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IPCG

INTERNATIONAL POLYMER COLLOIDS GROUP

Newsletter June 1998

IPCG Website

Bob Fitch has set up the IPCG www site, on http://www.newmex.com/IPCG_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

Fine Particle Synthesis and Characterization
 American Chemical Society, Polymer Division, Fall National ACS Meeting
 23 - 27 August, 1998, Boston, Mass.
 Contact Warren Ford, wtford@osuunx.ucc.okstate.edu

Fourth 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>

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FIRST ANNOUNCEMENT

FOURTH INTERNATIONAL SYMPOSIUM ON POLYMERS IN DISPERSED MEDIA

11 - 15 APRIL 1999 - LYON (FRANCE)

Honoring Doctor Alain Guyot

Objectives and Scope :

Following the Symposia held in Lyon in 1984, 1989 and 1994, this new Symposium would like to focus on various aspects regarding polymers in dispersed media. In the past decade, many efforts have been directed on the design and characterization of such materials from nanoscale to macroscopic dimension. Moreover, due to their outstanding and specific properties, they are increasingly developed in a broad range of applications.

Topics :

1- Polymerization in dispersed media: kinetics, mechanisms, modeling and chemical engineering of homo and co-polymerization in emulsion, microemulsion, dispersion, precipitation polymerizations, etc.

2- Non conventional dispersions of polymer : reactive solvents, sol-gel process, dendrimers, ring opening polymerization, encapsulation, etc.

3- Properties and applications of dispersed polymers: rheology, films, composites, hybrids, materials for adhesives, coatings, conductors, biology, etc.

Call for papers :

The symposium will include invited lectures (30 min), oral communications (20 min) and a poster session (4 days).

SCIENTIFIC COMMITTEE

F. CANDAU (France)	J. C. DANIEL (France)	D. I. LEE (USA)
J. P. VAIRON (France)	C. JANIN (France)	M. S. EL-AASSER (USA)
S. SLOMKOWSKI (Poland)	R. G. GILBERT (Australia)	F. PIERSON (France)
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LIST OF INVITED SPEAKERS

(the following speakers have already accepted to present a lecture)

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J. P. PASCAULT (France)	S. SLOMKOWSKI (Poland)
J. Y. CAVAILLE (France)	K. TAUER (Germany)
S. OMI (Japan)	A. VAN HERK (The Netherlands)
D. CHARMOT (France)	C. WU (P.R.China)
R. WILLIAMS (Argentine)	M. A. WINNIK (Canada)
P. COUVREUR (France)	J.M. DESIMONE (USA)
M. OKUBO (Japan)	P. A. LOVELL (UK)
H. KAWAGUCHI (Japan)	W.B. RUSSEL (USA)
R. ALEXANDER-KATZ (Mexico)	

SECOND CIRCULAR

The second circular will appear by September 1998 and will contain a preliminary program including the main presentations as well as information on Meeting location, registration and accommodation. The number of participants is limited and the second circular will be only sent to those who notified us their interest. So, please return the Reply Form before July 31th 1998.

PUBLICATION

Selected papers and main lectures will be published by Macromolecular Chemistry and Physics as a Macromolecular Symposia issue.
Fourth International Symposium on :
"Polymers in Dispersed Media"
April 11 - 15, 1999
Lyon (France)

Reply to First Circular

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oral: yes no

poster: yes no

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International Workshop

Particles and Surfaces: Fundamentals, Techniques and Applications

March 13-16, 1999

Oud Poelgeest, near Leiden, The Netherlands

Organization:

G. J. M. Koper (Leiden University, The Netherlands),
M. Borkovec (Clarkson University, USA)

Confirmed Speakers and Discussion Leaders

- Z. Adamczyk (Polish Academy of Sciences, Krakow)
- G. Benedek (Massachusetts Institute of Technology, Cambridge, USA)
- W. Ducker (Virginia Institute of Technology, Blacksburg, Virginia, USA)
- J. Earnshaw (University of Belfast, Belfast, UK)
- M. Elimelech (University of California, Los Angeles, California, USA)
- D. Frenkel (Inst. of Atom. and Molec. Physics, Amsterdam, The Netherlands)
- P. G. de Gennes (College de France, Paris, France)
- D. Grier (University of Chicago, Chicago, Illinois, USA)
- D. Horn (BASF, Ludwigshafen, Germany)
- J. Israelachvili (University of Santa Barbara, Santa Barbara, USA)
- R. Kjellander (Goteborg University, Goteborg, Sweden)
- R. Klein (University of Konstanz, Konstanz, Germany)
- C.G. de Kruif (Institute for Dairy Research, Ede, The Netherlands)
- H. Lekkerkerker (University of Utrecht, Utrecht, The Netherlands)
- G. Maret (University of Konstanz, Konstanz, Germany)
- E. Matijevic (Clarkson University, Potsdam, USA)
- H. Mizes (Xerox Corporation, Webster, New York, USA)
- H. Reiss (University of Los Angeles, Los Angeles, USA)
- J. Ricka (University of Berne, Berne, Switzerland)
- P. Schaaf (Institute Charles Sadron, Strasbourg, France),
- P. Schurtenberger (Swiss Fed. Inst. of Technology, Zurich, Switzerland)
- T. van de Ven (Pulp and Paper Research Center, Montreal, Canada)
- D. Weitz (University of Pennsylvania, Philadelphia, USA)
- H. Wennerstrom (University of Lund, Lund, Sweden)

Focus and Scope

The workshop focuses on interaction and aggregation of colloidal particles in bulk suspensions and at interfaces. The aim is to bridge between fundamental colloid science and actual applications. The workshop will communicate our current understanding of equilibrium and dynamic effects in such systems, the role of electrostatic, dispersion and depletion interactions, and irreversible formation of clusters, gels and particle deposits on surfaces. These fundamental issues will be challenged by problems encountered in actual biological and industrial applications.

Program

Registration starts in the afternoon of Saturday March 13, 1999 and the workshop closes in the afternoon of Tuesday March 16, 1999. The four days program will consist of 18 invited lectures given by experts in the field, discussions and extended poster sessions. Poster presentations are strongly encouraged.

Registration

The costs for participation at the workshop are NLG 1,200.- (approx. US \$ 600). These costs include conference fee, full board for the entire workshop and printed lecture notes.

Registration will proceed on a first-come first-served basis, and becomes effective with the receipt of the full payment. The registration is transferable and can be canceled until December 15, 1997. Thereby, the full registration fee will be reimbursed. The registration deadline is January 15. Please, register early, however. We already had an excellent response and expect to be booked out rather soon. The total number of participants (including speakers and discussion leaders) is limited to about 90.

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The role of polymeric surface in hydrodynamic stability of emulsifier-free acrylate latexes.

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The hydrodynamic stability of emulsifier-free latexes of acrylates differed in water solubility has been studied in view of dependance of their coagulation upon dynamics of taking latex particles together [1].

If aggregative stability of particles is connected with the ratio of electrostatic, structural and molecular forces of their interaction, so hydrodynamic stability depends upon hydrodynamic behaviour of liquid between the particles surface. In other words, the condition of unreversible coagulation of colloidal particles in view of the Theory of DLVO when they are taken together very slowly corresponds to the maximum value of potential energy of particles interaction equal to zero.

As followed from [2] the high relative rates of taking particles together are possible under dispersion agitation. The rates of two particles can be differed 100 cm/c when the distance between them are 50 micrometer.

The emulsifier-free acrylate latexes of meth- and butylacrylate significantly differed in water were synthesized. The zeta-potential of latexes was measured by using Ottewill method. The coefficient of structural forces was calculated by using experimental data on latex coagulum formed during polymerization, radius and concentration of particles according to the equations derived in [3]. The hydrodynamic stability is studied by using Maron method under rate gradient 146 [1/ s] and distance between two surfaces 6,5 cm. The gradient corresponds to critical rate of coagulation estimated in [1] and equal to the value more than 1000 cm/s.

The potential barrier was calculated in view of the modern theory of DLVO by using traditional equations of electrostatic, structural and molecular components of energy.

The kinetic energy of interaction of two particles when the distance between them is only one particle radius was calculated by taking into account the hydrodynamic conditions and dispersion properties.

According to the results of measurement the radius of pMA and pBA equals to 120 nm in both cases, zeta-potential increases from 56 to 75 mv and coefficient of structural forces also increases from $12 \cdot 10^{-6}$ to $62 \cdot 10^{-6}$ erg for pBA in comparison with pMA. The coefficient increase correlates to increasing the water contact angles of polymers: it changes from 18 to 89 grad.

The higher concentration of hydrodynamic coagulum of pBA latex was observed than pMA. It increases from 4 to 9%. The hydrodynamic stability of particles correlates to hydrophilic-hydrophobic properties of polymers. It increases with increasing the polymer hydrophilicity.

The maximum value of potential energy of particles interaction of pBA and pMA calculated equals to $3 \cdot 10^{-13}$ to the -13 th power and $5 \cdot 10^{-13}$ erg respectively. The main part in the total potential energy is added by electrostatic and structural components. The higher value of energy in case of pMA is achieved even at smaller value of zeta-potential of particles surface.

The kinetic energy of interaction of two particles when the distance between them is a particle radius equals to about $0.03 \cdot 10^{-13}$ erg. The lower value of kinetic energy in comparison with potential barrier indicates that hydrodynamic effect used in the study can cause only some decrease of particles stability. It is demonstrated by the coagulum concentration observed.

There was a trouble to estimate correctly hydrodynamic effect on stability of particles differed in polymer hydrophilicity because of the low value of kinetic energy calculated. In this connection the effect of kinetic energy on potential barrier was estimated in view of the study [4]. According to it particles repulsion should decrease the rate of slow coagulation at W times. This rate is proportional to $\exp(U/kT)$, where U - potential barrier, k - Boltzmann constant, T - absolute temperature. The decrease in potential barrier causes the decrease in W and increase in the coagulation rate. The maximum coagulation rate when potential barrier equals to zero corresponds the condition $W=1$. By taking into account hydrodynamic effect the coagulation factor W was calculated. The value of $\log W$ is proportional to 0.85 and 1.07 for pBA and pMA respectively. From these values followed that the coagulation factor is high in both cases, indicating at the high potential barrier of particles interaction. The value of decrease a risk of particles coagulation under hydrodynamic effect.

The process of rapid coagulation of particles when every collision is accompanied with their coalescence was described by a straight line dependence of concentration of particles and aggregation upon time [4]. The angle of its slope characterizes duration of coagulation of half the quantity of particles. This time of particles coagulation in aqueous phase at room temperature is inversely proportional to initial concentration of particles and aggregates in volume unit C_p . It varies with proportion 2.10 to the $1/\ln$ power to C_p . Taking into account latex concentration, particles radius and polymeric density, the duration of coagulation of half the quantity of particles was calculated. It equals to 3,23 and 3,45 s for pBA and pMA respectively. The duration of rapid coagulation increases with increasing polymeric hydrophilicity. This correlates to the data on slow coagulation when the coagulation factor characterized particles stability also increases with increasing polymer hydrophilicity.

Thus the consideration of hydrodynamic stability of emulsifier-free acrylate latexes in view of potential barrier of particles interaction and dependence of their coagulation upon dynamics of taking them together permits to estimate the effect of polymeric surface on coagulum formation.

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INTERNATIONAL POLYMER COLLOIDS GROUP NEWSLETTER

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Reported by José M. Asua

1998

EFFECT OF THE OXYGEN ON THE EMULSION POLYMERIZATION KINETICS. A STUDY BY REACTION CALORIMETRY

Lourdes López de Arbina, Luis M. Gugliotta, María J. Barandiaran and José M. Asua

ABSTRACT

The influence of the oxygen on the kinetics of chemically initiated seeded emulsion homopolymerization of styrene and the seeded emulsion copolymerization of styrene/butyl acrylate was investigated by reaction calorimetry. It has been observed a decrease on the inhibition period and an increase on the polymerization rate when the system is purged with nitrogen. It has also seen that the oxygen has a great influence on the polymerization kinetics, producing not only inhibition, but also decreasing the reaction rate. An increase of the dependence of the average number of radicals per particle with the initiator concentration with respect to theoretical predictions was observed in presence of oxygen. The overall experimental results show that after an inhibition period there is a continuous flow of oxygen from the gas phase, which causes the retardation on the polymerization rate.

KINETICS OF THE DISPERSION COPOLYMERIZATION OF STYRENE AND BUTYL ACRYLATE

José M. Sáenz and José M. Asua

ABSTRACT

The kinetics of the dispersion copolymerization of styrene and butyl acrylate in an ethanol-water medium was investigated in a batch stirred glass reactor. The effect of

the presence of oxygen, agitation, stabilizer concentration, ethanol/water ratio, styrene/butyl acrylate ratio, temperature, and initiator concentration on the particle size distributions, conversion-time curves and molecular weight distributions was investigated. It was found that the polymerization started in the continuous medium and, depending on the process conditions, the main polymerization locus shifted to the polymer particles. A consequence was that the more pronounced the shift the higher was PI. The shift was more marked when the size of the particles were small and when the solubility of the copolymer chains in the continuous medium was low. This solubility was the key factor in the process as it also affected substantially the particle size.

MATHEMATICAL MODELLING OF THE DISPERSION COPOLYMERIZATION OF STYRENE AND BUTYL ACRYLATE

José M. Sáenz and José M. Asua

ABSTRACT

A mathematical model for the prediction of particle growth and molecular weight distribution in dispersion copolymerization was developed. The model was validated by fitting conversion evolutions and molecular weight distributions in the dispersion copolymerization of styrene and butyl acrylate in an ethanol-water medium. It was found that the model provided good fitting of the experimental data under many conditions, but cases were found where the model could not fit the molecular weight distribution. Reasons for the lack of fitting were discussed.

MONODISPERSE POLYSTYRENE LATEX PARTICLES REACTIVE SURFACTANTS IN HETEROPHASE POLYMERIZATION XI.- PARTICLE NUCLEATION

Javier I. Amalvy , María J. Unzué, Harold A.S. Schoonbrood and José M. Asua

ABSTRACT.

The nucleation process in the emulsion polymerizations of styrene, methyl methacrylate and vinyl acetate stabilized by sodium dodecyl sulfopropyl maleate, a polymerizable surfactant (surfmer), was investigated. A nonpolymerizable surfactant, sodium dodecyl sulfate (SDS), was used as a reference. It was found that the presence of the surfmer did not affect the nucleation mechanism (micellar for styrene and homogeneous for MMA and VAc). The type of surfactant did not affect the dependence of the number of particles upon surfactant concentration for styrene, but the dependence for the surfmer was lower than that for SDS in the cases of MMA and VAc. This was interpreted in terms of formation of water-soluble oligomers that do not participate in the stabilization of the polymer particles.

