesis of temperature-sensitive micron-sized monodispersed composite polymer particles and its application

M.Okubo, H. Ahmad, T. Suzuki

Colloid Polym. Sci., **276**, 470-475 (1998)

Temperature-sensitive micron-sized monodispersed composite polymer particles were prepared by seeded copolymerization of dimethylaminoethyl methacrylate and ethylene glycol dimethacrylate with 1.77 μm-sized monodispersed polystyrene seed particles. The change in surface property at temperature above and below 35 °C was examined by differential scanning calorimetry, trypsin activity and the adsorption/desorption behaviors of low molecular weight cationic emulsifier as well as biomolecules.

(4) Production of Micron-sized Monodispersed Polymer Particles by Seeded Polymerization for the Dispersion of Highly Monomer-Swollen Particles Prepared with Submicron-sized Polymer Seed Particles Utilizing the Dynamic Swelling Method

M. Okubo, E. Ise, T. Yamashita

J. Polymer Science, Part A: Polymer Chemistry, **36**, 2513-2519 (1998)

For the purpose of extending the size range of polymer seed particles used in "dynamic swelling method" (DSM), first, it was verified theoretically that the submicron-sized polymer particles produced by emulsion polymerization can also absorb a large amount of monomer by DSM in both equilibrium and kinetic control states. Next, on the basis of the theoretical results, experimentally about 2.6 μm-sized styrene-swollen polystyrene (PS) particles were prepared utilizing DSM in the presence of 0.64 μm-sized monodispersed PS seed particles produced by emulsifier-free emulsion polymerization. Moreover, 2.5 μm-sized monodispersed PS particles were produced by seeded polymerization for the dispersion of the swollen particles at $30_{\circ}$C with 2,2'-azobis(4-methoxy-2,4-dimethylvaleronitrile) initiator.

(5) Preparation of micron-sized monodispersed highly monomer-"adsorbed" polymer particles having snow-man shape by utilizing the dynamic swelling method with tightly cross-linked seed particles

M. Okubo, T. Yamashita, H. Minami, Y. Konishi

Colloid Polym. Sci., **276**, 887-892 (1998)

Micron-sized, monodispersed highly styrene-"adsorbed" particles having snow-man shape were prepared by the dynamic swelling method (DSM) with tightly cross-linked polymer seed particles as follows. First, 3.8 μm-sized monodispersed polystyrene (PS)/poly(divinylbenzene) (PDVB) (PS/PDVB = 1/10 wt. ratio) composite particles produced by seeded polymerization utilizing DSM were dispersed in an ethanol/water (6/4, w/w) solution dissolving styrene monomer, and poly(vinyl alcohol) as a stabilizer. Secondary, water was post-added to the dispersion with a micro feeder at a rate of 2.88 ml/h at room temperature. The cross-linked seed particles adsorbed a large amount of styrene onto the surfaces and resulted in monodispersed highly styrene-"adsorbed" snow-man shape particles having about 10 μm in diameter.

Contribution to the IPCG Newsletter January 19, 1999

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Main activities of our group are on colloidal crystals, their morphology, crystal structure, crystal growth kinetics and effect of external fields such as an gravitational field, electric field, and centrifugal field. Microgravity effect on colloidal dispersions has been studied systematically using dropping, aircraft and rocket techniques. Multiple absorption phemomena of colloidal spheres, viscosity of colloidal gases, liquids and crystals, and surface tension of polyelectrolytes and their complexes with colloids are also included in our research fields.

Publications(1998-)

(1)"**Kinetic Analyses of the Colloidal Crystallization in Aliciholic Organic Solvents and Their Aqueous Mixtures As Studied by Reflection Spectroscopy**", T.Okubo and S.Okada, *J.Colloid Interface Sci.*, 204, 198-204(1998).

Reflection spectroscopy is made for the kinetic analyses of the nucleation and growthprocess of colloidal crystals of silica spheres(110 nm in diameter) in the exhaustively deionized suspensions of purely alcoholic organic solvents(methyl alcohol, ethyl alcohol and ethylene glycol) and aqueous mixtures with the alcohols(methyl-, ethyl-, n-propyl-, n-butyl-alcohols and ethylene glycol). Sphere concentrations studied range from 0.001 to 0.01 in volume fraction, rather high compared with those in water. Induction periods are from 5 to 2000 seconds, and prolong with decreasing sphere concentration. Nucleation rates are 10^{-3} to 10^{3} $mm^{-3}s^{-1}$ and increase sharply as sphere concentration increases. The crystal growth rates, v have been determined from increase of intensity in the sharpened reflection peaks. v ranges from 1 to 27 μm/s and decreases linearly as the reciprocal sphere concentration increases. Nucleation and crystallization rates decrease sharply as fraction of the organic solvents increases in the mixtures with water. Importance of the electrostatic intersphere repilsion through the electrical double layers and the cooperative and synchronized fluctuation of colloidal spheres in the crystallization processes is supported.

(2)"**Does Crystal growth in a Microgravity? Colloidal Crystals as Example**(in Japanese)", *Solid Physics*, 33, 80-84(1998).

Microgravity experiments made by our group recently on the kinetics of colloidal nucleation and crystallization processes are reviewed.

(3)"**Nonlinear Electro-Optics of Colloidal Crystals as Studied by the Reflection Spectroscopy**", T.Okubo, A.Tsuchida, S.Okada, and S.Kobata, *J.Colloid Interface Sci.*, **199**, 83-91(1998).

Nonlinear electro-optic behavior of colloidal crystals of colloidal silica spheres is studied by the reflection intensity measurements and the time-resolved reflection spectroscopy. Harmonic generation is observed for the reflection signal when a sine-wave electric field ranging from 0.01 Hz to 10 Hz is applied. The synchronous fluctuation of the colloidal spheres containing expanded electrical double layers in the crystal lattices will be one of the main causes for the electro-optics. It is deduced from the time-resolved reflection spectra analyses that the transformation between two subphases of lattice structures, fcc and bcc, is also important factor for the harmonic generation.

(4)"**Electro-optic Properties of Colloidal Crystals As Studied by Reflection Spectroscopy**", T.Okubo, A.Tsuchida, T.Tanahashi and A.Iwata, *J.Colloid Interface Sci.*, 207, 130-136(1998).

Electro-optic properties of colloidal crystals of silica spheres in the exhaustively deionized aqueous suspension have been studied by the reflection spectroscopy using T-type cell. Acoustic shear waves are induced when sinewave electric fields ranging from 0.01 to 1 Hz are applied. Modulation effects of the crystals on the applied a.c. fields such as phase delay, change in response intensity, waveform transformation and harmonics generation are observed. The shear waves propagate outside the electrodes where the electric field is absence. The synchronous fluctuation of the colloidal spheres includingfexpanded electrical double layers in the crystal lattice will be one of the main causes for the electro-optic nature of the crystals.

(5)"**Surface Tension of Biological Polyelectro;yte Solutions**", T.Okubo and K.Kobayashi, *J.Colloid Interface Sci.*, 205, 433-442(1998).

Surface tensions of biological polyelectrolytes in aqueous solutions are studied systematically as possible at the air-water interface by the Wilhelmy method. The polyelectrolytes measured are sodium chondroitin sulfates A and C, sodium poly-α,L-glutamate, poly-L-lysine hydrobromide, deoxyribonucleic acid, lysozyme and bovine serum albumin. Linear type macroions such as NaCR, NaPGA, PLL.HBr and DNA have no surface activity in a wide range of polymer concentrations below the critical polymer concentration, m*, and increases as the concentration increases above m^*. Surface activity of the undissociate state of macroions is rather high in general. Globule-like macroions such as LZ and BSA show high surface activity at isoelectric point above m^* accompanied with orientation of the molecules along the air-water interface. Separation into the hydrophobic and hydrophilic parts at the interfaces and balancing in their strenght are important for appearance of surface activity.

(6)"**Kinetic Analyses of Colloidal Crystallization in a Sinusoidal Electric Field as Studied by Reflection Spectroscopy**", T.Okubo and H.Ishiki, *J.Colloid Interface Sci.*, in press.

The effect of sinusoidal electric field on the crystal growth rates in colloidal crystallization of silica spheres (110 nm in diameter) in the exhaustively deionized aqueous suspensions has been studied by reflection spectroscopy.

Sphere concentration is 0.0016 in volume fraction. Nucleation time is shorter than 1 s. The crystal growth rates, *v* of the body-centered cubic lattices have been determined from increase in the cube-root of the intensity in the sharpened reflection peaks. The *v* value is 20 μm/s in the absence of electric field. *v* decreases from 20 to 8 μm/s as the voltage applied increases from 0 to 10 V at 1 Hz. *v* decreases from 30 to 15 μm/s when frequency increases from 0.01 Hz to 10 Hz at *E*= 6 V, and keeps constant irrespective of frequencies higher than 10 Hz upto 10 kHz. Interestingly, the crystallization of bcc lattices is enhanced at low frequencies between 0.01 and 0.5 Hz. Main causes for the retardation of the crystallization at high frequencies and voltages are (a)the additional translational fluctuation of the spheres and the surrounding electrical double layers by the electric field, and (b)the partial melting of the crystals by the shearing forces in an electric field. Importance of the electrostatic intersphere *repulsion* by overlapping of the electrical double layers and the cooperative and synchronized fluctuation of colloidal spheres in the crystallization processes are supported strongly.

(7)"**Electro-optics of Colloidal Crystals As Studied by the Reflection Spectroscopy**", T.Okubo, A.Tsuchida, T.Tanahashi, A.Iwata, S.Okada, S.Kobata and K.Kobayashi, *Colloid & Surfaces*, in press.

Responses in the colloidal structural changes induced by an alternating electric field(sine- and square-wave fields) have been studied by the reflection intensity measurements of colloidal crystals. The suspensions of colloidal silica spheres in water, ethyl alcohol and ethylene glycol, and their aqueous mixtures are deionized exhaustively with the mixed beds of ion-exchange resins for more than four weeks. Several characteristic modulation effects such as phase difference, changes in amplitudes and wave-forms and generation of the harmonics have been discussed. Furthermore, significant effects of the relative position between the observation and the electrode upon the electro-optics have been observed. This supports strongly that the electro-optic effects are ascribed to the accoustic shear waves in colloidal crystals.

(8)"**Electric Field Induced Shear Waves of Colloidal Crystals As Studied by the Electro-Optic Reflection Spectroscopy**", T.Okubo, A.Tsuchida, A.Iwata and T.Tanahashi, *Colloids & Surfaces*, in press.

Viscoelastic electro-optic properties of colloidal crystals of colloidal silica spheres in the exhaustively deionized aqueous suspension have been studied by the reflection spectroscopy. Acoustic shear waves are induced when a sine-wave electric fields from 0.01 to 1 Hz are applied. The shear waves propagate outside the electrodes, where the electric field is absence. The whole suspension of colloidal crystals oscillates synchronously with symmetry plane at the center of the electrodes. The phase differences observed around the cell are explaned by the symmetric structure of the shear waves.

(9)"**Electro-optic Effects in Colloidal Crystals** ", T. Okubo and M. Stoimenova, ACS Book, "*Polymers for Advanced Optical Applications*", Am.Chem.Soc., in press.

Colloidal single crystals of giant size(3 to 8 mm) have been observed in exhaustively deionized and highly diluted suspensions of monodisperse polystyrene and silica spheres. Kinetics of crystal growth is discussed briefly. Size of the single crystals increases sharply as sphere volume fraction decreases, and the crystal is largest at sphere concentration slightly higher than the critical concentration of melting. Dynamic aspects in the visco-elastic properties of colloidal crystals have been also discussed. g-factor, which indicate the magnitude of thermal motion, in colloidal crystals, range from 0.03 to 0.1, and are close in value to those of stable crystals of metals and proteins. Static and dynamic light-scattering measurements have been made for many kinds of colloiudal crystals. Three and two dynamic processes are extracted separately from time profiles od autocorrelation function of colloida crystals and liquids, respectively. Electro-optic effects of colloidal crystals are studied both by using the electric light-scattering technique and by reflection spectroscopy in a.c. electric fields. Two electro-optic relaxations are obtained and their relation to electrically-induced acoustic modes is demonstrated. Phase difference and higher order harmonics are clearly observed at low frequencies. The oscillating decay of the effects observed in a narrow low frequency range demonstarets their relation to undamped shear waves of the crystall lattice.

(10)"**Electro-optic Spectroscopy of Colloidal Systems**", M.Stoimenova and T.Okubo, "*Surfaces of Nanoparticles and Porous Materials*", J.A.Schwarz,Ed., Dekker, New York, in press.

Recent advancement on the elecvtro-optic properties of colloiddal suspensions are reviewed. Contents are Introduction, Electro-optic effects in suspensions of spherical particles, Electro-optic effects in suspensions of snisometric particles and References.

(11)"**Relation of Electro-accoustic Effects to Low Frequency Anomalies in Colloidal Electro-optices**", M.Stoimenova and T.Okubo, *Colloids Surfaces*, in press.

Low frequency anomalous electro-optic behaviour of colloids(deviations from Kerr low) concerns a series of phenomena in different systems widely studied by researchers involved in the field of colloids, polymers, polyelectrolytes, etc. Investigations on samples of isotropic spherical particles display electro-optic effects of similar characteristics, which are recognized as electrically induced acoustic modes. Therefore the analysis of the colloidal electro-optic spectra requires separation of anisotropy and density fluctuations prior to application of the method for determination of single particle constant.

(12)"**Kinetic Analyses of Colloidal Crystallization in a Microgravity. -Aircraft Experiments-**", T.Okubo, A.Tsuchida, T.Okuda, K.Fujitsuna, M.Ishikawa, T.Morita and T.Tada, *Colloids & Surfaces*, in press.

Nucleation and growth processes in colloidal crystallization of silica spheres are studied in a microgravity by the parabolic flights of an aircraft. Continuous circulating type stopped flow cell system has been used, and the time-resolved reflection spectra are measured. The cell system is composed of a peristaltic pump, a column containing a mixed bed of ion-exchange resins and a quartz observation cell. They are connected with PharMed tube in a closed circuit. Close-up observation with a CCD camera has been made. Nucleation dates decrease in a microgravity. Crystal growth rates of the face-centered cubic(fcc) lattices decrease in a microgravity(0G) by ca. 25% compared with those in a gravity(1G). One of the main reasons for the retardation is that the downward diffusion of spheres, which may enhance the inter-sphere collision, disappears in a microgravity. No convection of the suspension in a microgravity is also important.

(13)"**Kinetic Study of the Formation Reaction of Colloidal Silica Spheres by the Transmitted-light Intensity and Dynamic Light-Scattering Measurements**", T.Okubo, K.Kobayashi, A.Kuno and A.Tsuchida, *Colloid Polymer Sci.*, in press.

Kinetic analyses of the formation reaction of colloidal silica spheres, which are synthesized from ethyl silicate(EtSi), ammonia(NH_3) and a trace of water in ethanol, are made by the transmitted-light intensity and dynamic light-scattering methods. Sphere size vs. time profiles from the two methods agree well especially in the beginning of the reaction. The polymerization starts after an certain induction time(t_i) ranging several ten seconds to several minutes. ti increases as the concentrations of NH_3, EtSi and/or H_2O decrease. The apparent rates of the reaction, v' are estimated from the reciprocal periods between the intersection of the straight slope line with the initial and final holizontal lines in the cube-root of the absorbance vs. time plots. Log v' increases linearly with the slopes of 1, 2 and 0.5 as the logarithms of the concentrations of EtSi, NH_3 and/or H_2O increase, respectively. These results support the polymerization mechanisms of the formation of the small preliminary particles followed by their coalescence to the final large silica spheres.

(14)"**Kinetic Study of Formation Reaction of Colloidal Silica Spheres in a Microgravity Using Aircraft**", T.Okubo, A.Tsuchida, K.Kobayashi, A.Kuno, T.Morita, M.Fujitsuna and Y.Kohno, *Colloid Polymer Sci.*, in press.

Polymerization reactions of colloidal silica spheres via the hydrolysis and dehydration processes of tetraetyl ortho-silicate with ammonia and a tiny amount of water in ethyl alcohol have been studied in a microgravity by the parabolic flights of MU-300 rear-jet aircraft. Induction periods and polymerization rates are determined by the fast-scanning transmitted-light intensity measurements and the fast-scanning dynamic light-scattering method. Direct observation of the reaction mixtures is also made with a CCD video-camera. Reproducible and reliable data are obtained in a microgravity and compared with those in a gravity. Increase in the induction times and decrease in the polymerization rates are observed in a microgravity compared with those in a gravity. One of the main reasons for these observations are the fact that the translational Brownian movement of the reactants and/or product spheres is free from the downward translational movement in a microgravity. Very weak convection of the reaction suspensions in a microgravity are another important factor.

(15)"**Rotational Diffusion of Anisotropic-shaped Colloidal Particles in a Microgravity as Studied by the Free-fall Experiments**", T.Okubo, A.Tsuchida, H.Yoshimi and H.Maeda, *Colloid Polymer Sci.*, in press.

Rotational relaxation times(τ) and diffusion coefficients of ellipsoidal colloids of tungstic acid are studied in aqueous suspension in a microgravity by free-fall experiemts. τ-values are evaluated from the relaxation traces of optical transmittance of the suspension using the stopped-flow technique. Experimental errors at 0G are small compared with those at 1G, which is ascribed to the lack of the movement of impurities in suspension such as quite small dusts and bubbles and the convection of suspension in a microgravity. The limiting slopes of the relaxation curves in the plots of the transmittance against time at 1G depend on the flow direction of the suspension in the flow cell, whereas those at 0G keep zero irrespective of flow direction. Much more reliable data of the diffusion coefficients are obtained in a microgravity. However, the diffusion coefficients themselves are quite insensitive to the gravity.

(16)"**Absorption of Polyelectrolytes on the Colloidal Surfaces as Studied by the Electrophoretic and Dynamic Light-scattering Techniques**", T.Okubo and M.Suda, *J.Colloid Interface Sci.*, submitted.

ζ-Potential and the effective diameter of the colloidal spheres absorbed with the macro-cations and macro-anions are studied by the electrophoretic light-scattering and dynamic light-scattering measurements. Reversal of colloidal surface charges from negative to positive occurs abruptly above the critical concentration of macroions by the excess absorption of the macro-cations onto the anionic colloidal spheres,i.e., avalanche-type absorption. The effective diameter of colloidal spheres including the absorbed layers increases substantially by four to ten fold. In the presence of large amount of macro-cations aggregation of colloidal spheres mediated by the layers of absorbed macro-cations may occur.

(17)"**Alternative sign reversal in the ζ-potential and synchronous expansion and contraction in the absorbed multi-layers of poly(4-vinyl-N-n-butylpyridinium) cations and poly(styrene sulfonate) anions on colloidal silica spheres**", T.Okubo and M.Suda, Colloid Polymer Sci., submitted.

Alternative multiple absorbed layers up to ten of macro-cations [poly(4-vinyl-N-n-butylpyridinium bromide)] and macro-anions [sodium poly(styrene sulfonate)] are formed on colloidal silica spheres above the critical concentration of macroions, m^*. The m^*-value is the minimum amount of macro-ions to reverse the sign of ζ-potential of the spheres in the first absorption step. Alternative sign reversal in the zeta-potential and the expansive-contractive thickness changes are observed by the repeated and alternative addition of macro-cations first and macro-anions next. During the multiple absorption, pH and conductivity values decrease and increase continuously as number of absorbed layers increases. When the macro-anions are added first, the sign reversal in the ζ-potential and the reversible expansion and contraction do not occur. Breaking of the alternative mutiple–type absorption occurs when equivalency in the amount of dissociative groups of macro-cations and –anions is broken. Synchronous conformational changes of macro-cations and -anions in the multiple-absorbed layers, where balancing of the conformational rigidities with the multiple electrostatic attraction and repulsion between macro-cations and -anions are strongly supported

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SURFACE TENSION, STICKINESS AND ENGULFMENT

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ABSTRACT

The thermodynamic conditions for the engulfment of one set of particles by another has been given in terms of interfacial energies. Experimentally, it has been shown that a polymer with a high glass transition temperature can be engulfed by a particle of low glass transition temperature; also, that inorganic particles can be engulfed by polymer particles. As a precursor to the engulfment stage heterocoagulation can be used for bringing the particles together in a "sticking" mode. This appears to be a general process which is applicable to a number of scientific areas, e.g. in biology, phagocytosis, and in material science for the preparation of composite particles.

Contribution to IPCG Newletter From
Laboratoire de Chimie des Procédés de Polymérisation
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Evaluation of emulsion polymerisation kinetics using a non-linear state estimator.

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Shortened abstract of a paper to be presented at Polymers in Dispersed Media, Lyon, April 12-16, 1999

In previous papers from this research group [1-2] we introduced a combined hardware-software approach to the state estimation of both solution and emulsion copolymerisations. In this work, we present the results of the experimental evaluation of an up-dated version of this technique in the semi-batch copolymerisation of styrene and BuA.

The on-line estimator was tested under dynamic experimental conditions in order to follow the individual monomer conversions and during BuA/St emulsion copolymerisations. This on-line estimator allows us to "see" events such as particle nucleation that are fairly exothermic. The value of μ obtained on-line can be used with off-line measurements of N_p (e.g. from light scattering) to find values of (see Figure 1b,c). This technique has been applied to a number of experiments with Sty-BuA and it has been found that, outside periods of particle nucleation, remains fairly constant up to high conversions, and is relatively independent of particle size. We will continue to apply this method to a number of systems in order to determine how the kinetics varies as a function of process conditions.

[1] G. Févotte, T.F. McKenna, A.M. Santos "Modelling of the glass transition temperature of free radical polymers: An approach for control purposes". *Chem. Engng. Sci.*, 53, pp. 2241-2256 (1998).
[2] S. Othman, I. Barudio, G. Févotte, T. McKenna "On-line Monitoring and Modelling of Free Radical Copolymerisations: Butyl Acrylate and Vinyl Acetate," (*Polym. React. Engng. Vol 7(1), to appear 1999*).

A New Look at Kinetics and stabilisation phenomena in emulsion polymerisation

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Shortened abstract of a paper to be presented at Polymers in Dispersed Media, Lyon, April 12-16, 1999

Economic improvements to existing emulsion polymerisation processes can be achieved by several means, including: (i) improving control over rheological properties and viscosity (related to particle size and size distribution); (ii) increasing solids content of the latex (also related to particle size). High solids content without undesirably high viscosity can be obtained when the Particle Size Distribution (PSD) is polymodal [1,2]. However, although these studies provided recipes for obtaining polymodal PSDs and acceptable levels of viscosity, they did not attempt to examine the problem from a process engineering point of view: i.e. try to quantify the effect of particle size, and the concentration and type of surfactant on the evolution of the PSD and reaction kinetics. In order to obtain a well-defined PSD in emulsion polymerisation, it is necessary to have a complete understanding of several different, but interdependent phenomena, including particle nucleation, kinetics, latex stability, monomer type and concentration. We have chosen to study these parameters for a system composed of butyl acrylate (BuA), methyl methacrylate (MMA) and a carboxylic acid, and will concentrate on the influence of surfactant on particle number and size, and on the functionalisation of latexes with carboxylic acids.

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[2] F. Chu, J. Guillot, A. Guyot, *Colloid. Polym. Sci.*, **276**, 305-12 (1998).