Reactive Surfactants in Heterophase Polymerization

José M. Asua

Harold A.S. Schoonbrood

This work reviews the publications concerning the use of polymerizable surfactants (surfmers) in heterophase polymerization in terms of the mechanisms relevant during the process. The goal was to gain some insight about these mechanisms and to help the reader on the way in trying to find a suitable surfmer and to apply it in an appropriate way for a specific polymerization system.

MONODISPERSE POLYSTYRENE LATEX PARTICLES FUNCTIONALIZED BY THE MACROMONOMER TECHNIQUE

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ABSTRACT

Monodisperse core-shell latex particles functionalized with surface groups that were introduced by the macromonomer technique were obtained by means of a two-step emulsion polymerization process in a batch reactor at 70°C. In the first step the cores were synthesized by means of a batch emulsion polymerization of styrene (St), and in

the second step, the shells were formed by batch emulsion copolymerizations of St and different macromonomers using the seeds obtained previously. Macromonomers were synthesized by anionic « living » polymerization. They are constituted of a poly(ethylene oxide) hydrophilic block and a hydrophobic block or sequence end-fitted with an unsaturation. The latexes were characterized by gravimetry, transmission electron microscopy (TEM) and conductimetric titrations to obtain the conversion, the particle size distribution (PSD) and the surface charge density (ζ), respectively. The colloidal stability of the cores and final latexes were determined by measuring the critical coagulation concentration (CCC) at two pHs (7 and 2) using KBr as electrolyte. The surface charges of the latexes were moderately low, with corresponding moderately low CCCs. The presence of spacers, confirmed with disk centrifuge photosedimentometer (DCP) and photon correlation spectrophotometer (PCS), did not increase the CCC. During the CCC measurements, at high electrolyte concentrations, the reduced solubility of the spacer PEO moiety in the solution resulted in its collapse on the particle surface.

MOLECULAR WEIGHT DISTRIBUTION CONTROL IN EMULSION POLYMERIZATION

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

ABSTRACT

Emulsion polymers with well defined molecular weight distributions (MWD) were obtained by using a control strategy based on on-line measurements of both unreacted monomer and chain transfer agent (CTA). The control strategy includes a nonlinear model based controller that calculates the feed rates of monomer and CTA needed to obtain the desired MWD. This requires a mathematical model for the MWD that was developed based on independent measurements. The control strategy was assessed by computer simulation and experimentally verified by producing polymers with widely different MWDs in the styrene emulsion polymerization using CCl_4 as chain transfer agent.

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

Emulsion polymerization and copolymerization of allyl methacrylate

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Abstract

The emulsion polymerizations and copolymerizations of allyl methacrylate (AMA) or ethylene dimethacrylate (EDMA) with methyl methacrylate (MMA) or propyl methacrylate (PMA) were studied. Polymerizations or copolymerizations show two distinct non-stationary rate intervals with the maximum rate at medium conversion. The maximum rate of emulsion polymerization of AMA is proportional to 0.73 and 0.28 power of potassium peroxydisulfate (KPS) and sodium dodecylsulfate (SDS) concentrations, respectively. The particle size continued to increase with conversion up to a high conversion and the increase was more pronounced at low conversion. The similar particle size evolution for the polymerizations and copolymerizations of AMA and EDMA indicates the dominant role of agglomeration. The non-uniform particle morphology and the presence of reactive pendant groups promote the agglomeration of microgels between themselves and with the large particles carrying the reactive pendant groups. The number of particles is proportional to 0.54 and 0.67 powers of KPS and SDS concentrations, respectively. The promoted particle formation results from the decreased particle growth due to which the residence time of monomer-swollen micelles increases. The polymerization accompanied by crosslinking mainly occurs at the particle surface because of the restricted penetration of radicals and monomer into crosslinked particles.

Introduction

Reactive microgels are intramolecularly crosslinked macromolecules of submicron sizes. They can be prepared by the radical polymerization and copolymerization of multivinyl monomers. A drawback of these microgels is their colloidal instability due to the pendant double bonds at the surface, which may react easily with each other to form large aggregates. Stability of these microspheres increases in the presence of emulsifier. It is expected that the formation of microgels influences, by a complex way, the mechanism of emulsion polymerization.

In the conventional emulsion polymerizations; the micellar mechanism [1] and the homogeneous nucleation [2,3] may, in principle, be operating separately or simultaneously. The particle size and number are controlled by varying the initiator, emulsifier and monomer concentrations, temperature and ratio water/monomer, etc. In the emulsion crosslinking polymerization the relative contribution of micellar mechanism or homogeneous nucleation to the particle formation can be different; it depends on the weight

ratio crosslinker/comonomer, the monomer droplet size, the solubility of monomer in water, and the emulsifier concentration. Besides, the particle size control in such systems is very complex and remains an area of scientific interest. Information on the locus of initiation and particle formation is a necessary prerequisite for the understanding of the reaction mechanism of emulsion crosslinking polymerization.

The present article deals with the kinetics of the emulsion polymerization and copolymerization of AMA or EDMA and MMA or PMA accompanied by crosslinking, especially focusing our attention on the reaction mechanism of particle formation and growth.

Experimental

Methyl methacrylate (MMA), propyl methacrylate (PMA), ethylene dimethacrylate (EDMA), and allyl methacrylate (AMA), commercially available reagents, were purified by conventional methods and then, subjected to vacuum distillation under nitrogen. Potassium peroxydisulfate (KPS), sodium dodecyl sulfate (SDS) were used as commercially available, extra pure reagents. Twice-distilled water was employed as a polymerization medium.

Emulsion polymerizations were carried out in an ampoule at 50 °C according to the following recipe: monomer 10 g, water 90 g, SDS 1.3 g and KPS 0.03 g - if it is not stated otherwise. Ultrasonification was applied to provide the fine monomer emulsion. The polymerization technique was the same as that described earlier [4-6].

Results and Discussion

The conversion-time curves of emulsion polymerization of AMA initiated by KPS took on a sigmoidal shape typical for the emulsion polymerization, and the final conversion reached very close to 100% conversion. The dependence of the rate versus conversion was described by a curve with a maximum at ca. 50% conversion for runs with $[KPS] = 1.24$ and $6.18 \times 10^{-3} \text{ mol.dm}^{-3}$, respectively. This dependence shows two non-stationary rate regions which deviate from the classical micellar model and resemble the mini- or microemulsion polymerization. The increase in the rate was discussed in terms of the increase of the particle number (reactive crosslinked polymer microspheres) and also the decrease was in terms of the decrease of monomer concentration at the reaction loci. In the runs with the lowest KPS concentration ($0.247 \times 10^{-3} \text{ mol.dm}^{-3}$) the stationary rate interval was observed in the conversion range 20 - 50%.

From the slopes the linear relationships - the logarithmic plots of the maximum rate versus KPS concentration - the reaction orders were estimated to be 0.73 and 0.40 for AMA and PMA polymerization, respectively, the latter being in conformity with the micellar model [1]. From kinetic point of view of solution polymerization, the former exponent 0.73 suggests the deviation from an ordinary bimolecular termination to a unimolecular one as a reflection of the immobilization of growing polymer radicals in the crosslinked polymer matrix. The low swellability of crosslinked polymer particles or low monomer concentration within the particle core results in the shift of reaction loci into the particle surface. The pseudo - bulky kinetics is assumed to be operative in the particle surface layer as a result of the high radical concentration. The strong increase of R_p with KPS concentration is assumed to result from the decreased termination and the high particle (microgel) formation rate, as well. The exponents γ of 0.28 and 0.57 for AMA and PMA polymerizations ($R_p \propto [SDS]^\gamma$) deviate from the micellar model and deviation is much more pronounced with AMA. We may consider a rather high exponent of 0.6 or above by considering the strong interaction of SDS with the hydrophobic PAMA matrix and the chain transfer to AMA monomer. The low value 0.28 reflects the low

activity of SDS in the particle nucleation and stabilization. This may result from the fact that main growth events proceed during the formation of microgels with a slight interaction with SDS molecules. Besides, the crosslinked non-uniform microgels and particles disfavour the strong interaction with SDS.

The maximum rate ($R_{p,max} \cdot 10^5 \text{ mol.dm}^{-3} \cdot \text{s}^{-1}$) of polymerization became slow by the change to more facile crosslinking system in the following series:

$$R_{p,max} \times 10^5 / (\text{mol.dm}^{-3} \cdot \text{s}^{-1}): 118(\text{MMA}) > 48 (\text{AMA/MMA:10/90}) > 17.5(\text{AMA}) > 12 (\text{AMA/EDMA:95/5}) > 1.6 (\text{EDMA})$$

where the values in brackets denote the molar ratios. The strong decrease in the rate of polymerization of MMA by the addition of a small amount of AMA as crosslinker results from the decrease of a monomer concentration at the reaction loci due to the crosslinking or due to the shift of reaction loci to the particle surface. Besides, the entrapping of radicals and immobilization of monomer in the polymer network and the increased particle agglomeration also promote the decrease in the rate.

The low water solubility of AMA would disfavour the formation of surface active oligomer growing radicals able to enter the negatively charged micelles. The similar behaviour is also expected with EDMA, although the formation of crosslinked growing radicals will be enhanced as compared to AMA. The presence of microgel-like polymer at the particle surface or the high local viscosity will decrease the penetration of radicals into the particle interior and so, reduce the range of the reaction loci.

The final particle size decreased with increasing KPS and SDS concentrations, while the reversed dependencies were observed for the number of particles ($N_p \propto [\text{KPS}]^{0.54}$ and $[\text{SDS}]^{0.67}$). These data indicate that crosslinking promotes the particle nucleation and the formation of larger number of particles. The decreased particle or chain growth due to crosslinking increases the residence time of monomer swollen micelles in the reaction system. The particle size was observed to increase with conversion and the most remarkable increase was observed at low conversion range:

$$\text{AMA; } D \text{ (nm) vs. (conversion/\%): } 30 \text{ nm (5\% conv.)} < 45 \text{ (20)} < 60 \text{ (50)} < 65 \text{ (95)}$$

The similar particle time evolution was observed in the emulsion polymerization of EDMA and copolymerization of AMA or EDMA with MMA. This is attributed to a low colloidal stability of small particles and a dominant role of agglomeration on the particle growth. The agglomeration is very operative due to the presence of reactive pendant double bonds in the particle shell and non-spherical particle surface. The particle collisions lead to the irreversible agglomeration and generation of larger particles.

The number of polymer particles increased with increasing conversion and the most remarkable increase was observed at a low conversion. This finding indicates that the particle nucleation proceeds during the whole polymerization. The high concentration of SDS, the long residence time of monomer swollen micelles due to the depressed particle growth, the precipitation of microgel-like particles from the continuous phase and the release of the emulsifier from the large crosslinked particles as a reflection of particle shrinkage caused by the progress of crosslinking promote the nucleation of new

particles during the polymerization. Besides, the presence of non-uniform particles and their restricted interaction with SDS shift the equilibrium bound/free to free SDS molecules.

Conclusions

A common feature of the emulsion polymerization and copolymerization of AMA was the long rise to a maximum rate of polymerization with the two rate intervals. The polymer particles are formed through the precipitation of crosslinked oligomer radicals and followed interactions with monomer and emulsifier. The growth of polymer particles proceeds mainly by the agglomeration of non-uniform polymer particles with reactive double bonds. The suppressed penetration of radicals into the particle interior and the reduced swellability of crosslinked particles promote the polymerization at the particle surface. The depressed particle growth, the high concentration of emulsifier and the long residence time of monomer swollen micelles promote the nucleation events during the whole polymerization.

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Surfactant Co-thickening in Associative Polymer Solutions

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ABSTRACT: Associative thickeners act to thicken aqueous systems through the formation of non-specific hydrophobe associations. The formation of these "pseudomicellar" units is driven by the exclusion of the thickener hydrophobes from the aqueous phase by water. The associative strength and/or duration of hydrophobic clustering is governed by the chemical potential of the hydrophobes, which in-turn is related to the relative size, volume fraction and solubility of the hydrophobes in the continuous phase. The greater the relative size, volume fraction or insolubility of the hydrophobe in the continuous phase, the greater is the viscosity development as well as the shear-thinning character of the associative polymer solutions.

The formation of hydrophobic clusters can be greatly enhanced by the presence of the appropriate type and concentration of nonionic surfactant which will result in a dramatic increase in solution viscosity, commonly referred to as surfactant co-thickening. The selection of an "appropriate" surfactant is dictated by the solubility of the surfactant in the system which is, in turn, controlled by temperature, the nature of the surfactant hydrophobe, the degree of ethoxylation and the presence of co-solvents. Surfactant co-thickening is observed with surfactants of varying water-solubility. For water-miscible surfactants the maximum viscosity enhancement is observed at surfactant concentrations corresponding to approximately ten times the surfactant's critical micelle concentration. With water-dispersible surfactants however, much greater viscosity enhancement is possible with the maximum viscosity enhancement being obtained at concentrations an order magnitude greater than with water-miscible surfactants.

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reported by **Françoise CANDAU**

The following are summaries of progress in several research areas of our group.

Adsorption of hydrophobically associating polyacrylamides on clay.

(E. Volpert, J. Selb, F. Candau, N. Green, J.F. Argillier, A. Audibert, *Langmuir*, in press).

We have studied the solution properties and the adsorption behavior on alumino silicate surfaces of hydrophobically modified polyacrylamides synthesized by micellar copolymerization. This method allows one to prepare compositionally homogeneous polymer samples by an appropriate choice of the hydrophobic comonomer. The hydrophobic moieties associate in aqueous solution by hydrophobic interactions which increase the viscosity and lead to particular rheological properties. The strength of the hydrophobic associations depends on the structure of the hydrophobic comonomer and its distribution. Hydrophobic comonomers with a bulky structure lead to particularly strong thickening properties.

In the case of homopolyacrylamide, a classical high affinity adsorption isotherm is found with a plateau at relatively low concentration. The hydrophobic modification of the polymer with dihexylacrylamide comonomer enhances considerably its affinity to the silicate surface. In addition, the adsorbed amount increases continuously with concentration, this effect being particularly pronounced for copolymers of high molecular weights. Copolymers that show no associative properties in solution, i.e. no viscosity increase induced by intermolecular hydrophobic interactions, have an adsorption behavior similar to copolymers exhibiting strong thickening properties.

NMR measurements have revealed the crucial role of water molecules and/or hydrated cations adsorbed at the surface for the adsorption mechanism. The adsorption of the hydrophobically modified polyacrylamide results in significant replacement of the water layer at the clay surface. This is an indication of an entropy driven process. Force measurements have given experimental evidence that the adsorption proceeds in a large part by direct interaction of the hydrophobe with the silicate. This causes a change in the conformation of the adsorbed layer due to stronger surface/polymer interactions. Intra- and intermolecular interactions in the polymer layer have also an influence on the layer structure. The adsorbed layer has presumably a higher chain density than that formed by the homopolymer. This high polymer concentration in the adsorbed layer will favor hydrophobic interactions even for weakly associative polymers. The continuously increasing adsorbed amount is

due to chain reorganization in the adsorbed layer and to the formation of multiple layer adsorption through hydrophobic associations, i.e. adsorbed polymer chains that are not directly in contact with the surface.