INTEGRATED APPROACH TO MONITORING, STATE ESTIMATION AND CONTROL OF POLYMER REACTORS

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6th International Workshop on Polymer Reaction Engineering, DECHEMA Monographien, Vol. 134, 567-576, 1998, Wiley-VCH, Berlin.

An integrated approach to polymer reaction engineering combines the use of (as precise as necessary) kinetic models, models for the prediction and the control of polymer properties (e.g. T_g), the elaboration of hardware and software sensors, the use of non-linear state estimators for the interpretation of data from said sensors, and finally easily tunable non-linear controllers for the optimal and safe operation of reactors that produce polymer of a pre-specified quality. We will present results of on-line estimation of both copolymer composition and kinetic parameters in semi-batch emulsion and solution polymerisation, using the rate of polymerisation measured by reaction calorimetry. In addition to information related directly to the composition of the copolymer, one can also obtain on-line estimates of useful kinetic parameters.

ON-LINE MONITORING OF EMULSION COPOLYMERISATIONS USING HARDWARE SENSORS AND CALORIMETRY

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Submitted to Polymer Reaction Engineering

We have used a simplified model of emulsion polymerisation, along with an adaptive calorimetric approach and a set of non-linear state estimators to monitor the individual monomer conversions in a pilot scale polymerisation reactor for the production of methyl methacrylate/butyl acrylate/carboxylic acid polymers. The usefulness of reaction calorimetry for the monitoring of such systems is demonstrated. It is also shown that non-linear, high gain estimators can be used to monitor such systems even if they are based on simplified models that ignore polymerisation of the two principal monomers in the aqueous phase, and of the carboxylic acid. The advantages and disadvantages of several different types of on-line sensors for use in industrial situations are also reviewed.

It has been shown that the combined use of well-tested hardware sensors and robust process observation techniques can be used to provide accurate estimates of the evolution of copolymer composition under on-line conditions. The accuracy of the estimation of the evolution of the individual conversions was tested in laboratory conditions and found to be excellent. This shows it is possible to neglect the contribution of water phase polymerisation when dealing with only small amounts of hydrosoluble monomers. A more precise examination of this subject will be treated in a forthcoming article.

Finally, the use of an on-line energy balance, even if it is not required for monitoring the evolution of the composition has been shown to provide interesting information about the polymerisation process. It is probably therefore judicious to use it in whenever possible, especially given the very low cost factor associated with this type of analysis.

Encapsulation of Inorganic Particles by Dispersion Polymerization in Polar Media

2. Effect of Silica Size and Concentration on the Morphology of Silica-Polystyrene Composite Particles

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Following a previous work (Bourgeat-Lami, E., and Lang, J., *J. Colloid Interface Sci.* 197, 293 (1998)), encapsulation of silica beads has been achieved by dispersion polymerization of styrene in an aqueous ethanol medium using poly(*N*-vinyl pyrrolidone) as stabilizer. Silica beads, prepared according to the Stöber method, were coated prior to polymerization, by grafting 3-(trimethoxysilyl)propyl methacrylate (MPS) on their surface. A great number of silica beads per composite particle was previously found using silica beads with a diameter comprised between 49 and 120 nm. In the present work, bigger silica particles, with a diameter between 191 nm and 629 nm, are investigated. We demonstrate by TEM that only a few number of silica beads is then contained in the composite particles. By counting the composite particles containing precisely zero, one, two, three, four, and more than four silica beads, it appears clearly that encapsulation of only one silica bead can be obtained by simply increasing the size of the silica beads. Under our experimental conditions, the optimal silica diameter giving rise to composite particles containing only one silica bead turns out to be around 450 nm. We show that when increasing the silica beads size above this value the number of composite particles without silica beads increases, whereas when decreasing the silica beads size, the number of composite particles with two, three, four or more than four silica beads increases. In addition to the above variations in composition of the composite particles, changes in particles shapes were also observed as a function of the size of the silica beads and the styrene concentration in the polymerization medium. Hypothesis concerning all these variations are presented.

LIVING RADICAL POLYMERIZATION IN EMULSION

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As radical polymerization necessitates much less restricting conditions than other types of polymerizations and as it is employed for a wide range of monomers, there has been a strong impetus to design strategies allowing to control it. Up to now, different processes have been employed. One of the pioneer work, developed by Rizzardo *et al.*, consists in moderating the free radical reactivity by reversible termination with a nitroxide (Figure 1).[1] This discovery has stirred a lot of interest, as shown by the ever growing number of reports about this novel polymerization.[1] We, and others have recently disclosed that is is possible to control polymerization in emulsion using this technology.[2] Soon after, it was realized that it is possible to tune the reactivity of a free radical via the mediation of organometallic

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compounds (Figure 1). The use of organometallic compounds has appeared to be an attractive strategy,[3] since it allows a greater tunability of the adduct formed by the metal and the free radical, but it can create some compatibility issues with reaction media such as water.

We report here the development of an original organometallic based emulsion system that allows control for the polymerization of acrylics, methacrylics and styrene monomers. Emulsion polymerizations have allowed to synthesize lattices made of block copolymers such as styrene-butyl acrylate.

We were also able to synthesize similar lattices using the reversible transfer route (Figure 1, 3rd method). In this case, the initiator is a thiobenzyl glycolic acid that is water soluble. We were succesful in synthesizing lattices consituted of triblocks such as styrene-butylacrylate-acrylic acid copolymers.

Both systems as well as the physical properties will be described here.

$$IM_n^\circ + T \rightleftharpoons IM_nT$$

$$IM_n^\circ + MeX \rightleftharpoons IM_n^+ + Me^-X \rightleftharpoons IM_nX + Me$$

$$IM_n^\circ + IM_mX \rightleftharpoons IM_m^\circ + IM_nX$$

Figure 1: Methods for controlling radical polymerization. The first method is based on reversible trapping of a growing radical IM_n by a radical (SFRP). The second method consists in a transfer reaction betwween a growing radical IM_n and a metal halogen MeX to give a reduced metal moiety and a halogen capped dormant chain (ATRP). There can be non stoechiometry between the metal species (catalyst) and the halogen compound (initiator). The third method is a reversible transfer between a growing chain and a chain transfer agent terminated chain (RAFT).[4]

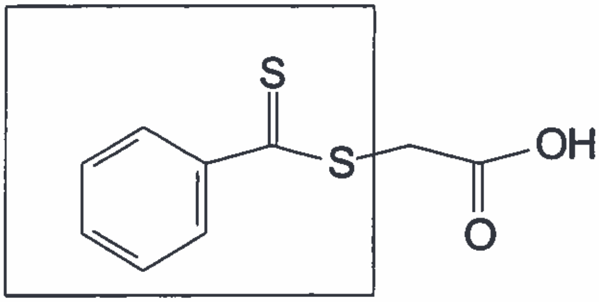

Figure 2: Thiobenzyl glycloic acid used for emulsion RAFT systems. The transferrable group is the $PhCS_2$ moiety. All chains are terminated by the CH_2COOH moiety.

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LIVING RADICAL POLYMERIZATION IN EMULSION

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More and more frequently, novel catalysts compatible with water or polar functionnalities are disclosed in open literature. For exemple, in ring-opening metathesis polymerization, ruthenium based catalysts allow the catalytic ring opening of an olefin in the presence of water (Figure1). It is possible to vary the solubility of the catalyst by changing the nature of the phosphine attached to it : water soluble, surface active or hydrophobic phosphines are evaluated to allow the synthesis in emulsion polymerization of metathesis polymers such as polynorbornene, or 1,4-polybutadiene.

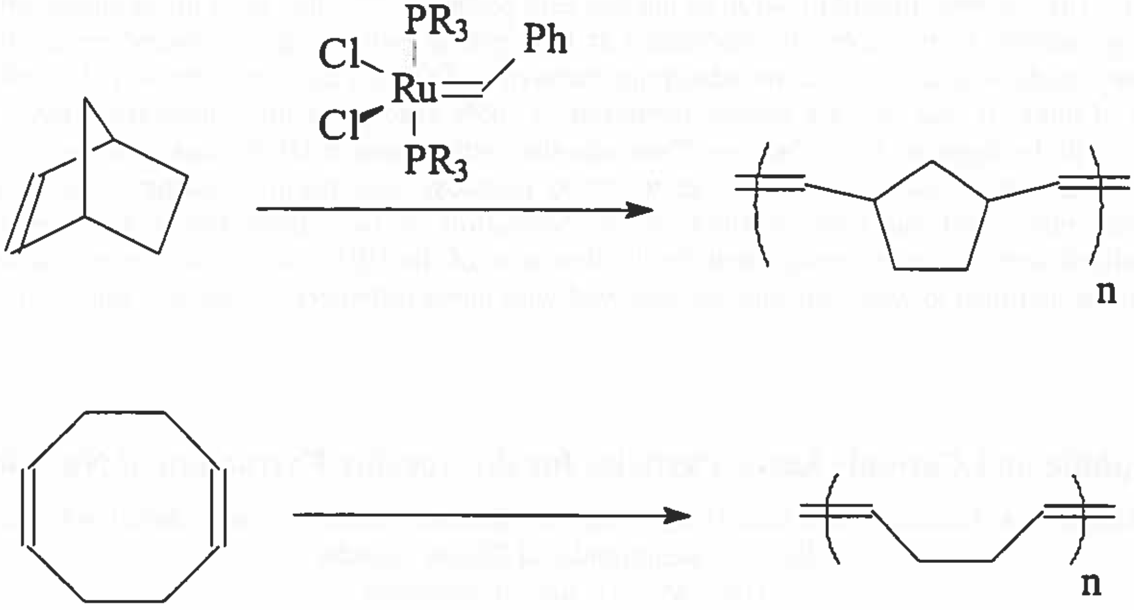

Figure 1 Ring-opening metathesis polymerization of norbornene and cyclooctadiene (to give polybutadiene-1,4).

Similarly, polyacetylene lattices are produced by the catalytic polymerization of alkynes.

Figure 2 Alkyne polymerizaiton in emulsion, to give polyacetylene lattices

The goal of this study is two fold :

- implementing new processes to old chemistry. Most ROMP polymers are produced by bulk or solution processes. For dicylcopentadiene, RIM process is used. Emulsion polymerization could potentially compete with usual processes, because it allows to control gel formation, formation of cyclic oligomers and the extent of depolymerization.
- producing novel lattices. ROMP polymerization is often living or close from living. The production of controlled architecture particles by this technique seems more feasible than by conventionnal radical techniques.

Amino-containing Cationic Latex-Oligodeoxyribonucleotide Conjugates : Application to Diagnostic test Sensitivity Enhancement

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Abstract : The covalent immobilization of nucleic acid probes (ODN) has been investigated onto amino-containing cationic hydrophobic (polystyrene) or hydrophilic poly[N-ispropoylacrylamide] latexes. A preliminary study was devoted to the adsorption behavior of ODN's as a function of pH, ionic strength and type of latex. It was found a drastic reduction of ODN adsorption upon increasing ionic strength, especially with hydrophilic-based latexes. Then, covalent attachment of ODN's onto the reactive particles was performed in a basic pH (>9) so as to avoid physical adsorption. Coating of the ODN-latex conjugates onto solid surfaces resulted in the formation of two dimensional assemblies. These functionalized surfaces were finally used for the detection of the HBV virus DNA, providing sensitivity improvement identical to what was already observed with linear polymers. (in press, Colloid and Surfaces A)

Hydrophilic and Cationic Latex Particles for the Specific Extraction of Nucleic Acids

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Bernard Mandrand and Claude Mabilat
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Abstract : The adsorption of BSA and RNA onto hydrophilic and thermosensitive poly[N-isopropylacrylamide] latex particles was described as a function of pH, ionic strength and temperature. The hydrogel poly[NIPAM] latex was synthesized by precipitation polymerization in the presence of a cationic amino-containing monomer. The latex obtained was characterized in terms of particle size, and electrophoretic mobility as a function of pertinent variables : pH, temperature and ionic strength. The adsorption of BSA onto the latex was investigated to identify the conditions at which the adsorbed amount of BSA was negligible. The adsorption of RNA was studied to establish the conditions which give rise to maximal adsorption of RNA. In order to favor the adsorption of RNA, desorption was investigated by changing the pH, ionic strength and temperature. The adsorption of BSA was found to be lower at 20°C than at 40°C. However, the adsorption of RNA is drastically affected by the pH and the ionic strength of the medium. Maximal adsorbed amounts were obtained at acidic pH, 20°C and low ionic strength. The adsorption is shown to decrease when the pH, temperature and ionic strength increase, implying that the adsorption was mainly governed by electrostatic interactions. Maximal release of RNA molecules was obtained at high ionic strength and basic pH. (in press. *Journal of Biomaterials Science, Polymer Edition*)

Hydrophilic magnetic polymer latexes :
1. Adsorption of ionic ferrofluids onto various particle seeds.