Synthesis and characterization of new hydrocarbon and fluorocarbon polymerizable surfactants.

(K. Stähler, J. Selb, P. Barthelemy, B. Pucci, F. Candau, *Langmuir*, in press).

A series of novel polymerizable hydrocarbon and fluorocarbon cationic surfactants (*N*-alkoxycarboxymethyl,*N*-[2-(*N*'-alkylacrylamido)ethyl],*N,N*-dimethyl ammonium bromide) potentially useful for the formation of multicompartement polymeric micelles were prepared. Micellization and surface active properties of these surfactants and of their mixtures were determined using electrical conductivity and surface tension measurements. The interaction between the fluorocarbon and the hydrocarbon surfactants in the aqueous micellar state can be described by the regular solution theory with an interaction parameter $\beta=1.25$ indicating the formation of one type of mixed micelles. The solubilization capacity of the pure and of the mixed surfactant systems for pyrene and for a new fluorocarbon azo dye were studied by UV absorption as a function of the surfactant concentration. It was found that the ability to solubilize these hydrophobic compounds depends strongly on the nature of the micellar core (hydrocarbon, fluorocarbon or mixed), the polarity of the dye, the micellar shape and the composition of the surfactant mixture.

Predicting the Effectiveness of Chain Transfer Agents in Emulsion Polymerizations

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In free-radical polymerizations, the cumulative and pseudoinstantaneous molecular weight distributions (MWDs) of a polymer contain the complete history of the chain stopping events that are responsible for polymer formation. In emulsion polymerizations, these chain stopping events include termination due to radical entry, transfer to monomer, chain transfer agent (CTA) or polymer, and bimolecular termination of polymer chains. Predicting MWDs in emulsion polymerization systems that contain added CTAs is complicated due to the partitioning behaviour of the CTA between the droplet and particle phases. Emulsion polymerizations that employ CTAs with very low water solubility, such as 1-dodecanethiol, can have non-equilibrium concentrations of CTAs in the growing polymer particles. This non-equilibrium concentration of CTA leads to difficulties in predicting the MWD of a polymer system. The ability to accurately infer MWDs from available on-line measurements, such as GC (gas chromatography) analysis of monomer and CTA concentrations, would be a valuable tool in monitoring industrial processes. This requires knowledge of the CTA and monomer concentrations in the polymer particles and of the polymerization conditions (e.g. zero-one or pseudobulk).

Through the analysis of pseudoinstantaneous MWDs, the relative effectiveness of a chain transfer agent, 1-dodecanethiol, is being studied in the seeded emulsion polymerization of styrene under zero-one and pseudobulk conditions. Samples are analyzed by GC to measure the total dodecanethiol concentration in the reaction mixture. Pseudoinstantaneous MWDs are obtained by taking samples over short conversion intervals and subtracting the subsequent cumulative MWDs after normalizing the GPC trace with respect to peak area and conversion. Based on models that have been developed to predict instantaneous MWDs for zero-one and pseudobulk systems [1], it is then possible to infer the concentration of chain transfer agent within the polymer particles during a short conversion interval, thereby enabling us to relate the dodecanethiol concentration in the particles to its overall concentration in the reactor. We are interested in then determining the feasibility of using only GC measurements to accurately infer instantaneous molecular weight distributions during an emulsion polymerization.

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Modelling Morphology and Molecular Weight Distribution Development in Emulsion Polymerization

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A mathematical model examining the morphology and molecular weight distribution development of styrene is being developed. The primary aim of the model is to study the existence of radial gradients in the polymer particles with respect to monomer concentration, radical concentration, and most importantly, molecular weight distribution and morphological development. While there have been reports which examined monomer and/or radical gradients in emulsion polymerizations [1,2], no previous modelling attempt has examined these effects on both the molecular weight distribution and morphological development. The model is initially being developed for seeded homopolymerization. The longer term objective is to extend it to copolymerization and possibly multicomponent polymerizations.

The parameters for all reactions, propagation, termination and transfer, are chain-length-dependent and all incorporate a diffusion controlled aspect via the Smoluchowski equation. In developing chain-length-dependent kinetics for this model three groups of radicals were used. "Tiny" radicals are the smallest length of radical in the model and are defined as those radicals entering the polymer particle and those capable of desorption and diffusion. "Short" radicals are those which are too long to desorb but are still small enough to undergo Fickian diffusion. Long radicals are those which are too long to undergo Fickian diffusion. This treatment of the kinetic parameters leads to a large number of kinetic parameters since there are three propagation rate constants, three rate constants for each type of transfer reaction and six modes of bimolecular termination resulting in six rate constants for each form of termination reaction.

The approach taken in developing the model uses ordinary differential equations to account for reaction and diffusion within the particles. The initial monomer swollen seed particles are divided into equal volume shells on which the ODEs are based. Each shell has an equation for the reaction and diffusion of species within that shell as well as a balance on volume to account for shell growth or shrinkage. The species of interest in the model are monomer, swelling agent, chain transfer agent, tiny radicals, short radicals, long radicals, monomer converted into polymer, dead tiny radicals and dead short radicals. There are also overall all mass balances on species of interest such as monomer, chain transfer agent and swelling agent. Since the polymerizing particle is divided into separate shells and each shell may or may not grow or shrink at the same rate each shell also has its own set of

kinetic and transport parameters. Solubility parameters are used as the basis for determining the interactions between the polymer particle, monomer droplets and the aqueous phase during interval II.

Two sets of code are used to model a complete polymerization. One set of code uses $10 \times (\text{number of shells}) + 7$ ODEs and $35 \times (\text{number of shells}) + 7$ parameters to model interval II. The results from this first set of code are used as the initial conditions for a second set of code that models interval III. The code used in interval III consists of $10 \times (\text{number of shells}) + 10$ ODEs and $35 \times (\text{number of shells})$ parameters. The equations used in both sets of code are generated using Maple and are exported as FORTRAN 77 code. The numerical integrator LSODE used in Microsoft PowerStation solves the FORTRAN 77 code. The model is now in its final stages of being debugged. Model predictions are being compared with experimental data from the literature for seeded styrene homopolymerization.

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Light Scattering Study of Diblock Copolymers in Supercritical Carbon Dioxide: CO₂ Density-Induced Micellization Transition

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The behavior of polymeric surfactant polyvinyl acetate (PVAc)-*b*-poly(1,1,2,2-tetrahydroperfluorooctyl acrylate) (PTAN) in supercritical carbon dioxide (CO₂) was investigated using static and dynamic light scattering. We observed three regions on the phase diagram of copolymer in supercritical CO₂: (i) a two-phase region at low CO₂ density; (ii) solutions of spherical micelles at intermediate CO₂ densities; (iii) solutions of unimers (individual copolymer chains) at high CO₂ densities. The aggregation number (the number of copolymer chains in a micelle) decreases with increasing density of supercritical CO₂ in region (ii). An increase of the CO₂ density corresponds to the improvement of solvent quality for both blocks of the copolymer (PVAc and PTAN). The hydrodynamic radius of micelles and unimers was measured using dynamic light scattering in regions (ii) and (iii), respectively. This light scattering study is the first to report a solvent density-induced transition between spherical micelles at lower supercritical CO₂ density and unimers at higher CO₂ density. The light scattering technique appears to be a very powerful tool for the analysis of the carbon dioxide density-induced micellization transition. This phenomenon is unique to supercritical fluids and demonstrates a convenient control over the polymer solubility.

Synthesis of Core-Shell Materials in CO₂ by Dispersion Polymerization

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The current project builds upon previous successes with dispersion polymerizations in CO₂ in the DeSimone group. Previously, dispersion polymerizations of both styrene and methyl methacrylate in supercritical CO₂ produced stable latexes of high molecular weight polymers. Following careful removal of CO₂ from the reactor, dry powders consisting of sub-micron sized spherical particles of polystyrene (PS) or poly(methyl methacrylate) (PMMA) were removed. Particle size and particle size distribution were manipulated by varying reaction

pressure, surfactant type, and surfactant concentration.

Core-shell materials consisting of PMMA and poly(acrylic acid) (PMMA/PAA) have been synthesized in liquid CO₂ by dispersion polymerization previously in the DeSimone group. In core-shell synthesis, the second stage monomer is added to a stable latex of the first polymer. It was observed by transmission electron microscopy (TEM) that varying the rate of addition of the second monomer, acrylic acid, resulted in several different chemical architectures, or distributions of the two polymers throughout the particles. These architectures included PAA-rich domains in the PMMA particles, core-shell, inverted core-shell, and concentric shells. In one instance, three different chemical architectures were present in one sample. It is desirable to exclusively produce one architecture in each sample. Furthermore, at moderate conversions, the latexes became unstable due to insolubility of the surfactant in liquid CO₂ as the monomer concentration was decreasing.

Current research has focused on the synthesis of core-shell materials in supercritical CO₂ to avoid the issue of latex instability. The monomer pair studied was styrene and methyl methacrylate since the homopolymerizations yield stable latexes at high conversion. The targeted mol % PS/mol % PMMA was varied, the rate of second stage monomer (MMA) addition was varied, and the order of monomer addition was reversed.

These core-shell materials were characterized. The ¹H NMR analysis indicated the relative amounts of PS and PMMA in the samples, and indicated that a small amount of copolymer was also formed. The scanning electron microscopy (SEM) images indicate particle size and particle size distribution. The core-shell particles, averaging 100 nm in diameter, were larger than the PS seed latex particles. The particle size distribution was dependent on the rate of second stage monomer addition and on the monomer feed ratio of styrene/MMA. The particle size distribution broadened as the rate of second monomer addition increased and also broadened as the ratio of styrene/MMA decreased.

This study of PS/PMMA core-shell materials prepared in supercritical CO₂ will continue. Ongoing TEM studies should elucidate the distribution of the PS and PMMA throughout the particles. Insight may be gained into the role of CO₂ and plasticization of these polymers based on the polymer distributions in the particles. In addition, other monomer systems will be examined for preparation of core-shell materials in CO₂.

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The titles of our current research projects are given in the **Contents** of our *Graduate Research Progress Reports*, No. 49, January, 1998, which can be found at the end of this report. Abstracts of several presentations made at the Annual Review Meeting of the Emulsion Polymers Institute's Industrial Liaison Program are given below.

1 Enhanced Droplet Nucleation in Miniemulsion Polymerization: A Kinetic and Mechanistic Study

P. John Blythe

Miniemulsions are comprised of relatively stable oil droplets, ranging in size from 50 to 500 nm, suspended in an aqueous phase. The stability of these systems arises from the use of an ionic surfactant and a low molecular weight, highly water-insoluble cosurfactant in the emulsification process. In miniemulsion systems, the main locus for nucleation is the monomer droplets due to their small size. However, nucleation of droplets is typically described as an inefficient process by which only a fraction of the initial droplets become particles.

It has been shown in styrene miniemulsion systems using cetyl alcohol as the cosurfactant that the addition of a small amount of sulfate-terminated polystyrene into the miniemulsion droplets before polymerization results in a large enhancement in the rate of polymerization and the number of droplets nucleated [C.M. Miller, *Ph.D. Dissertation*, Lehigh University, 1994]. Three possible explanations were proposed: [C.M. Miller and M.S. El-Aasser, *NATO ASI on Recent Advances in Polymeric Dispersions, Series E: Applied Sciences- Vol. 335*, Kluwer Academic Publishers, 1997] 1) the predissolved polymer increases the viscosity of the droplets which results in an increased probability that an entering radical will propagate in the droplets rather than desorb back into the aqueous phase; 2) polymer chains could disrupt the proposed ordered structure of cetyl alcohol (cosurfactant) and sodium lauryl sulfate (surfactant) at the interface creating openings in the structure through which radicals could enter the droplets; and 3) the polymer, coupled with the cosurfactant, may provide additional stability to the small, uninitiated monomer droplets allowing for a greater droplet number to be available for polymerization.

This presentation will report the effect on miniemulsion kinetics of varying the molecular weight and end-group of the predissolved polymer, the type of cosurfactant used, and the level of shear imparted to create the miniemulsion. The results will be used to: 1) determine which of the three proposed explanations correctly describes the cause for enhanced droplet nucleation in miniemulsion polymerization; and 2) formulate the proper assumptions to be used in mathematical modeling of the rate of polymerization versus time in 1% polymer miniemulsion systems.

2 Grafting Reactions Occurring in the Emulsion Polymerization of Vinyl Acetate Using Poly(Vinyl Alcohol) as Emulsifier

Bridgette M. Budhlall

Previously, the importance of the grafting of vinyl acetate (VAc) monomer onto the poly(vinyl alcohol) (PVA) emulsifier in emulsion polymerizations using potassium persulfate as initiator, was established by monitoring the reaction kinetics, particle nucleation, and grafting reactions during the course of a polymerization. It has been reported that the rates of polymerization, evolution of number of particles, amount of grafted polymer and the final latex properties are all

affected by the intramolecular sequence distribution of the residual acetate groups of the PVA. An attempt will be made to gain a more fundamental understanding of the grafting mechanisms occurring during the emulsion polymerization of vinyl acetate (VAc) using PVAs having different degrees of blockiness.

In this investigation, separation and characterization of the microstructure of the starting Poval PVAs and that of the poly(vinyl alcohol)-g-poly(vinyl acetate) [PVA-g-PVAc] were performed via several techniques.

The microstructure of the PVAs in terms of the differences in their acetate block sequence distributions (i.e., degree of blockiness) was investigated via 125 MHz ^{13}C -NMR and 500 MHz ^1H -NMR techniques. Sequence distributions of the acetate groups were obtained from the methine dyads, (OH, OH), (OH, OAc) and (OAc, OAc), in the ^{13}C -NMR spectra. The average sequence lengths of the acetate and hydroxyl groups were also determined via 125 MHz ^{13}C -NMR. A more accurate determination of the average sequence length can be estimated from the ^1H -NMR peaks of the methylene dyad protons, H(AA), H(AO) and H(OO) of vinyl alcohol and vinyl acetate residual groups. Combination of these two NMR techniques provides a powerful tool for gaining information on the architecture of the polymer. Successful separation of the Poval PVAs in terms of differences in their compositional distributions of acetate block sequences (i.e., degree of blockiness) was achieved via a high-performance liquid chromatographic (HPLC) technique. It was observed that a gradient elution with water/tetrahydrofuran (THF) using a reversed-phase mechanism on columns with wider pore polystyrene-based packing produced separations dependent on the degree of hydrolysis and sequence length distribution. 500 MHz ^1H -NMR studies on the effect of temperature on the aqueous solution properties of PVAs of differing residual acetate content and hydroxyl block size distribution, but similar block size are also reported. The data appear to indicate a correlation with the previously determined conformational changes of the macromolecule as a function of temperature and acetate block sequence lengths.