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Unité Mixte CNRS-bioMérieux

Abstract : With a view to preparing monosized hydrophilic functional magnetic latex particles based on a two-step strategy using anionic ferrofluids and cationic polymer latexes, the adsorption step was systematically investigated for a better control of the subsequent encapsulation step. The iron oxide nanoparticles were first obtained according to the classical precipitation method of ferric and ferrous chloride salt using a concentrated sodium hydroxide solution, whereas the polystyrene (PS), poly(styrene/N-isopropylacrylamide (NIPAM)) core-shell and poly(NIPAM) latexes were produced via emulsion and precipitation polymerizations, respectively. The polymer and inorganic colloids were then characterized. The adsorption of ferrofluid nanoparticles onto the three types of polymer latexes via electrostatic interaction was studied as a function of iron oxide particles concentration, charge density and the cross-linking density of the hydrophilic layer. The maximal adsorbed amounts of magnetic nanoparticles onto the various latexes were found to increase in the following order : polystyrene<poly(S/NIPAM)<poly(NIPAM). This significant difference has been discussed by taking into account the charge distribution in the hydrogel layer and diffusion phenomena inside the cross-linked hydrophilic shell. (*submitted to Colloid Polymer Science*)

Hydrophilic magnetic polymer latexes :
2. Encapsulation of adsorbed iron oxide nanoparticles.

Abstract : The encapsulation of seed polymer particles coated by anionic iron oxide nanoparticles has been investigated using N-isopropylacrylamide (NIPAM) as a main monomer, N,N-methylene bisacrylamide (MBA) as a crosslinking agent, itaconic acid (IA) as a functional monomer and potassium persulfate (KPS) as anionic initiator. The obtained magnetic latexes have been characterized with regards to particle size, iron oxide content and electrophoretic mobility. All of these properties have been examined upon varying several polymerization parameters : reaction medium, monomer(s) and crosslinking agent concentrations, nature of seed latexes and type of polymerization (batch vs shot process). Results showed that polymerization took place at the heterogeneous seed surface and provided hydrophilic, magnetic and monodisperse polymer particles. Magnetic content in the polymer microspheres strongly depends on polymerization procedure and varies between 6 and 23 weight percent. Partial iron oxide release during encapsulation and most particularly upon storage was found to occur. (*submitted to Colloid Polymer Science*).

Covalent immobilization of polythymidylic acid onto amine-containing polystyrene latex particles.

François Ganachaud, Abdelhamid Elaissari, Christian Pichot
Unité Mixte CNRS-bioMérieux

Abstract : The covalent grafting of a 35 base poly(thymidylic) acid (dT_{35}) onto aminated polystyrene latex has been studied. The oligonucleotide was first activated by 1,4-phenylene diisothiocyanate (DITC) before being bound onto the latex surface. Covalent binding reactions were performed as a function of various experimental conditions related either to the medium conditions (pH, ionic strength), or to the latex (charge type, surface charge density, adsorption of a surfactant). The discrimination between covalent binding and physical adsorption was determined by inducing complete desorption of the non-covalently grafted oligonucleotide using basic buffer, high ionic strength and a nonionic surfactant (Triton X-405). The amount of covalently grafted oligonucleotide could be directly correlated to the affinity between oligonucleotides and the latex particle surface. (*Submitted to Journal of Biomaterials Science, Polymer Edition*).

Cross-linked Poly(N-isopropylmethacrylamide) particles :
2- Colloidal Characterization

David Duracher, Abdelhamid Elaïssari, Christian Pichot
Unité Mixte CNRS-bioMérieux

Abstract : This article describes the colloidal and physico-chemical characterization of the prepared poly(N-isopropylmethacrylamide) (poly[NIPMAM]) latexes as reported in our first paper by *D. Duracher, et al in J. Polym. Sc. Polym. Chem. Ed. 1998*. The latex particles were first characterized by determining the lowest critical solubility temperature (LCST) using the turbidity method by measuring the optical density (OD) variation as a function of temperature. In addition, all latexes were characterized by measuring the electrophoretic mobility as a function of pH and temperature. Finally, the colloidal stability was examined by determining the Critical Coagulation Concentration (CCC) and the Critical Flocculation Temperature (CFT) and the corresponding results were discussed by taking into account the effect of both salinity and temperature on the solvency of poly[NIPMAM]. (*Submitted to Polymer Journal*).

Phase transfer of poly(ε -caprolactone) and poly(l,l-lactide)microspheres and their characterization

M. Gadzinowski[1], S. Slomkowski[1], Abdelhamid Elaïssari[2], Christian Pichot[2]
[1] Centre of Molecular and Macromolecular Studies Polisha Academy of Sciences, Lodz Poland)
[2] Unité Mixte CNRS-bioMérieux

Abstract : A method suitable for transfer of poly(-caprolactone) and poly(L,L-lactide) microspheres, synthesized by pseudoanionic dispersion polymerization of _-caprolactone and L,L-lactide in heptane-1,4-dioxane mixed solvent, from heptane to water was developed. This method consists of treatment of microspheres with KOH-ethanol in presence of surfactant. Three surfactants: nonionic (Triton X-405), anionic (sodium dodecyl sulfate (SDS)), and zwitterionic (ammonium sulfobetaine-2) were used in the studies. Partial hydrolysis of macromolecules of polyesters results in formation of hydroxyl and carboxyl groups in the surface layer of microspheres and enhances their stability in water based media. Minimal concentrations of surfactants, needed to obtain stable suspensions of particles, were equal $3\cdot10^{-2}$, $6\cdot10^{-2}$, $3\cdot10^{-2}$ mol/l for Triton X-405, SDS and sulfobetaine-2 respectively. In the case of poly(ε-caprolactone) microspheres suspensions in water were stable for all three surfactants for pH from 3 to 11. Suspensions of poly(L,L-lactide) were stable in the same region of pH only for SDS. Surface charge density determined by electrophoretic mobility varied for poly(ε-caprolactone) microspheres from $2.6\cdot10^{-7}$ mol/m^2 to $8.9\cdot10^{-7}$ mol/m^2, for particles stabilized with Triton X-405 and ammonium sulfobetaine-2, respectively. In the case of poly(L,L-lactide) microspheres surface charge density varied in the region from $3.9\cdot10^{-7}$ mol/m^2 (stabilizer: Triton X-405) to $7.4\cdot10^{-7}$ mol/m^2 (stabilizer: ammonium sulfobetaine-2). Carboxylic groups in the surface layer of poly(L,L-lactide) microspheres were used for covalent immobilization of 6-aminoquinoline, a fluorophore with amino group. Maximal surface concentration of immobilized 6-aminoquinoline was equal $1.9\cdot10^{-6}$ mol/m^2. For poly(ε-caprolactone) in microspheres molecular mass and molecular mass polydispersity parameter were initially equal $M_n = 40\ 800$, $M_w/M_n = 1.43$ whereas after treatment with KOH-ethanol-surfactant, leading to partial hydrolysis of this polyester, $M_n = 8\ 300$ and $M_w/M_n = 1.70$. For poly(L,L-lactide) microspheres treatment with KOH-ethanol-surfactant mixture changed molecular mass and molecular mass distribution of polymer constituting particles from $M_n = 38\ 000$ and $M_w/M_n = 1.12$ to $M_n = 19\ 300$ and $M_w/M_n = 1.53$.

Preparation of amino-functionalized core-shell latex particles for the covalent binding of peptides.

C. Lorenzo[1], T. Delair, A. Elaïssari[2], C. Pichot[2]
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Polymer latex particles are widely used as a carriers for biomolecules such as nucleic acids, antibodies, antigens, enzyme, in biomedical diagnosis. When used in the diagnosis applications as a solid phase, it was evidenced that using hydrophobic latex particles led to undesirable phenomena such as denaturation of the immobilized biomolecules (i.e. antigens and antibodies). One alternative route is to control the latex surface properties (i.e. as charge density and hydrophilic character) of the prepared support by the polymerization process. This can be ensured by combining both emulsion and precipitation polymerization of styrene and N-isopropylacrylamide (NIPAM) respectively. Then, the obtained latex particles exhibit a core (PS)-shell (P (NIPAM)) structure.
The purpose of this study is to report on the synthesis and characterization of such core-shell latexes bearing various amounts of surface amine groups. The particle size was controlled by the amount of NIPAM monomer in the polymerization recipe. The functionalization was performed by adding a given amount of aminopropylmethacrylamide hydrochloride (APM), NIPAM and methylenebisacrylamide (MBA). The surface yield incorporation of the functional monomer is examined through various analytical methods and the total conversion was determined by taken into account the water soluble polymer. The final latexes particles were characterized in terms of size distribution, electrokinetic properties, colloidal stability etc. The covalent binding of peptides is currently investigated after activation step of latex particles or using a reactive bifunctional spacer.

Fonctionalization of lipid cationic emulsions and grafting of a fusogenic peptide : application in oligonucleotide encapsulation

T. Trimaille, A. Schnoerringer, C. Chaix, T. Delair, C. Pichot in collaboration with H. Texeira,
C. Dubernet, P. Couvreur (Faculty of Pharmacy, University Paris VI)

This is new research area of the group based on our experience in the covalent grafting of biologically active macromolecules onto polymer particles. It was initiated through the frame of a interdisciplinary collaboration research, named"Oligonucleotide antisense targetting", especially with a leading group having a long term expertise in the design and application of polymer-based synthetic vectors for therapeutic purposes. The aim of the research is to conceive submicron capsules containing oligonucleotide antisense and also bearing fusogenic peptides (enable to destabilize the endosomal membran under acidic pH), a strategy which artificially mimicks the role of a virus.

In this context, the main objective of our group is :

i) to induce the precipitation of a reactive polymer (poly[maleic anhydride-alt-methyl vinyl ether) at the interface of submicron cationic emulsions ;

ii) to further chemically graft a 20-residues fusogenic peptide.

Work is currently devoted on the modification of the reactive polymer so as to import appropriate HLB properties favoring both the precipitation step and the stabilization of the functionalized cationic emulsions. Resulting nanocapsules are characterized with respect to particle size and distribution (by photon correlation spectroscopy) and surface charges (by electrophoretic mobility).

Synthesis and characterization of functionalized poly(N-ethylmethacrylamide) thermosensitive latex particles

P. Hazot, T. Delair, A. Elaïssari, C. Pichot
Unité Mixte CNRS-bioMérieux

The aim of this new research work is to prepare thermosensitive polymer particles functionalized with phenyl boronic acid. Boronic acids are well known to form complexes (esters) with diols and this property will be used to modify the surface properties of silica plane supports. In addition to the increase in the available specific surface area of such functionalized surfaces, the thermosensitive character of the polymer particles should allow to also monitor the HLB properties. In order to get thermal sensitive particles, exhibiting a relatively high phase transition temperature, N-ethylmethacrylamide (NEMAM) was selected as a main monomer. Current studies are performed on the radical-initiated precicipation polymerization of NEMAN, using ethylene glycol dimethacrylate (EGDMA) as crosslinking agent, N-phenyl boronic acid methacrylamide as functional monomer and postassium perfulfate as initiator. Latex particles are characterized with respect to particle size and distribution, water-soluble polymer formation and LCST.

<u>RECENT PUBLISHED PAPERS</u> (Unité Mixte CNRS-bioMérieux)

Surface characterization of amine-containing latexes by charge titration and contact angle measurements
F. Ganachaud, B. Boulai, L. Véron, P. Lantéri, A. Elaïsari, C. Pichot
Colloids and Surfaces A, 137, 141-154 (1998)
Atomic Force Microscopy as a Quantitative Technique : Correlation between Network Model Approach and Experimental Study
Perrin, A. Elaïssari, A. Theretz, A. Chapot
Colloids and Surfaces B, 11, 103-112 (1998)
Effect of Charge Nature on the Adsorption of Single-Stranded DNA Fragments onto Latex particles
A. Elaïssari, J.P. Chauvet., M.A. Halle, O. Decavallas, C. Pichot, Ph. Cros
Journal of Colloid and Interface Science, 202 (1998)
Surface functionalization of polystyrene nanoparticles with liposaccharidic monomers : preparation, characterization and applications
Charreyre M.T., Revilla J., Elaïssari A., Pichot C., Gallot B.
Journal of Bioactive and Compatible Polymers (in press)
Synthesis and Characterization of Surface-cyanofunctionalized poly(N-isopropylacrylamide) latex
Zhou G., Elaïssari A., Delair Th., Pichot C.
Colloid & Polymer Science 276, 1131-1139 (1998)
Cationic amino-containing N-isopropylacrylamide-styrene copolymer particles : 2-surface and colloidal characteristics
Duracher D., Sauzedde F., Elaïssari A., Pichot C., Nabzar L.
Polymer Colloid Science, 276, N°10, 920-929 (1998)
Cationic amino-containing N-isopropylacrylamide-styrene copolymer particles : Electrokinetic and colloidal stability
Nabzar L., Duracher D., Elaïssari A., Chauvetaux G., Pichot C.
Langmuir, 14, 5062-5069 (1998)
Acid-Base Approach to Latex Particles Containing Specific Groups Based on Wettability Measurements "

Journal of Colloid and Interface Science, 208, 81-89 (1998)

Bouali B., Ganachaud F., Chapel J.P., Pichot C., Lanteri P.

Contribution to the International Polymer Colloids Group Newsletter

Gérard RIESS

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During 1998, 5 PhD students working in our group on block copolymers and colloidal systems submitted their thesis.

J.F. STUMBE synthesized ω dihydroxy polystyrenes by controlled free radical polymerization of styrene in the presence of thioglycerine. ω dihydroxy functionalized PS of M_n between 1000-2000 could be obtained with excellent yield. They can be used as precursors for the preparation of PS-PEO block copolymers.

F. VANRENTERGHEM has developed a series of functionalized latexes which can be crosslinked by flash-curing.

P. HOERNER has examined the micellization of Pbut-PEO, hydrogenated Pbut-PEO and poly(t butylstyrene) – PEO block copolymers.

Ph. PETER was interested in the controlled agglomeration process of PS and PVC latexes by using PS-PEO or PMMA-PEO block copolymers (in micellar form or as hairy latexes of small particle size). Monomodal or bimodal distributions could be obtained with adjustable size in the range of 1-40 µm. The morphology and the porosity of the agglomerated particles were examined in connection with their application possibilities in PVC plastisols.

Y. SULLY has studied the emulsion polymerization of styrene, MMA and BA, as well as the copolymerization of these monomers by using PMMA-PEO block copolymers as emulsifiers. These systems were also examined in mini-emulsion polymerization.

Polyesters from lactides and ε-caprolactone. Dispersion polymerization versus polymerization in solution.

S.Slomkowski, S.Sosnowski, M.Gadzinowski

Polymer Degradation and Stability, 59, 153-160 (1998)

Abstract

Polymerizations of lactides and caprolactone, carried out in 1,4-dioxane:heptane mixtures in a presence of poly(dodecyl acrylate)-*g*-poly(ε-caprolactone) surface active agent, yield polymers in form of microspheres. Polymerizations are initiated in solution. Shortly after initiation particles are nucleated and the main part of propagation proceeds in heterogeneous systems which consist of growing microspheres suspended in the 1,4-dioxane-heptane-monomer media. These dispersion polymerizations differ in many aspects from the corresponding polymerizations in solution. Suspensions of microspheres are significantly less viscous than polymer solutions with the same polymer content. For example, viscosity of suspension of polylactide microspheres (microsphere diameters $\overline{D}_n = 2.7$ μm) in heptane is 14 times lower than that of the THF solution of the same polylactide (polymer content in suspension and in solution 5 wt%). High local concentrations of active centers and monomers inside of microspheres result in fast polymerization. For polymerizations of caprolactone in dispersed systems a given degree of monomer conversion is achieved from ten to twenty times earlier than for the corresponding polymerizations in solution. Dispersion polymerizations yield polylactides and poly(caprolactone) with $1.05 < \overline{M}_w / \overline{M}_n < 1.29$. Polylactide and poly(ε-caprolactone) microspheres with a high values of monodispersity parameter ($\zeta = \overline{D}_n / (\overline{D}_w - \overline{D}_n) > 10$) are obtained in polymerizations carried out in presence of surface active agent with a ratio of molecular weight of poly(ε-caprolactone) grafts and molecular weight of poly(dodecyl acrylate)-*g*-poly(caprolactone) copolymer close to 0.23. The microspheres can be isolated from suspension by gravitational sedimentation. Depending on the post-synthesis treatment it is possible to obtain poly(L,L-lactide) microspheres with controlled degree of crystallinity.

Mechanism of particle formation and kinetics of the dispersion polymerization of cyclic esters

S.Slomkowski, M.Gadzinowski, S.Sosnowski

Macromol. Symp., 132, 451-462 (1998)

Abstract: Pseudoanionic and anionic polymerizations of ε-caprolactone and lactides in 1,4-dioxane:heptane mixtures containing poly(dodecyl acrylate)-*g*-poly(ε-caprolactone) yield polyesters in form of microspheres. Monitoring partition of active centers between solution and microspheres revealed that particles are formed during initial period, when macromolecules reach their critical masses (ca 1 000) and became insoluble. Then, propagation proceeds inside of microspheres into which monomer diffuses from solution. Monitoring of variation of the number of particles in a unit volume of reaction mixture with time indicated that after a primary nucleation the delayed nucleation and aggregation are absent. In effect, microspheres with narrow diameter distribution are obtained. Kinetic measurements revealed that in the dispersion pseudoanionic (initiator $(CH_3CH_2)_2AlOCH_2CH_3$) and anionic (initiator $(CH_3)_3SiONa$) polymerizations of ε-caprolactone the overall rates of monomer conversion are from 10 to 30 times higher than for the corresponding polymerizations in solution (THF solvent). Analysis of kinetic equations indicated that the observed faster monomer conversions in polymerizations in dispersed systems are due to the high local concentrations of active centers and monomer in growing microspheres.

Diameters and Diameter Distributions of Poly(L,L-lactide) Microspheres by Ring-Opening Polymerization of L,L-Lactide and from Earlier Synthesized Polymers

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Center of Molecular and Macromolecular Studies, Polish Academy of Sciences,
Sienkiewicza 112, 90-363 Lodz, Poland

ACS Symp. Ser. R.M.Ottenbritte, S.W.Kim (eds)

Microspheres made of bioabsorbable polyesters are used as carriers of drugs and/or other bioactive compounds. Diameters and diameter distributions of microspheres are the most important parameters determining areas of their applications. Various methods used for preparation of microspheres yield particles in different ranges of diameters and diameter distributions. Microspheres with the most narrow diameter distribution ($<D_v/D_n> < 1.20$) and with number average diameter ($<D_n>$) in the region from 2.5 µm to 6.4 µm could be obtained either by the direct or by seeded dispersion polymerization of L,L-lactide.

Polymeric Microspheres and Related Materials for Medical Diagnostics

Stanislaw Slomkowski [1], **Beata Miksa** [1], **Dorota Kowalczyk** [1], **Teresa Basinska** [1], **Mohamed M. Chehimi** [2], **Michel Delamar** [2]

[1] Center of Molecular and Macromolecular Studies,Polish Academy of Sciences
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[2] Institut de Topologie et de Dynamique des Systémes, Université Paris 7, 1 rue Guy de la Brosse, 75005 Paris, France

ACS Symp.Ser. W.-T. Law, N.Akmal, A.M.Usmani (eds), submitted

Summary

In this paper there are described selected synthetic methods allowing to obtain polymeric microspheres with functional groups (e.g. aldehyde, carboxyl, hydroxyl, and thiol), suitable for covalent immobilization of biologically active compounds, mainly proteins. Procedures allowing to adsorb and/or covalently immobilize (in controlled manner) macromolecules of proteins, in particular human serum albumin (HSA), gamma globulins (γG), horseradish peroxidase (HRP), and glucose oxidase (GOD) onto surface of microspheres and results of evaluation of their biological activity after immobilization are described. Examples of application of microspheres with immobilized antigens and/or antibodies in aggregation tests are given. There are discussed also *dry tests* based on polymeric microspheres and methods allowing to obtain monolayers of microspheres immobilized onto solid supports, which could be used for fabrication of biosensors.

Inorganic-Organic Systems with Tailored Properties Controlled on Molecular, Macromolecular, and Microscopic Level

S.Slomkowski [1], B.Miksa [1], M.M.Chehimi [2], M.Delamar [2], E.Cabet-Deliry[2], J.P.Majoral [3]

[1]Center of Molecular and Macromolecular Studies,
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Reactive and Functional Polymers, submitted

Summary

Methods suitable for modification of quartz and glass (plates and beads) on molecular, macromolecular, and microscopic level are described in this paper. Modification led to composite materials with core containing quartz (fused silica) or glass and outer shells composed of layers of γ-aminopropyltriethoxysilane (small molecules), dendrimers with aldehyde groups and/or Starburst PAMAM dendrimers with amino groups (macromolecules), and with one particle thick assemblies of poly(styrene-divinylbenzene-acrolein) microspheres with aldehyde groups at their surface (microscopic objects). Monitoring by AFM quartz plates with immobilized dendrimers revealed that their surfaces are relatively smooth with roughness parameter R_g close to 2 nm and with diameters and maximal height of objects covering surface in form of bumps close to 4 nm, i.e. to diameters of single macromolecules of dendrimers. XPS studies of surfaces of modified quartz plates and glass beads unequivocally confirmed attachment of γ-aminopropyltriethoxysilane, dendrimers, and microspheres. Quantitative analysis revealed that dendrimer layers are 3.7 nm and 3.2 nm thick, for G5 and PAMAM dendrimers respectively. Indicating that these macromolecules form monolayer structures. XPS and SEM studies of quartz surface covered with layers of γ-aminopropyltriethoxysilane, G5 and PAMAM denrimers and subsequently with poly(styrene-divinylbenzene-acrolein) microspheres indicated that saturation of the surface coverage with these particles are achieved at the degree of coverage close to 0.60, i.e. to the maximal value attainable in the case of rapid covalent immobilization of spherical particles. Surfaces of quartz plates and glass beads, with outer layers containing G5 dendrimers and/or poly(styrene-divinylbenzene-acrolein) microspheres and thus, equipped with aldehyde groups, were used for covalent immobilization of human serum albumin (HSA). AFM studies revealed that macromolecules of HSA from dilute protein solution are attached onto surface of G5 dendrimers in such a way that they form clusters composed of not less than 50 protein

macromolecules each. X-ray photoelectron spectroscopy used for monitoring of surfaces with immobilized poly(styrene-divinylbenzene-acrolein) microspheres which subsequently were exposed to contact with solution of HSA revealed that macromolecules of HSA are readily attached onto immobilized microspheres.