The microstructure determination of the grafted PVA-g-PVAc was performed by means of 500 MHz ^1H , quantitative ^{13}C and spin echo ^{13}C -APT NMR techniques. Compared to other free radical polymerizable monomers, vinyl acetate polymerizations are characterized by a high degree of chain transfer, which partially controls the kinetic chain length. It has been shown that grafting in these polymerizations occurs by three reactions: (a) chain transfer to polymer (which results in a trifunctional branch point in the polymer molecule); (b) chain transfer to monomer (which gives a polymer molecule with a terminal double bond); and (c) polymerization of the terminal double bond in which an entire polymer molecule adds to a growing polymeric radical. The reaction leading to the formation of graft copolymers in this research is the transfer to polymer in which the polymer is PVA. The grafting mechanism entails abstraction of a H atom on the PVA by a sulfate ion radical followed by reaction of the free radical formed with the VAc monomer forming PVA-g-PVAc. Three possible grafting sites have been proposed for H abstraction: (1) the methine C-atom of the PVA backbone; (2) the methylene C-atom; and (3) the methyl C-atom of the residual acetyl groups pendent to the polymer backbone. The results obtained from these studies will be used to determine which of the three proposed grafting sites predominates in the emulsion polymerization of VAc using PVA as emulsifier and potassium persulfate as initiator.

3 Effect of Agitation on the Scale-Up of Reactors for Emulsion Polymerization

Manish N. Dave

The agitation characteristics that exist in small bench-scale vessels differ greatly from those that exist in larger pilot plant scale and manufacturing scale vessels. It is thus necessary to produce agitation characteristics in bench-scale vessel and larger production vessels that result in the same polymer characteristics and properties. Thus the aim of this work is to study the effects of shear stress and mixing on coagulum formation, particle size and distribution and the extent of crosslinking. The systems used to carry out this research are the n-butyl methacrylate (BMA)

homopolymerization system and the n-butyl methacrylate/n-methylol acrylamide (BMA/NMA) copolymerization system. Both systems end with 40% solids contents.

In order to generate the different mixing and shear stress conditions, three Rushton turbine impellers of different size were used. The polymerizations were then carried out at three different agitation speeds for each impeller. The reactions were carried out in a two-liter glass reactor in the semi-batch mode.

From the results obtained, it is seen that coagulum formation is directly proportional to the shear stress for both the homopolymerization and copolymerization systems. There is no noticeable effect of the different shear and mixing conditions on the particle size and distribution and on the extent of crosslinking. Further it has been shown that this latex system can be treated as a Newtonian fluid. It has also been observed that there is no secondary nucleation and all the monomer added contributes to the further growth of the particles.

4 Living Free-Radical Emulsion Polymerization of Styrene Thummanoon Prodpran

Living polymerization is a chain growth process without transfer and termination by coupling or disproportionation reactions. This kind of process leads to so-called living polymers, which may spontaneously resume their growth whenever fresh monomer is supplied to the system. The important characteristics of living polymers are controlled molecular weights, desired end-groups and low polydispersities. Living polymerization is most often observed in chain reactions which proceed with polar growing species such as ions (in anionic and cationic polymerization) or organometallic compounds. However, it has been reported that polymers with narrow molecular weight distributions can also be obtained by a free-radical polymerization process if the process proceeds by a living mechanism, with no premature termination, and if all the propagating chains are initiated at about the same time, which is similar to what occurs in an anionic polymerization process. Nitroxide stable radicals such as 2,2,6,6-tetramethylpiperidine-1-oxyl (TEMPO) are widely used to create the living mechanism in synthesis of narrow molecular weight distribution polystyrene by living radical polymerization in bulk, as well as in solution and suspension.

The application of living free-radical polymerization using TEMPO is being studied in this research project in order to determine the feasibility of carrying out polymerization of this system via a miniemulsion polymerization route. From the preliminary experiments, stable latexes (~20% solids) with relatively low molecular weight polydispersities were obtained. The increase of molecular weight with conversion was observed, which indicates the characteristic of a living system. However, there was also an increase in the molecular weight polydispersity and the number of polymer particles with conversion; this is attributed to the presence of an inevitable thermal generation of free radicals at the high reaction temperature (125°C).

5 Influence of the Homopolymer of Sodium Dodecyl Allyl Sulfosuccinate (TREM LF-40) on the Kinetics of the Emulsion Polymerization of Styrene Xiaoru Wang

The kinetics of the emulsion polymerization of styrene using the reactive surfactant TREM LF-40 indicated that N_p was not directly proportional to R_p (i.e., $N_p \propto [S]^{0.39}$, $R_p \propto [S]^{0.76}$). To understand this, the seeded emulsion polymerization of styrene is being investigated employing analogous conventional, polymerizable and polymeric surfactants. The slope-intercept method is used for analysis of the reaction kinetics to obtain the radical entry (k_i) and exit (k_t) coefficients. Different radical entry and exit rate coefficients were found for the systems employing a conventional surfactant, SLS, and poly(TREM LF-40); both entry and exit coefficients were lower for reactions with the poly(TREM LF-40) present on the surface of the latex particles. This

could be explained by the formation of a 'hairy' layer of the poly(TREM) surfactant on the polymer particles, which decreases the radical diffusion rate into and out of the polymer particles.

The influence of the poly(TREM) concentration on the kinetics of the seeded emulsion polymerization of styrene was studied. No significant effects were found over the concentration range employed. To help understand the reasons for this, the poly(TREM) was characterized. Dialysis was used to purify the poly(TREM) of residual initiator and other ionic species. Vapor pressure osmometry (VPO) was used to measure the molecular weight of the poly(TREM), ($M_n = 6000(300)$), which is a polyelectrolyte. Serum replacement was utilized to obtain the adsorption isotherm behavior; a_s was found to be $480\text{\AA}^2/\text{molecule}$. Surface tension measurements were used to obtain the CMC of poly(TREM) in water and in latex (2% solids); these were 0.17 mM and 0.51 mM, respectively.

Future work will focus on the mechanism and detailed kinetics of emulsion polymerization of styrene with different surfactant forms, especially the polymeric surfactant.

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

Enhanced Droplet Nucleation in
Miniemulsion Polymerization Utilizing an
Oil-Soluble Initiator
(S.W. Gross and P.J. Blythe)

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

Copolymerization of Styrene and Butadiene
Monomers via Miniemulsion
(D. Li)

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

Solid-State NMR Characterization of
Composite Latexes Containing a
Macromonomer
(K. Landfester)

Composite Particles Based on a Core of
PBUA/PMMA and a Shell of PMMA
Studied by Solid-State NMR
(K. Landfester and S. Kirsch)

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

Submicron Latex Preparation by Living
Radical Polymerization
(T. Prodpran)

Encapsulation of Inorganic Particles via
Miniemulsion Polymerization

(B. Erdem)

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

Influence of the Homopolymer of Sodium
Dodecyl Allyl Sulfosuccinate (Trem LF-40)
on the Kinetics of the Emulsion
Polymerization of Styrene
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Grafting Reactions Occurring in the
Emulsion Polymerization of Vinyl Acetate
Using Poly(Vinyl Alcohol) as Emulsifier
(B.M. Budhlall)

Effect of Agitation on Scale-Up of Reactors
for Emulsion Polymerization
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Micron-Size Structured Particles via
Dispersion Polymerization
(D. Wang)

Electrokinetic Lift Effects Associated with
the Transport of Latex Particles in Capillary
Hydrodynamic Fractionation (CHDF)
(A.D. Hollingsworth)

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

Film Formation from Latex Blends
(J. Tang)

Hybrid Composite Latexes
(P. Jeong)

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

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 eight Ph.D. students and a post-doctoral researcher. Eric Furst, Dean Wang, Albert Lee, and Poe Ratanbanangkoon, along with John Pople, a post-doctoral researcher, are advised by Alice P. Gast. Szu Wang, Mike Yacilla, 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 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.

Investigation of Two-Dimensional Streptavidin Crystallization

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

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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. Growth of 2D streptavidin crystals has been used to study molecular interactions in protein arrays. Streptavidin molecules bound to biotinylated lipids 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.

Changes in protein-protein interactions are accompanied by pH alterations and genetic manipulation. Under conditions of $\text{pH} > 7.0$, dendritic X-shaped morphologies are formed and show C222 symmetry. Needle-like crystals observed at acidic conditions ($\text{pH} < 4$) correspond to reported P1 symmetry. Between pH 4.5 and 6.5, several unique domain shapes exist which are composed of different coexisting crystal ratios. One of these phases is a new crystal type with P2 symmetry. These observations suggest that it is possible to control 2D protein self-assembly by directed manipulation of protein interactions, which could result in protein arrays with desired properties. Experiments are currently in progress which alter interactions between contact amino acids in streptavidin arrays via site-directed mutagenesis.

Light Scattering in Magnetorheological Fluids

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Stanford, CA 94305-5025

Abstract:

Magnetorheological fluids are suspensions of colloidal particles which acquire dipole moments when subjected to an external magnetic field. At sufficient field strengths and concentrations, the dipolar particles rapidly aggregate to form long chains. Subsequent lateral cross-linking of the dipolar chains is responsible for a rapid liquid to solid-like rheological transition. It has been proposed that strong Landau-Peierls thermal fluctuations of the dipolar chains are responsible for long-range lateral interactions between chains that may alter the aggregation kinetics and rheological response of these fluids.¹ In this study, we use diffusing wave spectroscopy (DWS) to probe the dynamics of the dipolar chains. The measured particle displacements are independent of the magnitude of the dipolar interactions at short times, but characterized by a constrained, sub-diffusive motion at long times that slows as the dipolar interactions are increased. Our observations show good qualitative agreement with Brownian dynamics simulations of dipolar chains.

¹ T.C. Halsey and W. Toor, *J. Stat. Phys.* 61, 1257 (1990).

Structure and Dynamics of pH Dependent Polyelectrolyte Micelles

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Abstract:

We use light scattering methods to study the structure of 2-(dimethylamino)ethyl methacrylate / 2-(diethylamino)ethyl methacrylate (DMAEMA/DEAEMA) block copolymers. In water, these polyelectrolyte copolymers form micelles whose structure changes with varying solution pH and ionic strength. We employ dynamic light scattering (DLS) to measure the micelle size as a function of varying solution conditions such as pH, ionic strength, and polymer concentration. For polymer volume fractions of 0.1% and 0.5% we find a critical pH of 7.5, where the single chain unimers aggregate to form micelles. Below the critical pH, the chains remain dispersed as unimers. We measure similar micelle radii at both concentrations. We also investigate the effects of the solution ionic strength on the micelle structure. In addition to characterizing the structure, we are interested in using fluorescent probes to study exchange dynamics and the dynamics associated with the breakup and formation of these micelles.

Fundamental Studies of Filled Systems

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Stanford, CA 94305-5025

Abstract:

There are a host of important problems in the study of polymer rheology which can be characterized as non-continuum or nonlocal and these are typically associated with the influence of boundaries or constrained environments on the stress-strain rate relationship. The burgeoning interest in these problems arises from the growing need to process materials at a molecular level. In most cases new physical principles need to be applied to such problems because the most fundamental relationships need to be derived anew. Moreover there highly constrained flow fields are now only beginning to be experimentally interrogated, but the early data suggests that qualitatively new rheological behavior needs to be understood in these cases. We propose to examine two problems that can serve as paradigms for rheological model-building in this field of study: a) biaxial squeezing flow of flexible chains in solution when the pore or channel thickness is comparable to the radius of gyration of the polymers with hydrodynamic interactions, b) rheological behavior of a colloid-polymer composite in shear and elongational flow. The numerical technique we are currently developing for the systems above is large scale Brownian dynamics simulations of Kramer's bead-rod chains. In a parallel experimental effort, we are using small angle neutron scattering to investigate structures of colloid-polymer mixtures and colloid-polymer composites in various flow conditions.

Contribution from the group of Ton German at Eindhoven University of Technology to the IPCG Newsletter (electronic edition), (helly@chem.tue.nl), <http://www.chem.tue.nl/spc/>).

**I Summary of the Ph.D. thesis of John Geurts,
“Latices with intrinsic crosslink activity”,
Eindhoven University of Technology, 1997**

The investigation described in this thesis is directed towards the preparation, characterization and film formation behaviour of so-called "two pack in one pot" systems. These systems consist of a blend of complementary reactive latices. The reaction between the complementary reactive polymers does not occur in the pot, because they are incorporated in separate latices which do not interact due to the stabilizing layer around the particles. The particles containing the complementary reactive polymers come into contact with each other when the water is evaporating. So crosslinking occurs when the latex is applied onto a substrate and the process of latex film formation occurs.

Two kinds of complementary reactive systems have been investigated, i.e. the epoxy-amino and the acetoacetoxy-amino system. For this purpose three types of functional latices were synthesized: epoxy-, acetoacetoxy- and amino-functional latices. In the first part of this thesis the preparation and characterization of the different functional latices is described. The epoxy- and acetoacetoxy-functional latices were prepared by emulsion copolymerization of butyl methacrylate (BMA) with glycidyl methacrylate (GMA) or of BMA with acetoacetoxyethyl methacrylate (AAEMA). One of the most important factors that had to be controlled in the emulsion polymerization is the molecular weight of the reactive copolymers formed. The molecular weight determines the rate of interdiffusion of the complementary reactive polymer chains during the last stage of the film formation (autohesion) and thereby influences the rate of crosslinking.