Phase transfer of poly(ε-caprolactone) and poly(L,L-lactide) microspheres and their characterization

Mariusz Gadzinowski[1], Stanislaw Slomkowski[1], Abdelhamid Elaïssari[2], Christian Pichot[2]

Colloid and Polymer Science, prepared for submission

[1] Center of Molecular and Macromolecular Studies, Polish Academy of Sciences
Sienkiewicza 112 90-363 Lodz, Poland.

[2] Ecole Normale Superiéure de Lyon, Unite Mixte CNRS-bioMérieux
46 allée d'Italie 69364 Lyon Cedex 07 France.

Abstract

A method suitable for transfer of poly(ε-caprolactone) and poly(L,L-lactide) microspheres, synthesized by pseudoanionic dispersion polymerization of e-caprolactone and L,L-lactide in heptane-1,4-dioxane mixed solvent, from heptane to water was developed. This method consists of treatment of microspheres with KOH-ethanol in presence of surfactant. Three surfactants: nonionic (Triton X-405), anionic (sodium dodecyl sulfate (SDS)), and zwitterionic (ammonium sulfobetaine-2) were used in the studies. Partial hydrolysis of macromolecules of polyesters results in formation of hydroxyl and carboxyl groups in the surface layer of microspheres and enhances their stability in water based media. Minimal concentrations of surfactants, needed to obtain stable suspensions of particles, were equal $3\cdot10^{-2}$, $6\cdot10^{-2}$, $3\cdot10^{-2}$ mol/l for Triton X-405, SDS and sulfobetaine-2 respectively. In the case of poly(ε-caprolactone) microspheres suspensions in water were stable for all three surfactants for pH from 3 to 11. Suspensions of poly(L,L-lactide) were stable in the same region of pH only for SDS. Surface charge density determined by electrophoretic mobility varied for poly(ε-caprolactone) microspheres from $2.6\cdot10^{-7}$ mol/m^2 to $8.9\cdot10^{-7}$ mol/m^2, for particles stabilized with Triton X-405 and ammonium sulfobetaine-2, respectively. In the case of poly(L,L-lactide) microspheres surface charge density varied in the region from $3.9\cdot10^{-7}$ mol/m^2 (stabilizer: Triton X-405) to $7.4\cdot10^{-7}$ mol/m^2 (stabilizer: ammonium sulfobetaine-2). Carboxylic groups in the surface layer of poly(L,L-microspheres) were used for covalent immobilization of 6-aminoquinoline, a fluorophore with amino group. Maximal surface concentration of immobilized 6-aminoquinoline was equal $1.9\cdot10^{-6}$ mol/m^2. For poly((ε-caprolactone) in microspheres molecular mass and molecular mass polydispersity parameter were initially equal M_n = 41 700 M_w/M_n = 1.19 whereas after treatment with KOH-ethanol-surfactant, leading to partial hydrolysis of this polyester, M_n = 8 300 and M_w/M_n = 1.09. For poly(L,L-lactide) microspheres treatment with KOH-ethanol-surfactant mixture changed molecular mass and molecular mass distribution of polymer constituting particles from M_n = 52 800 and M_w/M_n = 1.05 to M_n = 22 200 and M_w/M_n = 1.93.

Report from the Institute of Polymeric Materials, University of Pardubice
Reporter: Jaromir Snuparek

Main activity of the group has been synthesis of binders for water-borne paints by emulsion polymerization. Acrylic monomers have been investigated predominantly. The investigation is focused on preparation of copolymers containing higher contents of functional comonomers as AA, MAA, HEMA, AAm, MAAm, on copolymerization of monomers with different polarity in semi-continuous process as well as on the particle growth. Film-forming propertiers of binders and basic properties of water-borne paints have been investigated mainly from the point of view of their corrosion protection efficiency. New types of corrosion protective pigments have been used in paint formulations. We are collaborating with group for rheology in the Institute of Macromolecular Chemistry, Academy of Sciences of the Czech Republic in Prague. The rheological behaviour of highly carboxylated copolymers and interction of associative thickeners with different copolymer particles has been studied with support by Grant Agency of the Czech Republic.

Graduate research (PhD. students) in polymer colloids and their applications

Inverse emulsion polymerization of acrylic monomers.
(D.Benda) - finished 1997

Synthesis and film-forming properties of higly carboxylated acrylic latices.
(D. Kubik)

Butyl Acrylate/Styrene/HEMA copolymer latices.
(G. Baghaffar) - finished 1998

Butyl Acrylate/Styrene/methacryl amide copolymer latices - copolymerization, particle formation, properties.
(M. Kaška)

Interaction between carboxylic groups containig latices and reactive inorganic pigments.
(P. Gřesová)

Interaction of acrylic copolymer latex particles and new coalescing aids during film-formation.
(M. Rozhon)

Recent papers

Benda D., Šňupárek J. and Čermák V. :
Inverse Suspension Polymerization of Hydrophilic Acrylic Monomers in the Static Phase.
J. Dispersion Sci. Technol. 18 (2), 115 (1997).

Benda D., Šňupárek J. and Čermák V. :
Inverse Emulsion Polymerization of Acrylamide and Salts of Acrylic Acid.
Eur. Polymer. J. 33 (8), 1345 (1997).

Kalendová A., Šňupárek J. and Kalenda P. :
Nontoxic Spinel-Type Pigments in Anticorrosive Coatings in *Symposium Series 689 - ACS Organic Coatings for Corrosion Control*, (Ed. Gordon Bierwagen), Washington, D. C. 1998, pp. 366 - 379

Quadrat, O., Mrkvičková, L., Walterová, Z.,Titkova, L., Bradna, P. and Šňupárek, J.:
Structure anf Flow behaviour of crosslinked ethyl acrylate-methacrylic acid copolymer dispersion particles
Colloid Polym. Sci. 276, 879 - 886 (1998)

Submitted papers:

Light scattering study of the effect of polymerization time on structure of dispersion particles based on ethyl acrylate-methacrylic acid copolymers.

L. Mrkvičková [a], Z. Walterová [a], O. Quadrat [a], P. Bradna [b] and J. Šňupárek [d]

[a] *Institute of Macromolecular Chemistry, Academy of Sciences of the Czech Republic, 162 06 Praque 6, Czech Republic*
[b] *Spofa-Dental Co., Černokostelecká 84, 100 30 Prague 10, Czech Republic*
[d] *Department of Polymers, University of Pardubice, 532 10 Pardubice, Czech Republic*

Abstract: Structural changes of colloid particles of ethylacrylate-methacrylic acid copolymer after addition of alkali or methanol by means of light scattering method were investigated. With increasing monomer feeding time of semicontinuous emulsion polymerization solubility of dispersion particles diminished, which was a consequence of a crosslinked structure of the constituent copolymer. At the low polymerization times or at a high content of methacrylic acid in the copolymer the particle dissolved. On the other hand, when polymerization of copolymer with lower methacrylic acid content continues to higher polymer solids, the particles are insoluble and disintegrate only to smaller subparticles or swell as a whole.

Submitted to Colloid Polym. Sci.

Thickening of acrylic latices with dispersions of crosslinked ethyl acrylate - methacrylic acid copolymers

O. Quadrat[a*], L. Mrkvickova[a], Z. Walterova[a], P. Stern[b], P. Bradna[c] and J. Snuparek[d]

[a]*Institute of Macromolecular Chemistry, Academy of Sciences of the Czech Republic, 162 06 Prague, Czech Republic*
[b]*Institute for Hydrodynamics, Academy of Sciences of the Czech republic. 166 12 Prague 6, Czech Republic*
[c]*Spofa - Dental Co., Cernokostelecka 84, 100 30 Praha 10, Czech Republic*
[d]*Department of Polymeric Materials, University of Pardubice, 532 10 Pardubice, Czech Republic*

Abstract: Thickening of three model latices of copolymers of ethylacrylate with 0 - 2 wt.% od acrylic acid with dispersions of ethylacrylate - methacrylic acid copolymer crosslinked with 0.25 - 5 wt.% of *N,N'*-methylenebisacrylamide was investigated. Measurement of the static light scattering revealed that the highest thickening effect occured when after alkalinization from the thickener a sufficient amount of highly swelled crosslinked particles arose. Viscoelastic properties of this basic matrix is a decisive factor for the rheological behaviour of thickening material.

To be submitted to Progress Org. Coatings

Effect of water-soluble crosslinker on the growth and properties of ethyl acrylate-methacrylic acid emulsion copolymer particles

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Running head: Properties of crosslinked latices
Key words: Polymer colloids, emulsion polymerization, particle growth, particle properties

Abstract: Model ethyl acrylate-methacrylic acid copolymer latices and latices of particles crosslinked by copolymerizing small amounts of water soluble *N,N'*-methylenebisacryl amide were prepared by non-seeded semicontinuous emulsion copolymerization. Dynamic and static light scattering measurements, indicated a little higher degree of polydispersity in the case of crosslinked particles, especially in initial stages of polymerization. The hydrodynamic volume of alkalinized particles controlling viscosity properties of dispersions decreased with the time of polymerization and in the case of crosslinked copolymer, at about 60 min reached virtually the constant value. The different character of the particle structure was confirmed by differences in particle disintegration after alkali addition or in the presence of methanol.

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MA. Winnik Newsletter to international polymer Colloids group, January 1999

Fusion fragmentation in nonionic Triton X-100 surfactant micelle

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Abstract: We have discovered a method for measuring the fusion-and-fragmentation rates for nonionic surfactant micelles in water. A Pyrene-labeled triglyceride **1** with negligible water solubility can be solubilized in Triton X-100 micelles in which it exhibit a Poisson distribution up to 4 molecules of **1** per micelle. When excess surfactant is added to a solution of Triton X-100 micelles containing sufficient **1** that the fluorescence spectrum is dominated by excimer emission, the monomer emission intensity grows in at the expense of excimer emission. Since **1** is insoluble in water, exchange requires fusion of two micelles followed by fragmentation. This process follows second order kinetics, from which we calculate a second order rate constant $k_{ex} = 1.15 \times 10^6\ M^{-1}s^{-1}$.

AIR PRODUCTS POLYMERS

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Contribution to the IPCG News Letter

Reporter: Helmut Zecha

This is the first contribution from a new company:
Air Products Polymers, a Joint Venture of Air Products and Wacker Chemie in the field of polymer emulsions. This company was formed on 1st October 1998.

The main fields for the German Product and Process R&D group are

- Vinyl acetate / Ethylen copolymers
- Vinyl acetate homo and copolymers
- Acrylics

Main application fields are:

- Adhesives
- Nonwoven Binders / Textile
- Paints.

This contribution summarizes some work on rheology of dispersions and for a special project regarding the vinyl acetate dispersion polymerization in supercritical carbon dioxide.

Both contributions will be presented as posters at the Symposium on Emulsion Polymers, 217th ACS Meeting, March 21-25, 1999, in Arnaheim, California.

VISCOSITY OF BIMODAL DISPERSIONS

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Introduction

Experimental studies on the shear viscosity behavior for different kinds of polymer emulsions, mainly on those with polydisperse or bimodal particle size distributions, are relevant to final emulsion application properties. Some experimental results have already been published for bimodal latexes [1-5] and other dispersions [6-8] and this study will complement the literature by checking known model approaches [9] for a quantitative description and prediction of viscosity data.

It is well known that the shear viscosity of a polymer colloid depends on hydrodynamic, Brownian and direct particle interaction, i.e. on: i) the viscosity and the properties of continuous phase, ii) the volume fraction of particles, iii) the particle sizes and iv) the thickness and the properties of the particle surface layer. The hard sphere volume of the particles may increase to an effective hydrodynamic volume for different reasons, such as: i) extended double layers at very low ionic strength, ii) swelling of particles and iii) adsorption / grafting of stabilizing agents. Experimental access to the surface layer thickness is essential for the interpretation of viscosity under shear.

A key parameter for all model equations describing the influence of particle volume concentration on viscosity is the available volume for the motion of the particles $(1-\Phi/\Phi_M)$. There is clear evidence that the maximum volume fraction (Φ_M) depends on shear with the lower and upper limits $\phi_{M,0}$ and $\phi_{M,\infty}$ if Peclet number Pe varies between $Pe \to 0$ and $Pe \to \infty$. This change of the particle arrangement is the only reason for the (small) shear thinning of monodisperse hard sphere dispersions. Little attention has been paid to the fact that the arrangement of particles does not only depend on shear but also on the volume fraction of particles itself. Increasing the concentration as well as increasing the shear rate causes the particles to change their arrangement. From published experimental studies and calculations it has been shown that the maximum packing fraction increases for increasing polydispersity of unimodal and bimodal / multimodal particle size distributions (PSD) [6,10]; this increase in Φ_M is more pronounced for multimodal PSD.

Vinyl Acetate Dispersion Polymerization in Supercritical Carbon Dioxide

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Introduction

Dispersion polymerization of vinyl monomers in liquid and supercritical carbon dioxide (SCCD) has gained much attention within the scientific community in recent years as an environmentally benign alternative to water-based emulsion and solvent-based dispersion polymerization[1]. Most of the experimental results published to date have been obtained with (meth)acrylates and styrene as monomers, whereas vinyl acetate (VAC) has been rarely used. In SCCD VAC dispersion polymerization reported in the literature, reaction runs are very lengthy, resulting in colloidally unstable particles with comparably low polymer molecular weight and low yields[2].

It has been shown that the selection of a sterically stabilizing surfactant is crucial for succesfully carrying out high-yield heterophase reactions leading to colloidally stable particles of high molecular weight polymers. These steric stabilizers are amphiphilic in that part(s) of the molecule is soluble in the solvent SCCD (these are CO_2-philic moieties) whereas the rest of the molecule is insoluble (CO_2-phobic groups) but compatible with the polymer particles. Typical CO_2-philic moieties in those molecules are siloxanes and fluorine-containing structures. In the present paper, a new siloxane-based comb-like graft copolymer stabilizer structure is described which effectively stabilizes VAC dispersion polymerization in SCCD.

During the course of VAC dispersion polymerization in SCCD, the initially homogeneous reaction mixture is transformed to a heterophase system, and this transformation is dependenct on monomer conversion, stabilizer type and volume fraction, and monomer-to-polymer-to-SCCD ratio. Based on solubility measurements which simulate the homogeneous-heterogeneous transition during the reaction, the concept of a continuously operating reactor for hetero-phase processes will be briefly discussed.

The Rheology of Aqueous Polyurethane Dispersions

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The rheological properties of aqueous polyurethane dispersions are reported from the dilute regime up to mass concentrations in excess of 40 wt %. In the dilute limit these materials show classical polyelectrolyte behavior. Particle sizes decrease with increasing ionic strength and at very low ionic strength the intrinsic viscosity passes through a minimum. Non-Newtonian behavior was observed as the concentration was increased with the development of an apparent yield stress at the highest concentration probed. Stress sweep experiments showed that deviation from the linear viscoelasticity started at strains of less than 5 % for the moderately concentrated dispersions. The Cox-Merz rule was obeyed by these dispersions only at strains in the linear viscoelastic region and at concentrations below the gel point. As the ionic strength is increased, viscosities pass through a minimum. These phenomena are discussed in terms of the interplay of particle deformability and the interplay of electrostatic and steric forces.

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NON-EQUILIBRIUM MORPHOLOGY IN LATEX PARTICLES - EFFECT OF SEED POLYMER T_G

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Earlier we had investigated the non-equilibrium morphology development in particles which were prepared with polar seed polymer particles and non-polar second stage polymer. Here we used both a high T_g, polar seed (PMMA) and separately, a low T_g, polar seed (PMA) with polystyrene (PS) as the second stage. Without surfactant present (i.e. stability achieved via charged end groups from the initiator), the equilibrium morphology for these systems is known to be close to inverted core shell. Despite this situation, it is quite simple to keep the PS at the outside of the of the particle when PMMA is used as the seed polymer. On the other hand, it is unlikely that the same condition can be achieved when the softer PMA is used as the seed polymer, unless perhaps the PMA is crosslinked. Given this set of results it has been interesting for us work with a variety of polar seed polymers having T_g's in between the extremes of the PMMA (T_g = 119°) and the PMA (T_g = 14°). This was accomplished by creating copolymer seed latices at various ratios of MMA and MA to achieve the desired T_g. Our goal was to study the influence of the seed polymer T_g under varying conditions of reaction temperature and monomer feed rates.

Experimental

Various copolymer seed latices were created using surfactant free emulsion polymerization with potassium persulfate initiator at 80° and at solids concentrations of 7-10% by weight. The MMA/MA monomer ratios were varied to produce seed polymer T_g's over the range of 52 - 98° and the second stage reaction temperatures were 50, 60 or 70°. The seed particle sizes were approximately 350 nm in diameter and the second stage reactions were carried out without the use of surfactant. In all cases the ratio of second stage polymer to seed polymer was 1:1 by weight. Styrene monomer was fed over a variety of times, from batch conditions (infinite feed rate) to feed times of longer than 9 hours. Resulting composite latices were investigated via transmission electron microscopy (TEM) of microtomed sections which had been stained with ruthenium to darken the PS phase. The seed copolymer T_g was determined by DSC and copolymer composition verified by NMR.

Analysis of Results

The morphology of the latices varied from highly occluded structures to the classic core-shell particle. All of the resulting TEM's were characterized as having one of the structures shown in Figure 1 which shows a variety of morphologies form core-shell to inverted core-shell. Type 0 is core-shell (CS), types 1 and 2 are called occluded core-shell (OCS), type 3 is occluded (OCC), type 4 is occluded inverted core-shell (OICS), and type 5 is inverted core-shell (ICS). Table 1 shows the effect of the different seed polymers on the final morphology when the reaction temperature was at 70° and the styrene was fed over a period of 4.2 hours. In each of these cases the radical flux to the particles was kept constant at $4*10^{13}$ radicals/m^2,s. As can be seen, the 52^{O} seed produced a highly occluded particle indicating that polystyrene radicals penetrated the particle deep enough to allow phase separation throughout the particle. Progressively higher seed polymer T_g's clearly appear to prevent the polystyrene from penetrating as far as do the lower T_g polymers. Of course these results apply specifically to the conditions of feed rate and temperature used in those experiments.

Table 2 lists the morphology results obtained as the feed rate of the styrene was varied. The use of all of seed polymers resulted in highly occluded particles for batch reaction conditions indicating that the reaction kinetics proceeded more quickly than phase separation and growth at these conditions. In all cases when we compare the results for a single seed polymer as the monomer feed rate is slowed, we observe the progression from highly occluded structures under batch conditions to CS when the monomer is fed over 4 to 9 hours. The lower the seed polymer T_g, the less well defined the shell for these experiments.

Table 3 shows the effect of reaction temperature for seed polymer T_g's at 52 and 88° at a monomer feed time of about 4 hours. For the lower T_g seed the effect of dropping the reaction temperature from 70 to 50° is very dramatic, changing the morphology from highly occluded to CS. Clearly the conditions that allow penetration of the polystyrene radicals within the seed particles are very different in these two situations.

The above results show that the T_g of the seed polymer can play a major role in determining the morphology of these particles. To make a general analysis one must combine all of the effects of glass points, feed rates, reaction temperature, and radical flux to appreciate the morphology results.

Figure 1

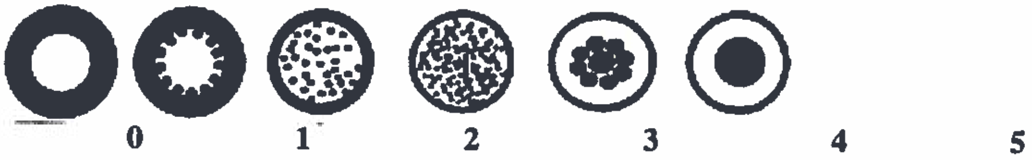

Table 1

Seed T_g	Reaction Temp.	Feed Time (hrs)	Morphology Type
98	70	4.2	CS type 0
88	70	4.2	CS type 0/1
77	70	4.2	OCS type 1/2
52	70	4.2	OCC type 3/2

Table 2

98	70	0 (batch)	OCC type 3
98	70	1.25	CS type 0/1
98	70	4.2	CS type 0
88	70	0 (batch)	OCC type 3
88	70	1.25	CS type 1
88	70	4.2	CS type 0/1
77	70	0 (batch)	OCC type 3
77	70	4.2	OCS type 1/2
77	70	9.2	OCS type 1/2

Table 3

88	70	4.2	CS type 0/1
88	60	4.2	CS type 0
52	70	4.2	OCC type 3/2
52	50	4.2	CS type 0/1

Low Resolution Raman Spectroscopy applied to on-line monitoring of mini-emulsion polymerization.

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Overview.

Raman spectroscopy has become recently a preferred technique for the on-line monitoring of dispersion polymerization[1]. Raman spectroscopy offers two specific advantages for these systems. First it is rather insensitive to the presence of water, and the total amount of water in the emulsion also has little to no influence. Secondly when combined with a visible light excitation laser it can use standard glass fiber conduits to allow use of a flexible remote sensor. We have used a low cost / low resolution Raman spectrometer (LRRS) to monitor emulsion polymerization and more particularly miniemulsion polymerization.

Raman spectrometer [2].

The instrument consists of a solid state laser emitting at 785 nm. The excitation and the Raman scattered light is collected by a glass fiber with a laser-line rejection filter. The Raman spectrum is collected by a CCD array. The spectral resolution is 30 cm^{-1}. The optical fiber probe is directly immersed into the reactor. Cleaning of the probe head is required to avoid excessive fouling and excessive loss of signal.

Experimental conditions.

A monodispersed polystyrene latex was made by semi-continuous polymerization with a particle size of 125nm, and a solid content of 28.4%. Known amounts of styrene monomer were added to the emulsion and allowed to swell for 48 hours. The resulting latices were used to establish the linear relation between conversion and peak area ratio (see interpretation and figure 2a).

Miniemulsions[3] typically involved sodium dodecyl sulfate, di-octyl sulfoccucinate and hexadecane to provide colloidal stability. Styrene and butyl acrylate were used after purification on an alumina column. The mini-emulsions were prepared by using a Branson ultrasonicator. Emulsions having 100 to 200 nm diameter were typically generated with a "solid content" up to 65%. The emulsions were placed in a jacketed reactor with either a magnetic stirrer for low volume, low viscosity samples or mechanical stirring for higher shear requirements. Sodium-persulfate was used as initiator. Polymerizations were carried out at 70°C.

Results and interpretation[4].

Figure 1 shows several spectra characteristic of the miniemulsion polymerization of styrene, 102 nm, 31.3% solid content. The vinyl stretch at 1600nm is characteristic and decreases as a function of monomer concentration. The 1000nm peack is characteristic of the "breathing" of the phenyl ring and remains fairly constant all through the polymerization. By integrating those peaks and calculating their ratio it is possible to correlate the peak ratio to the ratio of monomer over monomer plus polymer, i.e. conversion. Figure 2a plots the conversion of samples of known concentration as a function of peak area ratio. The relation was found to be linear.During the polymerization of miniemulsions, samples were taken manually for gravimetric analysis and Raman spectra were recorded at given intervals. Figure 2b shows that a fair correlation between the two methods was found. By using more complex mathematical procedures, such as common factor analysis, better correlations are found.

Conclusion.