Two main problems occurred when using GMA and AAEMA in the emulsion polymerization: partial hydrolysis of the epoxy-, or acetoacetoxy groups and premature crosslinking of the latex particles during emulsion polymerization. Hydrolysis was prevented by reducing the reaction temperature. However, this did not reduce the amount of crosslinking since this was caused by small amounts of difunctional monomers present in the monomers GMA and AAEMA. The effect of these dimethacrylates could be reduced by reducing the molecular weight by means of chain transfer agents. The chain transfer agents used and studied included mainly CBr_4 , CBrCl_3 and the catalytic chain transfer agent cobal oxime boron fluoride (CoBF). When using these chain transfer agents

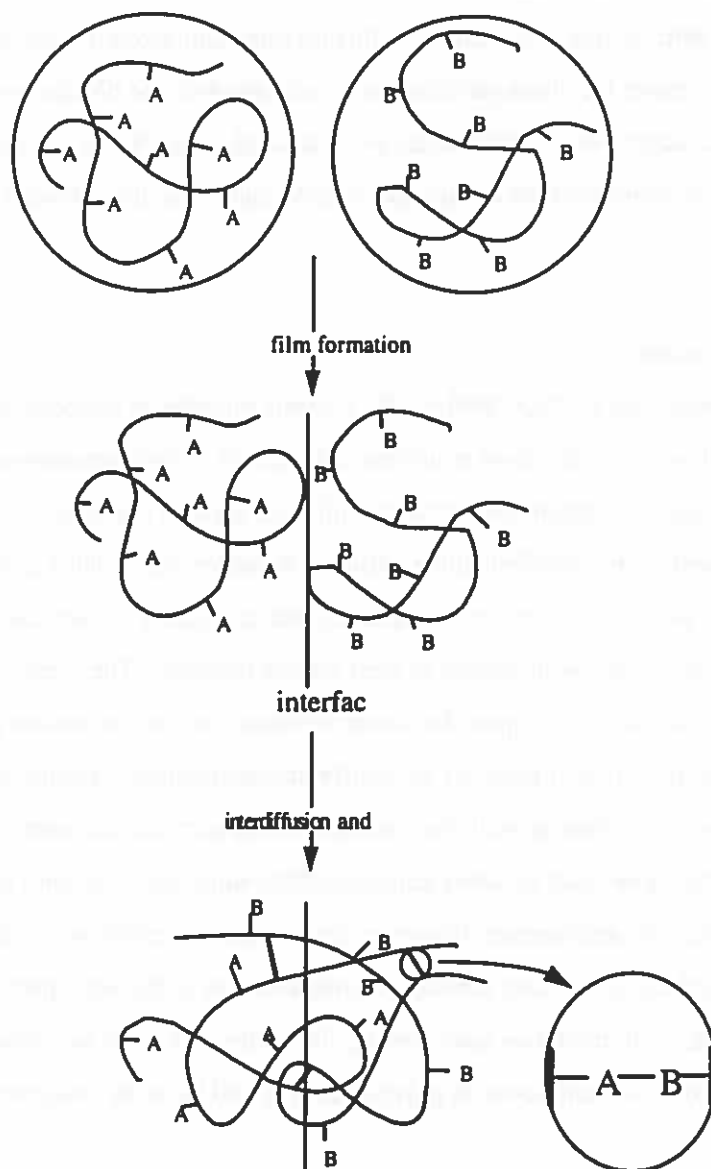
epoxy- and acetoacetoxy-functional latices were prepared with a molecular weight ranging from 1000 to \bullet g/mol.

Amino-functional latices were prepared by means of emulsion copolymerization with amino-functional methacrylate comonomers, which were synthesized for this purpose. The most suitable amino-functional monomer from the group of the ω -amino-1-alkyl methacrylates proved to be 5-amino-1-pentyl methacrylate (APMA). Other monomers synthesized were aminoethyl-, -propyl-, -hexyl- and -undecyl methacrylate. These monomers were synthesized as either the hydrochloric- or p-toluenesulfonic acid salt. APMA was incorporated in latices in a semi-continuous emulsion copolymerization process, which proved to be necessary due to the limited stability of APMA after neutralization of the p-toluenesulfonic acid salt.

The second part of this thesis describes the film formation of the "two pack in one pot" latex blends. Before investigating this system, model experiments were performed to investigate the effect of several parameters on the film formation. The first parameter is the influence of particle size and, especially of bimodal particle size distributions on film formation. By means of measurements of the minimum film formation temperature (MFFT) and atomic force microscopy it was shown that bimodal particle size distributions can have an effect on the packing of particles during film formation. Usually a homogeneous particle size distribution resulted in a nicely packed matrix of particles. A bimodal particle size distribution in most cases disturbed the packing, resulting in a high MFFT and a film containing more voids. The conclusion was that in order to exclude major effects of bimodality when studying "two pack in one pot" systems the particle sizes of the complementary reactive latices should be as identical as possible.

A model study of the epoxy-amino reaction and the acetoacetoxy-amino reaction showed that these reactions were influenced by many parameters in the actual "two pack in one pot" system. The parameters that were identified as having an influence on the reaction included the type of backbone monomer used, the T_g of the copolymers, the drying temperature and hydroxyl-containing components present in the system (which catalyze the reactions). This made it impossible to give an exact value for the reaction rate constant of the epoxy-amino and acetoacetoxy-amino systems. The best values that could be given were a maximum and a minimum reaction rate constant, which were used in model calculations of the "two pack in one pot" systems.

In the last part of this thesis the crosslinking during film formation of "two pack in one pot" systems is described. First, a model was developed that could give an insight in the effect of the parameters molecular weight and reaction rate on the crosslinking. These model calculations were used to enlighten the experiments performed. Crosslinking in the films casted from "two pack in one pot" systems was followed by means of gel content determinations, DMTA and FTIR. All experiments showed that crosslinking did occur during film formation. The effectiveness of crosslinking was a consequence of the competition between polymer-polymer molecular interdiffusion and polymer-polymer reaction. When the reaction is very fast (acetoacetoxy-amino) interdiffusion of the polymer chains is blocked at the interface because of the formation of densely crosslinked material at the interface. It was expected that lowering the molecular weight of these polymers would increase the rate of interdiffusion and thereby the rate of crosslinking. This trend was not observed because the molecular weight distribution of the emulsion copolymers was broad. As a consequence, low molecular weight material diffuses rapidly thereby crosslinking the complementary reactive polymer. This results in a high gel fraction, but also in a low crosslink density.



Principle of "two pack in one pot" systems, A and B represent the complementary reactive groups.

**II Summary of the Ph.D. thesis of Hennie Zirkzee,
“A Novel Approach to the Encapsulation of Silica Particles. Mechanisms and Kinetics”,
Eindhoven University of Technology, 1997**

This thesis describes the concepts, kinetics and process control concerning encapsulation reactions of inorganic silica particles, via an emulsion polymerization process. Previous studies demonstrated that encapsulation of pigment particles can be performed with reasonable success. The formation of undesired pigment particles, however, could not be prevented, which results in a decrease of the efficiency of the encapsulation reaction. Additionally it was shown that the encapsulation efficiency is highly dependent upon the applied process conditions, which are not always well defined. Therefore, the objective of this investigation is to obtain insight into the mechanisms of the encapsulation process at the molecular level, and its dependence on the applied process conditions. For this purpose the encapsulation system should be well defined. The inorganic pigment particles used are silica particles, prepared by the Sol-Gel process. These silica particles are spherical and exhibit a narrow particle size distribution. In this investigation two physical modification procedures have been used, to make the silica particles more hydrophobic: the blockcopolymer procedure and the twin-tailed surfactant route. Both routes are evaluated in this thesis, according to concepts, kinetics and process control of the encapsulation procedure. The basic results and conclusions will be given here.

Blockcopolymer route

The blockcopolymer used is PEO-PBMA, which forms micelles in aqueous solutions as well as in water-ethanol solutions. When phase equilibria is regarded, it has been shown that the modification of the silica particles is essential in order to adsolubilize styrene monomer at the surface of the silica particles. When next to the modified silica particles, micelles and/or latex particles are present, most of the styrene will be adsolubilized in the particles and micelles. Polymerization and Encapsulation reactions have been studied with respect to their kinetic behavior. The presence of ethanol in the system has a considerable effect upon the kinetic behavior in the continuous phase as well in the particle phase. The presence of particles with different morphology has an considerable effect on the kinetic behavior of the system as well. For modified silica particles the entry rate will be lower and the exit rate will be higher than for latex particles of the same size. For both particle morphologies pseudo-bulk kinetics are appropriate. However, the radical concentration in the modified silica particles is significantly lower than the radical concentration in the latex particles (when present). This effect, together with monomer partitioning, illustrates that when secondary nucleation, during encapsulation, occurs the main locus of polymerization will be in the polymer particles. As a result

the efficiency of the encapsulation process decreases. Secondary nucleation in these polymerizations, will occur when the surface area offered by the silica particle species is not enough to irreversibly adsorb all surface active oligomers. Unfortunately, secondary nucleation can not be prevented in batch reactor systems. Benefit of secondary nucleation can be made, however, by heterocoagulate these particles on the surface of the silica particles.

Twin-tailed surfactant route

Diocetadecyldimethylammonium Bromide (DODAB) is used as twin-tailed surfactant in this investigation. Preliminary to the encapsulation study, the polymerization in DODAB vesicles has been investigated. It appeared that the characterization of the individual stages of the process is of paramount importance. Characterization studies showed that the morphology of the DODAB vesicles is dependent upon the preparation procedure. Vesicles are thermodynamic metastable and exhibit a phase transition temperature, which influences phase equilibria phenomena and polymerization kinetics.

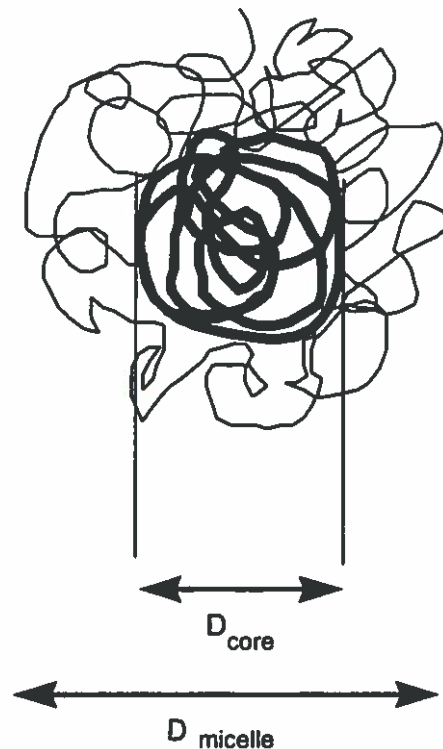
Phase equilibria of solvents in DODAB vesicles has been studied as function of temperature. When the temperature is above the phase transition temperature much more solvent can be incorporated in the bilayer than when the temperature is lower than the phase transition temperature. Next, it appeared that bulkthermodynamics do not describe the phase behavior of these systems, but the microstructure of the bilayer should be taken into account. Results also indicate that micro-phase separation can occur, possibly leading to solvent rich parts and DODAB rich parts in the bilayer. The kinetic behavior of polymerizations in DODAB vesicles deviates from a conventional emulsion polymerization. The polymerization starts at a relatively high volume fraction of hydrocarbon DODAB chains. This implies that the basic reactions events are diffusion controlled. Diffusion of species in these bilayers is characterized by lateral and transmembrane diffusion. The coefficient for transmembrane diffusion is many orders lower than for lateral diffusion, as determined by ESR. Therefore, entry and exit events, that are characterized by transmembrane diffusion will be diffusion controlled. Whether polymerization in vesicles exhibit a zero-one or pseudobulk behavior is still uncertain.

Studies concerning modification of silica particles with DODAB revealed that DODAB adsorbs on silica as a bilayer. Phase equilibria with solvents within these modified silica particles showed the same behavior with respect to temperature, as in the case of DODAB vesicles. The adsorption isotherm has been determined qualitatively. When too much DODAB is used, conditions for a mixed system are created, i.e. modified silica particles and DODAB vesicles. When a separation procedure is performed, prior to the encapsulation reaction, selective encapsulated silica particles with polystyrene are obtained. The temperature and the reaction time of the encapsulation reaction seems

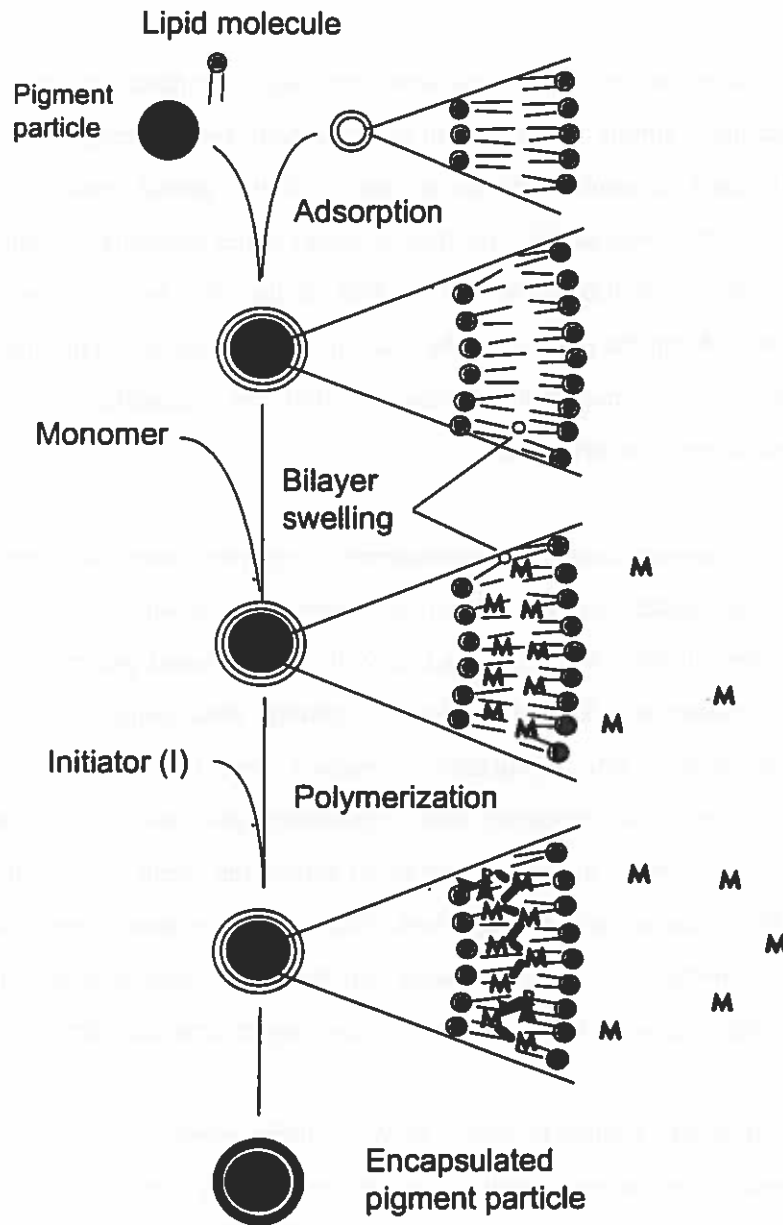
to be important with respect to the particle morphology of the encapsulated silica species. Theoretical thermodynamic considerations suggest that the system DODAB-polystyrene is able to phase separate, which changes the morphology. However, the polymerization is kinetically controlled, and therefore phase separation phenomena can be suppressed by tuning the applied experimental conditions, i.e. low polymerization temperatures.

The overall conclusion is that encapsulation of silica particles is possible via the twin-tailed surfactant route. Additionally, a considerable understanding is obtained about the concepts and kinetics of polymerization and encapsulation reactions in general, using these bilayers. However, at this stage the concepts of these polymerization reactions are described and many fundamental questions concerning phase equilibria and polymerization kinetics are existing.

This implies that there is sufficient area for future research, concerning this topic.



Schematic diagram of a blockcopolymer micelle



Schematic representation of the encapsulation route using bilayer forming surfactants

**III Summary of the Ph.D. thesis of Bart Manders,
“Pulsed Initiation Polymerization. Applications in Homogeneous and Heterogeneous
Radical Systems”,
Eindhoven University of Technology, 1997**

In this thesis, investigations are presented about the use of pulsed initiation polymerization experiments to determine kinetic parameters in homogeneous and heterogeneous radical systems. The advantage of pulsed initiation methods is that it allows partial control over initiation and termination events of a polymerization. This leads to peaks in the molecular weight distribution. The position of these peaks is controlled by the product of the time between two pulses and the propagation frequency. When the position of the peaks in the molecular weight distribution is known (e.g. from size exclusion chromatography measurements), the propagation rate coefficient or the monomer concentration may be determined.

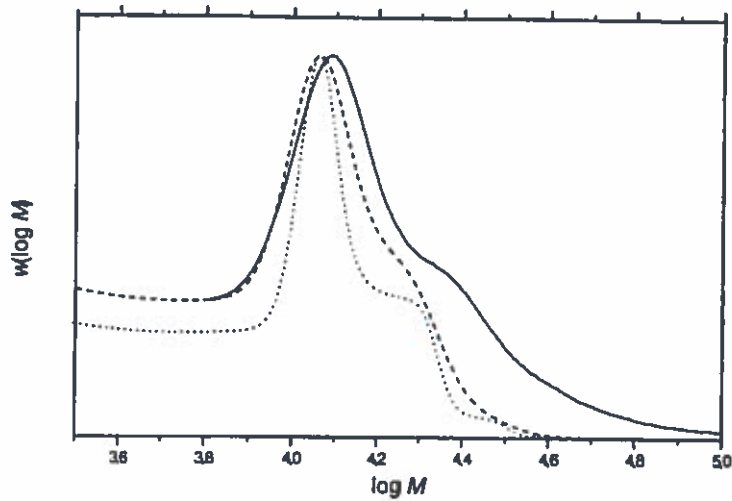
Simulations, both of homogeneous and heterogeneous systems, were performed for a better understanding of the processes that play a role in determining the exact position of the peaks in the molecular weight distributions. Two main cases may be distinguished, assuming instantaneous and non-instantaneous termination kinetics. When simulating instantaneous termination, the best estimate of the propagation rate coefficient is obtained using the peak maximum of the peak resulting from the controlled initiation and termination processes. For non-instantaneous termination, which is normal in homogeneous systems, the peak maximum leads to an overestimation of the propagation rate coefficient. This last observation corroborates results from other simulations. Furthermore, it was concluded that the pulsed laser polymerization method can not be used as possible evidence of the existence of chain length dependent termination.

The pulsed laser method was applied to bulk systems to obtain information on the propagation rate coefficient of styrene, vinyl acetate, methyl acrylate and butyl acrylate. For styrene, the data compares well with other data obtained with both the PLP method and other methods. During the polymerization of the fast propagating monomers, vinyl acetate and both acrylates, deteriorating effects occurred that obscured the peaks in the molecular weight distribution resulting from pulsed initiation. Because the method allows consistency checks, the correctness of each data point could be assessed. Based on these checks, guidelines have been proposed to circumvent the deteriorating effects, leading to consistent data that compared well with other data obtained with the pulsed laser method.

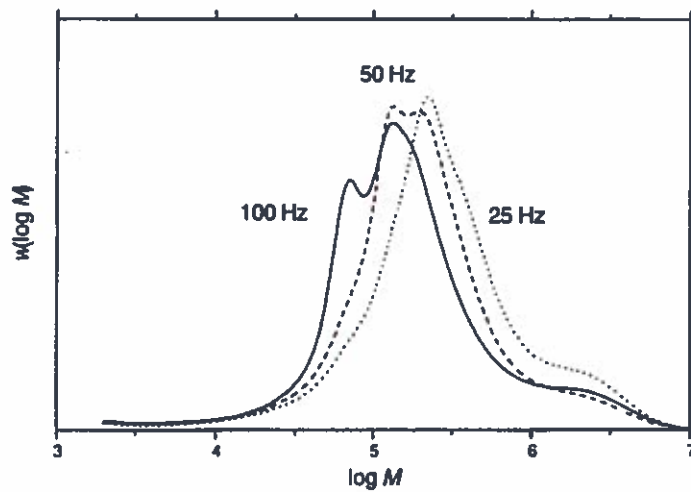
In heterogeneous systems, like latices, information about the monomer concentration is very important to understand and model emulsion polymerization processes. Pulsed laser polymerization experiments can provide this information. Again, the method allows for consistency checks to be performed. The main advantage of the method is that it gives an estimate of the monomer concentration at the site of reaction, which is the parameter that is used in modeling emulsion polymerization. A disadvantage is the fact that a latex is not transparent to the laser light and that as a result experimental conditions at which the experiments should be performed are hard to find. Therefore, an alternative initiation source was introduced, a pulsed electron beam. As electron penetration characteristics are better understood, with this initiation method, correct experimental conditions are easier to obtain. The method was also applied to bulk systems and in both cases no differences from a pulsed laser in combination with a photo initiator were observed.

Pulsed laser polymerization was also applied to the analysis of the copolymerization of styrene and methyl methacrylate. The terminal model is not able to describe at the same time the kinetic data that are obtained together with copolymer composition data. Therefore, the implicit penultimate unit model was used to describe these data. It is observed that one of the radical reactivity ratios of the penultimate unit model is not obtained with great precision. This is attributed to the equation that describes the propagation rate coefficient as function of the monomer feed composition. Two possible solutions are suggested. The precision of the radical reactivity ratio may be increased by using statistical design methods to perform the experiment at optimal feed compositions or by measuring a different quantity, the ratio of the radical concentrations with a different end unit.

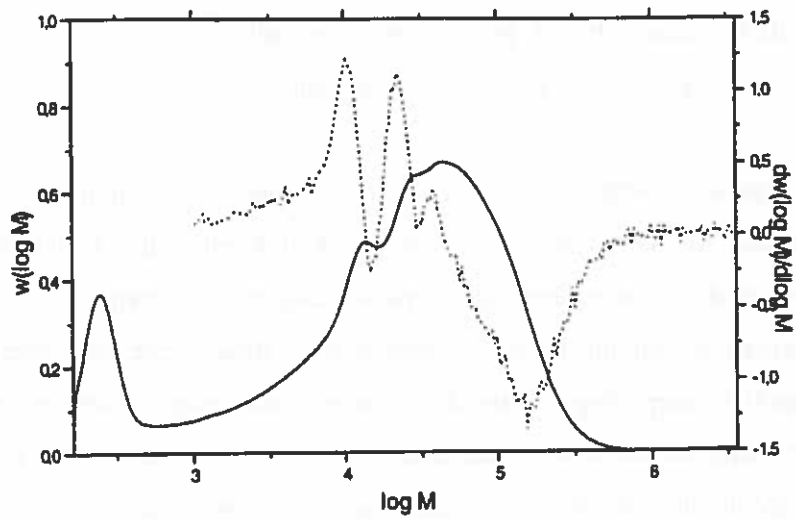
In total, the pulsed laser polymerization method proved to be a valuable and robust method to obtain values of kinetic parameters for a great variety of systems.



Experimental molecular weight distribution obtained at 29.7 °C (solid line, styrene PLP experiment with frequency 10 Hz) and simulated molecular weights distributions (dotted line, calculated with $[R_{1.}]^0 = 5.0 \cdot 10^{-6} \text{ mol L}^{-1}$, dashed line, Gaussian broadened distribution calculated using $\sigma_v \cdot b = 0.05$).



Comparison of resulting MWDs from PLP experiments of bulk BA, performed at approximately $-7.5 \text{ }^\circ\text{C}$, with different pulse repetition rates (as indicated in figure).



MWD of a PEBP experiment with PS4 performed at room temperature at a repetition rate of 5 Hz, for 3000 pulses.

IV Short communication "New Vesicle-Polymer Hybrids: The Parachute Architecture"

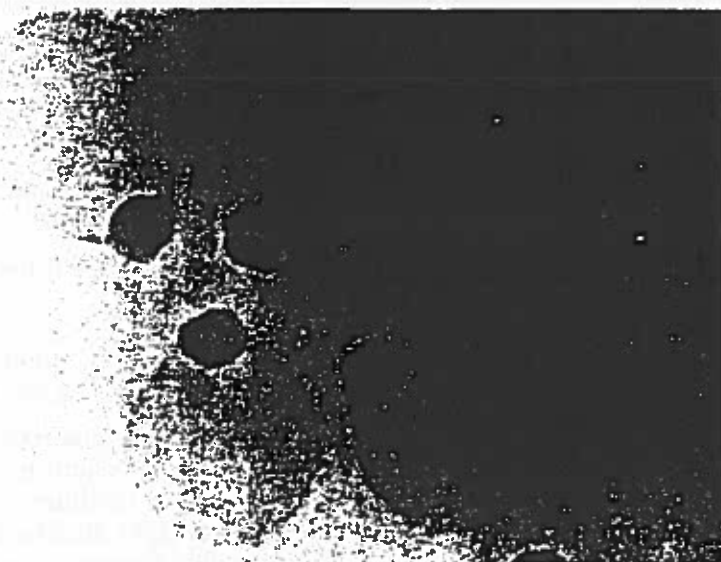
M. Jung , D.H.W. Hubert , P.H.H. Bomans, P.M. Frederik,
J. Meuldijk, A.M. van Herk, H. Fischer, A.L. German

The influence of organised media on polymerisation reactions results in many cases in interesting morphologies of the polymeric material. In the present study, vesicle bilayers were used as ordered medium for the free radical polymerisation of styrene. Cryo-electron microscopy gives evidence that the polymerisation induces phase separation phenomena leading to parachute-like morphologies. Based on general knowledge about vesicles and polymerisations in heterogeneous media, explanations for the observed phenomena are given in a recent publication¹. In this contribution a concise summary is presented.

Polymerisation *in* vesicles comprises the free radical polymerisation of monomer molecules, inserted into the bilayer as host molecules. The concept proposed by Murtagh and Thomas^{2,3} is to immobilise the amphiphiles within the aggregate in order to improve vesicle stability, and thus its life-time. Particularly, drug delivery systems require an increased life-time to allow delivery of their cargo to the desired place without premature vesicle break-up.

Although some publications have appeared following the pioneering study of Murtagh and Thomas, the question of the final morphology could not be fully clarified and remained a matter of speculation. A strong influence of the confined medium on the polymerisation reaction is expected and the crucial question is, how the growing macromolecules will arrange within the vesicle bilayer.

Our present cryo electron microscopy study clearly demonstrates that, at least under the present experimental conditions, interesting phase separation phenomena occur within the vesicles during the course of the polymerisation. Parachute-like structures are obtained, in which a single polymer particle is formed that remains confined to the vesicle bilayer. To the best of our knowledge, these hybrid vesicle-polymer architectures have never been observed before.



Polymerisation leads to exciting new structures: small solid spheres are linked to bilayer structures, typically one sphere per vesicle, to form parachute-like geometries, where the bilayer resembles the unfolded parachute and the polymer sphere resembles its cargo. When analysing a representative series of micrographs at various magnifications, the following interesting main characteristics are found: (i) nearly all observed parachutes contain only one polymer particle, and (ii) smaller vesicles contain smaller polymer particles. Clearly, a large number of polymer chains (approximately 1000 chains in a typical polymer particle of 50 nm diameter) are concentrated at one point in the vesicle bilayer.

These findings represent a unique case: although intra-bilayer phase separation takes place and the polymer leaves its template, an eventual separation of polymer and vesicle does not occur and a stable dispersion is obtained. At this moment the precise mechanisms are still rather speculative, but the observation that *each* vesicle contains *one* polymer particle makes it highly likely that the compartmentalisation of monomer together with a hindered inter-vesicular exchange of monomer and amphiphile can prevent a disproportional growth of polymer in only a small fraction of the vesicles at the expense of the others. Currently, investigations are underway to unravel the relevant mechanisms and to determine the scope of the present findings.

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

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

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

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 $\ln(\text{number molecular weight distribution})$, 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.

A theoretical study of propagation rate coefficients for methacrylonitrile and acrylonitrile. DM Huang, MJ Monteiro, RG Gilbert, Macromolecules, in press.

The propagation rate coefficients for methacrylonitrile (MAN) and acrylonitrile (AN) were calculated using transition state theory and high-level ab initio molecular orbital theory. The calculations take particular account of internal rotations in the transition states. Frequency factors and rotational potentials were found to be insensitive to the level of theory used (except that the semi-empirical AM1 method does not perform very well), because of cancellations in the partition function ratio in transition state theory; however, two of the internal rotations studied were found to be sensitive to the chain length of the radical used in the calculations. Activation energies were found to be extremely sensitive to the level of theory. At the highest level of theory used, the calculated frequency factor for MAN was slightly lower than experiment, while the activation energy was 2.6 kJ mol^{-1} higher than experiment. Theoretical comparison of propagation of MAN and AN was used to explain differences observed experimentally in activation energies and frequency factors of methacrylates and corresponding acrylates. The higher frequency factors for methacrylates are largely due to hindrance caused by the methyl groups to the three transitional modes in the transition state which correspond to the three external rotational degrees of freedom of the monomer in the reactants (but not a result of increased hindrance to methyl rotation itself in the transition state). The higher activation energies of methacrylates arises from differences in hindrance and loss of delocalization in the transition states of the methyl-substituted and unsubstituted monomers.

Measurement of diffusion coefficients of oligomeric penetrants in rubbery polymer matrices. MC Griffiths, J Strauch, MJ Monteiro and RG Gilbert.

The diffusion coefficients of oligomeric radicals in monomer-polymer systems have a major influence on properties such as polymerization rates and molecular weight distributions. The present work reports the results of an extensive set of studies of diffusion coefficients of rubbery ternary systems comprising polymer, diluent and oligomer, determined by pulsed-field-gradient NMR, at 25 and 40°C. Oligomers of methyl methacrylate (MMA) and of butyl methacrylate (BMA) were synthesized using catalytic cobalt chain transfer agent to produce macromonomers with a terminal double bond. Where necessary, these were fractionated by preparative GPC to obtain samples ranging from dimeric through to decameric; typical polydispersities were 1.08. Pulsed-field gradient NMR is facilitated by being able to monitor the proton NMR of the CH_2 hydrogens on the double bond. Matrices used were high molecular weight polyMMA

and polyBMA, the weight fraction of polymer (w_p) being varied by adding appropriate amounts of diluent (the saturated equivalents of MMA and BMA, viz., methyl isobutyrate and butyl isobutyrate). Above c^* (the concentration at which chains start to overlap), all data for diffusion coefficients D_i of an oligomer of degree of polymerization i could be fitted with acceptable accuracy by $D_1(w_p)/D_i(w_p) = i^{0.664 + 2.02w_p}$, for both BMA and MMA oligomers in both MMA and BMA matrices; the same relation also fits earlier data on styrene oligomers in polystyrene. If more accurate scaling parameters are obtained experimentally for smaller oligomers, these can be used to predict data for higher oligomers with even better reliability. For MMA monomer in pMMA, where free-volume parameters are available, the predicted dependences of monomer diffusion coefficient on w_p and temperature are in accord with experiment.