Low resolution Raman spectroscopy is a particularly good and cost effective tool to monitor on-line the monomer conversion of both miniemulsion polymerization and conventional emulsion polymerization. We established that the method is fairly insensitive to overall solid content, presence of water and particle size. Furthermore, by using chemometrics it is possible to monitor the copolymerization of acrylics and styrenics without chromatographic separation. Some improvements need to be made with the probe to reduce fouling and loss of signal.

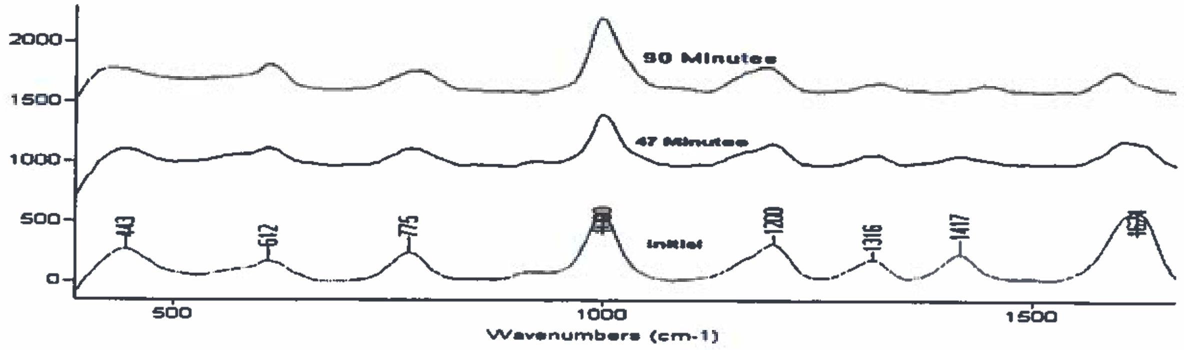

Fig. 1. Raw low resolution Raman spectra of a PS miniemulsion polymerization at various time intervals.

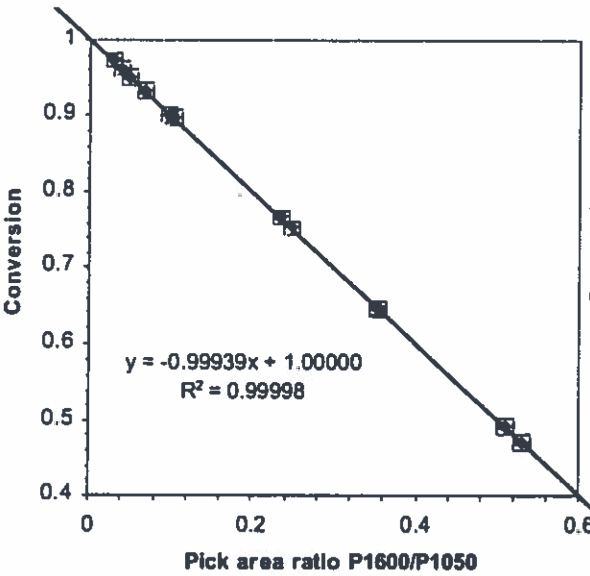

Fig. 2a. Linear relationship between pick area ratio and monomer conversion for two PS lattices.

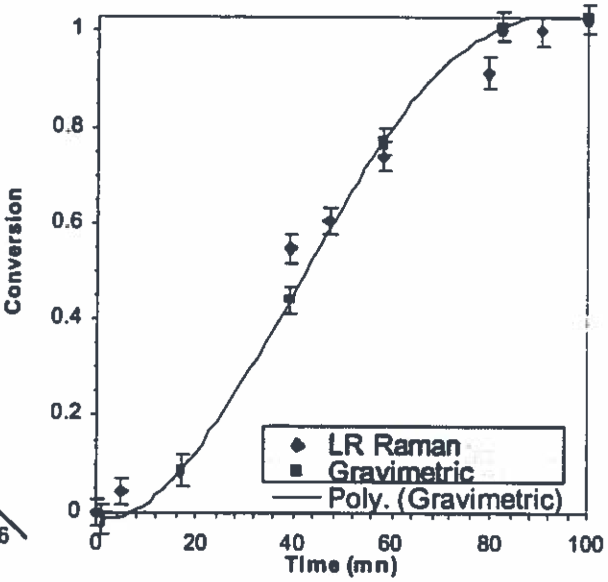

Fig. 2b. Comparison between gravimetric and on-line LRRS for a PS miniemulsion polymerization.

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Contribution to Miniemulsion Polymerization Technology

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Introduction.

Miniemulsion polymerization (mEP) is a very powerful technique to prepare dispersed polymeric system. This process is at its best in applications involving dispersing in water organic molecules with very poor water solubility. An excellent review of this field has been done recently by David Sudol and Mohamed El-Aasser[1].

Application to small particle size, high solid.

The combination of a dynamic surfactant (di-octyl sulfossucinate), a high surface activity surfactant (sodium dodecyl sulfate) and high energy sonication, can generate miniemulsions of particle size averaging 100nm. Hexadecane was used to provide great inhibition to the Oswald-ripening coalescence mechanism. Such small average particle size provides not only great shelf stability, but also provides low coagulum levels and high "droplet versus new particle" nucleation ratios. As mentioned by Miller et al.[2], renucleation is still present in mEP. Figure 1 and 2 are typical illustrations of this issue. The number of particles (diameter measured by light scattering (Nanosizer)) plotted as a function of conversion shows an initial increase of the number of particles (plus droplets) up to conversions close to 30%. Maturing of the emulsion by limited coagulation occurs during the rest of the polymerization.

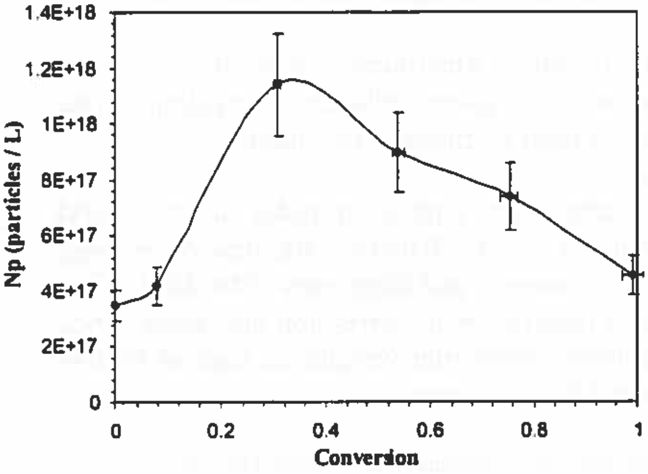

Fig. 1. Particle number as a function of convertion for PS crosslinked DVB (2 wt.%), at 40% solid content, initiated with 3mmol dm-3 NaPS at 70°C.

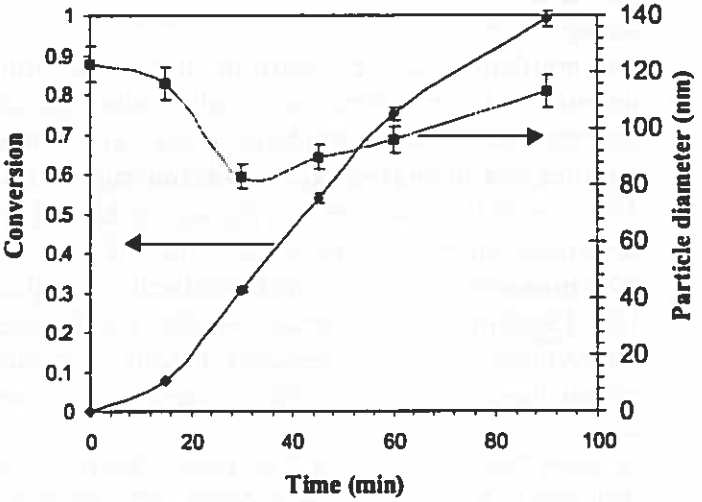

Fig. 2. Evolution of the conversion and particle size as a function of time for the same PS miniemulsion as in figure 1.

This "double" surfactant technique has allowed us to prepare mEP with solid contents up to 60%. The miniemulsion was prepared with an initial organic phase content of 65% and was characterized by a paste/cream-like viscosity. By addition of salt and water, the organic content was reduced to 60%, and the viscosity dropped to ~100cp. During polymerization at 75°C the viscosity increased significantly, but no coagulum was formed. After cooling the mEP recovered a 100cp viscosity. Consequently it is demonstrated that miniemulsions of solid contents of industrial relevance[3] can be produced in a simple batch process.

Continuous miniemulsion polymerization.

To further the demonstration of industrial relevance of the mEP process, several research laboratories have been developing continuous processes[4]. At the University of New Hampshire, a simple experimental setup has been built. It involves three rotating piston pumps, an ultrasound flow cell and a modified tubular reactor. Figure 3 outlines the principles of the setup.

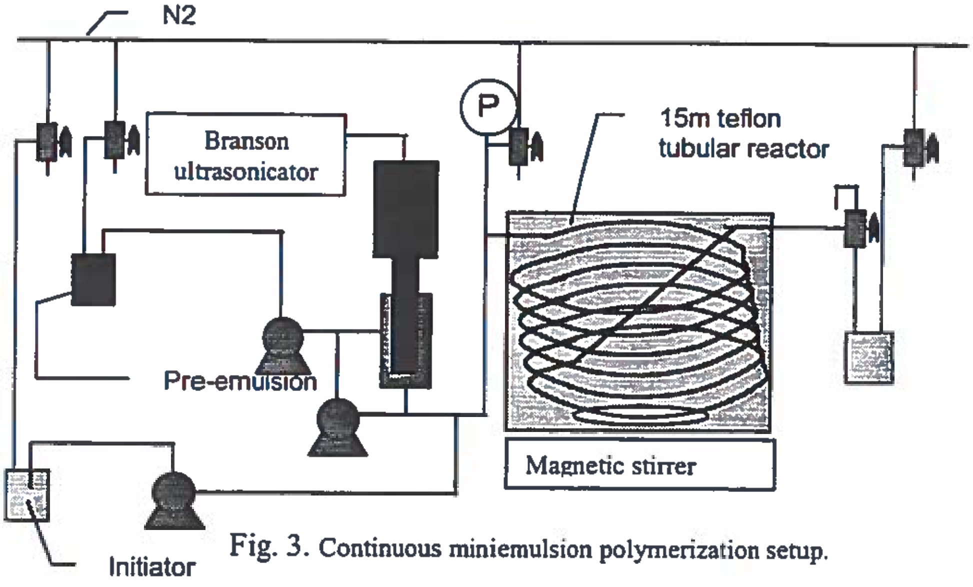

Fig. 3. Continuous miniemulsion polymerization setup.

Mixing of the aqueous initiator solution after ultrasonication was found to work best. We also found that using a "recycle" loop [illegible]und the continuous [illegible]ell of the sonic p[illegible]s critical to m[illegible]a homogeneous [illegible] miniemulsion [illegible]e of rotating pis[illegible]s allowed us [illegible]y pressurize th[illegible]or and also allo[illegible]to pump high [illegible]ity miniemulsions. Strong cooling of the flow-through cell is absolutely necessary. Optional insertion of air bubbles at regular intervals also avoided issues related to residence-time distributions. Average residence times have been varied from 15 minutes to 4 hours.

Application to controlled radical polymerization.

The use of the "double" surfactant technique in combination with a unimolar nitroxy-styryl controller allo[illegible]s to control the mEP of styrene at 130°C. Kinetics are first order with monomer con[illegible], while molecular weights are of narrow polydispersity (Mw/Mn=1.3 to 1.6). Experim[illegible]ecular weights (Mn) increased linearly with conversion and some block copolymers h[illegible]prepared directly in miniemulsion. Molecular weights as high as 80,000 g/mole have b[illegible] with conversion which reached 60% in 4hours.

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