Measurement of transfer constant for butyl acrylate free-radical polymerization. S. Maeder and R.G. Gilbert. Macromolecules, in press.

Arrhenius parameters for the transfer constant to monomer (C_M) for the free-radical polymerization of butyl acrylate (BA) are determined by a combination of techniques. A seeded emulsion polymerization with conditions designed so that "zero-one" kinetics are obeyed, i.e., where entry of a radical into a particle causes instantaneous termination, and such that transfer to monomer can be shown to be the dominant chain-stopping event. The seed comprised small polystyrene particles, which reduces the likelihood of chain transfer to polymer provided the polymer:monomer ratio is sufficiently low. Since the dominant chain-stopping events are then entry and transfer to monomer, C_M can then be obtained from the number molecular weight distribution for different initiator concentrations and conversions and isolating the component due to transfer to monomer. The transfer constant so obtained, over the temperature range 50–72°C, fits $C_M = (0.016 \pm 0.003) \exp(-15.2 \pm 0.6) \text{ kJ mol}^{-1}/RT$.

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.

The adsorption behavior of cationic polymer particles onto the wool fiber surface has been investigated in this study. In particular, the role of the lipid layer surrounding the wool fibers and the oxidation of wool has been studied in terms of polymer adsorption. For this, polymer particles consisting of crosslinked polystyrene cores and with surface ammonium groups have been synthesized. These colloidal particles are solely stabilized through electrostatic repulsion. It was shown that, under conditions where no polymer particles are adsorbed onto untreated wool, a monolayer is adsorbed onto wool in which the lipid layer has been removed. Wool oxidized with peroxomonosulfuric acid displays a very similar behavior in terms of wetting characteristics and polymer adsorption to untreated wool, despite an increased amount of cysteic acid on the fiber surface. X-ray photoelectron spectroscopy results indicate that the lipid layer is still intact after this oxidative treatment. A monolayer of polymer particles can be observed on the wool after the removal of the lipid layer. The enhanced adsorption of polymer particles onto untreated and oxidized wool from which the lipid layer has been removed indicated that this layer represents a major adsorption barrier to cationic polymer particles.

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, in press.

An extensive model is given for the particle size distribution (PSD), particle number, particle size and amount of secondary nucleation in emulsion polymerisations. This incorporates what are thought to be all of the complex competing processes: aqueous phase kinetics for all radical species arising from both initiator and from exit (desorption), radical balance inside the particles, particle formation by both micellar and homogeneous nucleation mechanisms, and coagulation (the rate of which is obtained using the Healy-Hogg extension of DLVO theory). The predictions of the model are

compared to extensive experimental results on rates, time evolution of the particle size distribution, and relative amounts of secondary nucleation, for styrene initiated by persulfate with sodium dodecyl sulfate and with sodium dihexyl sulfosuccinate as surfactants. For this system values of almost all of the many parameters needed for the model are available from independent measurements, and thus no significant parameter adjustment is plausible. Accord with experiment is imperfect but quite acceptable, supporting the validity of the various mechanisms in the model. Effects such as the experimental variation of particle number with ionic strength, as well as calculated coagulation rate coefficients as functions of particle size, suggest that coagulation of precursor (i.e., newly-formed) particles is a significant effect, even above the cmc. The modelling also suggests why secondary nucleation occurs readily in systems stabilised with polymeric surfactant.

Use of mechanistic principles to make modified natural rubber latex products by emulsion polymerization. N. Subramaniam, R. Balic, J.R. Taylor, M. Griffiths, M.J. Monteiro, R.G. Gilbert, C.C. Ho, I. Abdullah, P. Cacioli, J. Nat. Rubber Res. 12, 223-31 (1997).

A novel class of materials, comprising an artificial polymer inside natural rubber latex particles, so that the new polymer is extensively grafted to the cis-polyisoprene, can be made if the artificial polymer is of very low water solubility, with the natural rubber latex used as seed. This avoids the problem of secondary particle formation and subsequent engulfing of the resulting precursor particle into the pre-existing latex particles, which gives inhomogeneities in the conventional means of making modified NRL through such seed technology.

The following publications have appeared since the previous Newsletter:

Termination rate coefficients from molecular weight distributions. P.A. Clay, D.I. Christie, R.G. Gilbert. ACS Symposium Series 685, pps 104-19: Advances in Free-Radical Polymerization, ed. K. Matyjaszewski. American Chemical Society, Washington DC, 1998.

Chain transfer to monomer in the free-radical polymerizations of methyl methacrylate, styrene and α -methyl styrene. D. Kukulj, T.P. Davis, R.G. Gilbert. *Macromolecules*, 31, 994-9 (1998).

Designer polymer colloids. M. Monteiro, R.G. Gilbert, *Chem. in Aust.*, 64, 12-14 (1997).

Catalytic chain transfer in miniemulsion polymerization. D. Kukulj, T.P. Davis, R.G. Gilbert. *Macromolecules*, 30, 7661-6 (1997).

Transition-state theory model for the diffusion coefficients of small penetrants in glassy polymers. A.A. Gray-Weale, R.H. Henchman, R.G. Gilbert, M.L. Greenfield and D.N. Theodorou. *Macromolecules*, 30, 7296 -7306 (1997).

Emulsion polymerization in a hybrid carbon dioxide/aqueous medium. M.A. Quadir, R. Snook, R.G. Gilbert and J.M. DeSimone. *Macromolecules*, 30, 6015-23 (1997).

ESR Measurements of propagation rate coefficients for styrene free radical polymerisation. MP Tonge, A Kajiwara, M Kamachi, RG Gilbert. *Polymer*, 39, 2305-2313 (1998).

Critically evaluated rate coefficients for free-radical polymerization, 2. Propagation rate coefficients for methyl methacrylate. S. Beuermann, M Buback, TP. Davis, RG Gilbert, RA Hutchinson, OF Olaj, GT Russell, J Schweer, AM van Herk. *Macromol. Chem. Phys.*, 198, 1545 (1997).

**Contribution to the International Polymer Colloid Group Newsletter
August 1997**

from

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Below is given a summary of a recent work, utilising the DROP instrument that was described in the last Newsletter. The screen snapshot did not make it very well through the copy machine. For those who are interested in the method, see <http://www.uio.no/~fhansen/dropinst.html> With this work, we are getting closer to the "old" polymer colloids topics.

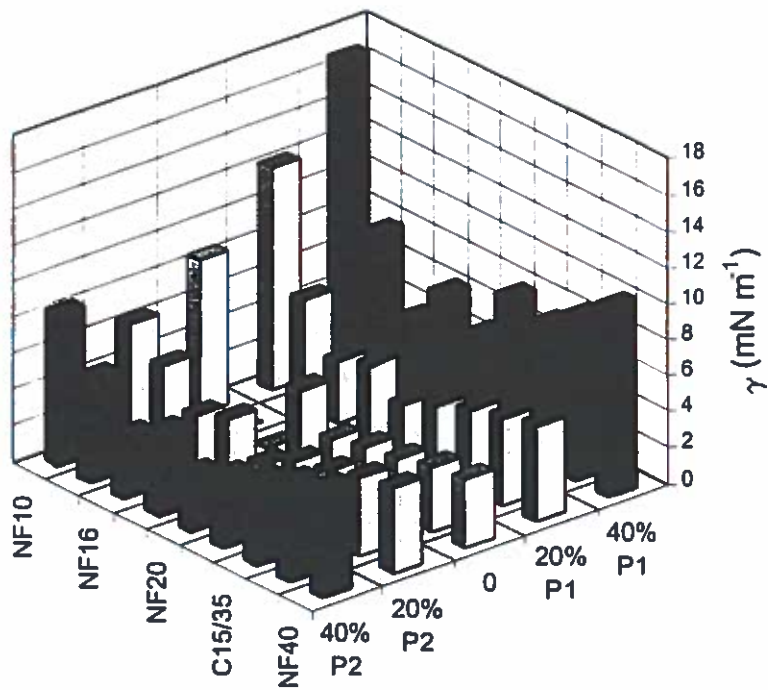
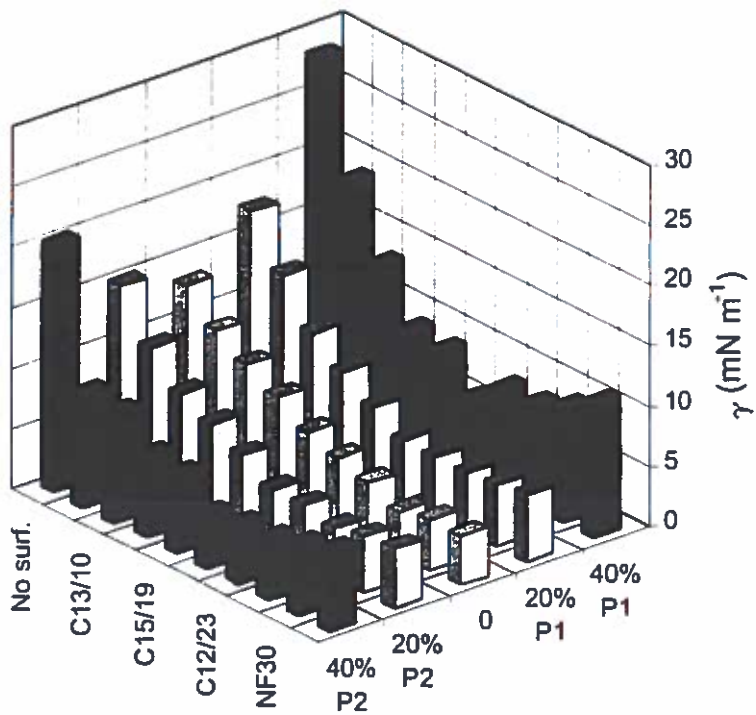
The Interfacial Tension Between Acrylic Monomers and Polymers and Non-ionic Surfactants Investigated by the Automatic Sessile Drop Method.

Finn Knut Hansen and Jørgen Hveem

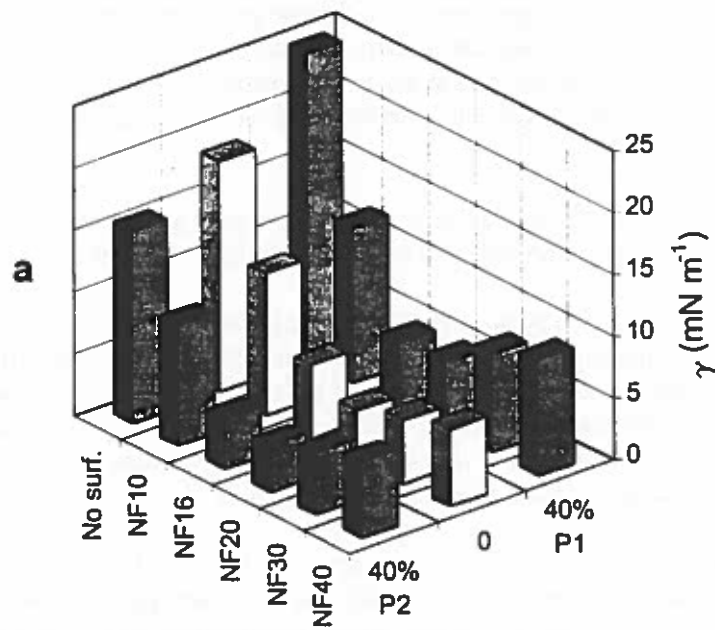
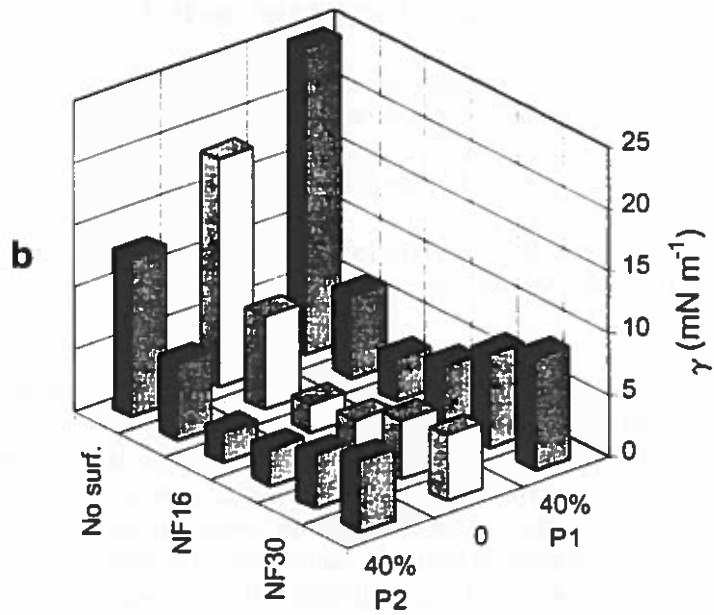
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Abstract

Time dependent interfacial tensions between CCl_4 , butyl acrylate (BA) and methyl metacrylate (MMA) and water have been measured, using nine different aryl and alkyl poly(oxyethylene) surfactants with between 10 and 40 OE-groups. The effect of adding two BA/MMA (Polymer 1) and BA/MMA/Acrylic Acid (AA) (Polymer 2) polymers to the monomer systems has also been evaluated. In all systems the interfacial tension, after a very fast initial drop, decreases slowly due to dissolution of the surfactant inside the oil. The magnitude of this decrease is dependent of the hydrophilicity of the surfactant and the oil. The equilibrium values, when plotted against the HLB of the surfactants show a minimum that shifts towards higher HLB as the oil's polarity increases. BA and CCl_4 show similar behavior, but with MMA as a more polar oil. Added polymer generally decreases the time dependent drop because of decreased surfactant solubility in monomer/polymer mixtures. The BA/MMA copolymer also generally increases the interfacial tension both with and without surfactants, but the increase is less with surfactants around the surface tension minimum. A BA/MMA/AA terpolymer neutralizes or even reverses the increasing effect in the BA/polymer system because of this polymer's more hydrophilic nature. Below are given some results. This work is submitted to J.Colloid Interface Sci.



The (a) start (γ^{EZT}) and (b) end (γ^{120}) values of the interfacial tension between MMA with 20 and 40% of polymer 1 and polymer 2 and solutions of the 9 surfactants.



The (a) start (γ^{EZT}) and (b) end (γ^{120}) values of the interfacial tension between BA with 40% of polymer 1 and polymer 2 and solutions of the 5 NF-POE surfactants.

International Polymer Colloids Group Newsletter

Contribution from Dr Alex van Herk

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In our group at Eindhoven University, currently 15 PhD students and 2 Post-docs are active in the area of polymer chemistry with a strong emphasis on emulsion polymerization:

PhD-students

Bas Pierik	: Catalytic chain transfer agents/CRP applied in emulsion polymerization
Martine Slawinski	: Emulsion copolymerization of styrene/butadiene and acrylic acid
Martin Jung	: Polymerization kinetics in ordered systems like vesicles
Camiel Peerlings	: In-situ preparation of polymer blends in emulsion copolymerization
Mark van den Brink	: On-line Raman spectroscopy in emulsion copolymerization
Wilfred Smulders	: Living Radical Polymerization applied in emulsion polymerization
Hans de Brouwer	: Preparation of functional telechelics in emulsion polymerization
John de Kock	: Chain length dependent termination in free radical polymerization
Paul Cools	: Gradient polymer elution chromatography
Harry Phillipson	: Gradient polymer elution chromatography
Gregory Chambard	: Intramolecular composition drift
Mike Schellekens	: Block copolymers as adhesion promoters for polyolefin coatings on metals
Stefan Bon	: Controlled radical polymerization
Eelco Hamersveld	: Vegetable oils in waterborne paints
Dominique Hubert	: Special particle morphologies including vesicle polymerization

Post-Docs

Amaia Montoya Goni	: Addition-fragmentation type reactive surfactants in emulsion polym.
Jozef Park	: Film formation of crosslinkable latex systems

In my contributions to the IPCG Newsletter I will mainly focus on the kinetic and mechanistic aspects of emulsion (co)polymerizations, including topics like composition drift, monomer partitioning and the application of pulsed initiation polymerization in heterogeneous systems. Complementary, Prof. German's contributions will cover the other aspects of the projects including functional monomers, reactive latices, vesicle polymerization, emulsion polymerization processes and microstructural characterization of emulsion copolymers.

To introduce the activities in the field over the past years first I will give an overview of the research strategies we followed so far, then I will focus on one specific topic which will be PLP in vesicles this time and finally a list of the pertaining publications of the past year will be given.

RESEARCH STRATEGY

MODELING AND COMPOSITIONAL CONTROL IN EMULSION CO- AND TERPOLYMERIZATION

The elucidation of the microstructure of copolymers has become feasible for some years now. Not only it is possible to determine the intramolecular microstructure in terms of e.g. sequence distributions, but also the analysis of the intermolecular microstructure in terms of molecular weight distribution and chemical composition distribution¹. Although the effect of the molecular weight distribution on properties of the polymer products is well recognized, the dramatic effects of the chemical composition distribution are certainly not, and are often neglected for convenience. Recently it was shown that copolymers of styrene and methylacrylate with the same average chemical composition but with different compositional distributions exhibited dramatic differences in mechanical properties like fracture toughness, elongation at break and E-modulus². Therefore, it is very important to be able to determine the chemical composition distribution, preferably in combination with the molecular weight distribution (MMCCD)^{3,4} and also to understand how these distributions are formed during the polymerization process. In our group much effort has been put in understanding the relations between process conditions in emulsion copolymerization and microstructure, on one hand, and between microstructure and properties, on the other hand.

We developed a model of the emulsion copolymerization process (SIEMCO)⁵ that is able to predict the kinetics and the microstructure of the formed copolymers. Recently we extended this concept to the microstructure of emulsion terpolymers (TRISEPS)⁶.

Through better understanding of the kinetics and of the thermodynamic aspects of emulsion copolymerization it became also possible to control the composition drift and to prepare copolymers with a narrow chemical composition distribution^{2,6}.

The quality of the modeling depends on the accuracy of the parameters used. One of the important aspects of copolymerization in heterogeneous systems like emulsion polymerizations is the partitioning of the monomers over the different phases present. The relevant monomer partitioning equilibria have been predicted and experimentally verified. It was observed that in all systems investigated with moderately water-soluble monomers the monomer ratio in the monomer droplets equals that in the polymer particles⁷. In the computer simulations the empirically determined monomer partitioning equilibria have been used which can be determined by gas chromatography, by conductimetry⁷, but also (in reacting systems) through pulsed laser^{8,9} and pulsed electron beam polymerizations.

Another important aspect is determination of the kinetic parameters like the propagation rate constants (k_p), the termination rate constants (k_t) and the transfer constants (k_{tr}). Pulsed laser polymerization technique is very suitable to obtain accurate propagation rate constants in homogeneous systems^{10,11}. This technique can also be applied to transparent microemulsions⁸ and even to regular lattices⁹. The new technique of pulsed electron beam polymerization¹² is even more powerful in latex systems and can be used to obtain the propagation rate constants directly in emulsion polymerizations (normally it is assumed that k_p 's determined in solution or bulk polymerizations can be transferred to emulsion systems). Heterogeneous systems, in which the radicals are compartmentalized, also conveniently allow measurement of the transfer constants through e.g. pulsed-initiation polymerization⁹. Rate constants, specific to emulsion polymerization systems like radical entry and exit coefficients can be obtained by gamma radiolysis¹³.

The quality of the predictions of kinetics and microstructure has improved very much due to the improvement of the methods of obtaining kinetic and thermodynamic parameters relevant to homogeneous and heterogeneous polymerizations. This development will also have its impact on the possibilities of designing intelligent process strategies aimed at obtaining well-defined products with better properties.

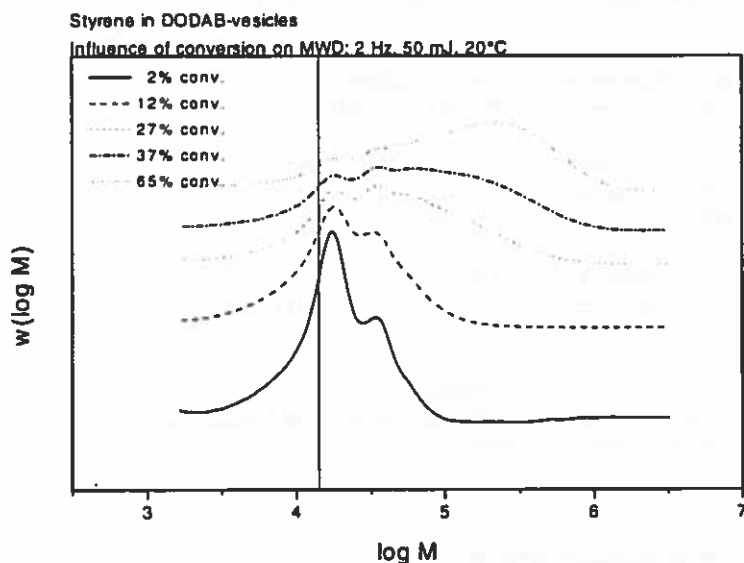
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PLP IN VESICLES

Martin Jung, PhD

The influence of organized media on polymerization reactions results in many cases in interesting morphologies of the polymeric material. In a recent study¹⁰, vesicle bilayers were used as ordered medium for the free radical polymerization of styrene. Cryo-electron microscopy gives evidence that the polymerization induces phase-separation phenomena leading to parachute-like morphologies¹⁰ (small latex particles linked to the vesicle bilayer, one per vesicle). On the basis of general knowledge about vesicles and polymerizations in heterogeneous media, the resulting morphologies can be explained. Also pulsed laser polymerizations were performed in these vesicle bilayers¹⁴ in order to obtain information about the local monomer concentrations at the site of polymerization. Assuming that the propagation rate coefficients, obtained in homogeneous media, can be applied in vesicle polymerizations, it was found the local monomer concentrations on the site of polymerization amounted to about 4 mol/l. In respect to the observed morphology of small latex particles (around 50 nm) linked to the vesicle bilayers, this low value seems reasonable.



It was also observed that below a certain concentration of photoinitiator the GPC traces no longer show the typical PLP structures. It is necessary for the chains to be initiated and terminated by the radicals generated by the laser pulses. Therefore at each pulse more than one radical per particle should be generated. If the concentration of the photoinitiator is too low (with respect to the number of particles) or the photoinitiator is consumed below a certain concentration the typical PLP peaks in the GPC trace are lost. The latter effect is observed when the GPC traces are followed as a function of conversion. At low conversion (and still sufficient photoinitiator present) the normal PLP peaks are visible in the GPC. At higher conversion one would expect the PLP peaks to shift to lower molecular weights (because the monomer concentration drops). This is not observed, instead high molecular weight material is produced for which termination is no longer controlled by the laser pulses but by alternative processes like transfer to monomer and normal bimolecular termination. In fact, from plotting the logarithm of the number distribution against the molecular weight, a chain transfer constant of $C_{tr}=5 \cdot 10^{-4}$ can be derived for styrene at 60 °C. So it is clear that during the experiment, as a consequence of the consumption of photoinitiator, the average number of radicals produced per pulse and per particle drops below one. Therefore the pulsed initiation polymerization experiment in heterogeneous systems like the vesicle polymerizations can render additional information on the compartmentalized system.

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Chlorination of Natural Rubber Latex Films

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Natural rubber (NR) latex film chlorinated by chlorine gas generated in situ from acidified hypochlorite solution at room temperature was characterised by FTIR-ATR. The presence of -CHCl-, -CCl₂- and -COOH groups were detected on the chlorinated surface. These were confirmed by SEM-EDX data using the Cl.K_α and O.K_α peaks. The level of surface chlorination increased with chlorination time and chlorine dosage as expected. The hydrophilic nature of the surface improved with the presence of these groups on the surface as reflected in a lower (water) contact angle compared with the control. Optical and scanning electron microscopy (SEM) studies show an increase in surface mean roughness, R_a, of the chlorinated surface with extent of chlorination. Severe cracking of the film surface at high chlorine concentration and extended reaction time was evident. The practical aspect of these observations in relation to the chlorination of NR latex glove manufacturing would be discussed.

1. INTRODUCTION

Chlorination, as a means of chemical modification, is often employed on NR latex film surface to reduce surface frictional resistance. This is particularly so in the manufacture of examination and household NR latex gloves to improve donning property and to reduce surface tackiness. The most direct method of chlorination is by treatment with acidified hypochlorite solution. The method is not without its shortcoming, the major one being health and safety hazards. In addition, it is beset with poor reproducibility of chlorination levels, possible deterioration in physical properties such as, ozone, wear and heat aging resistance. In spite of all these, chlorination remains the simplest and convenient way out for overcoming the donning problem of gloves. However, there is relatively little reference in the literature on the chemistry of surface chlorination of NR latex film. Early work by Noakes¹, Roberts et al² and Aziz³ gave some insight into the general chlorination process. However, investigation on its direct application on NR latex glove appears to be completely lacking. It is hoped that the present systematic study can shed some light on the mechanism of the surface chlorination process of NR latex film and thus help bring about an

improvement in the chlorination procedure which is beneficial to the industry.

2. EXPERIMENTS

Preparation of samples

Raw NR latex (HA) was used to prepare the sample. Weighed latex (10 ± 0.5 g) was poured into the leveled glass plate (12 cm X 18 cm), and allowed to dry overnight at room temperature.

Chlorination process

Chlorine gas was generated from sodium hypochlorite solution, (~ 10 % available chlorine) and dilute hydrochloric acid, (10 % w/w). Latex film still attached to the glass plate was chlorinated directly by immersing it in the solution in a closed chlorination tank.

FTIR ATR spectroscopy

A Perkin-Elmer system 2000, FT-IR spectrometer with total internal reflectance or attenuated total reflectance (ATR) accessory was used to obtain the spectrum. The penetration depth was about 5-10 μm from the chlorinated surface. A total of 128 scans was accumulated at 4 cm⁻¹ resolution. The area under

A STUDY OF NATURAL RUBBER LATEX FILM FORMATION BY ATOMIC FORCE MICROSCOPY

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Many applications of natural rubber latex depend on the coalescence of the latex particles to form a continuous film upon drying. The physical and mechanical properties of the final product are very much dependent on the extent the latex particles are able to coalesce and fuse into each other. Any factors that hinder the film formation process would result in poorly formed film and a drop in performance. The recent rapid development in atomic force microscopy has opened up new scope for this technique to be used in film formation study of soft polymeric materials such as natural rubber latex particles. With this technique it is possible to monitor the surface morphology of the film over a period of time which is not usually possible with other techniques. Effects of non rubber constituents, additives of rubber chemicals, leaching procedure on film formation were investigated. Results provide a better understanding of the film formation process of natural rubber latex.

INTRODUCTION

Surface morphology of latex film and its formation are important aspects of synthetic latex technology. Much effort has been directed towards understanding the mechanism of film formation and elucidating the structure of the latex film. A number of theoretical models have evolved over the years^(1,2,3,4). There are also numerous reports on the experimental aspect of film formation^(5,6,7,8). Morphological study of the film surface by conventional electron microscopies^(9,10,11) has contributed much to the knowledge of the film forming process. More recently atomic force microscopy (AFM) has become a very powerful tool in the study of latex film morphology because it can provide high-resolution three-dimensional images of the film surface without any sample pretreatment. It can be operated in an essentially non-destructive mode and is extremely useful for film aging studies where samples can be re-examined many times as a function of time^(12,13,14). Some latex film can be imaged within a few minutes after preparation thus, enabling the

nascent stage of film formation to be monitored⁽¹⁵⁾.

In contrast, there was very little work done on this aspect of natural rubber (NR) latex, even though NR latex is used extensively in the manufacture of gloves, prophylactics, catheters and other dipped-goods which also involve film formation of the latex particles. Apart from the much larger particle size and wider size distribution, one obvious difference between synthetic and NR latex is that for NR latex, the film forming process in most commercial applications is usually brought about by a destabilising agent: chemicals in the dipping process and heat in the heat-sensitized gelation process⁽¹⁶⁾. It is thought that once initial contact between the latex particles is achieved by gelation following the uniform destabilisation of the latex particles, dehydration of the aqueous phase retained in the interstices of the three-dimensional gel network of latex aggregates follows. In addition, since commercial high-ammonia NR latex contains a host of non-rubber constituents and other processing additives that are retained in the aqueous phase in the

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The immobilisation of biomaterials at polymeric surfaces is an important interfacial phenomenon spanning a wide spectrum of disciplines, from biofouling of shiphull to biocompatibility of surgical implants. Immunoassay is an area which partially depends on the immobilisation of binder proteins on polymeric substrate for detection of trace amount of biomolecules. Stable and reproducible binding of antigens or antibodies to a solid substrate is a pre-requisite for high resolution modern immunoassay. The success of the assay relies on the good control of selective adsorption and binding of the appropriate biomolecules by the immobilised binder proteins at the substrate surface. In solid phase immunoassay, the solid matrices are often based on simple adsorption antigens or antibodies on polymer substrates such as polypropylene (PP) and polystyrene. Covalent binding is sometimes introduced to overcome problems such as non-specific adsorption of immunoreagents and desorption. Thus a detailed understanding of the adsorption processes is urgently needed to provide better control and manipulation of protein adsorption at the interface.

To date many physical techniques have been applied to the study of protein adsorption at the solid-liquid interface, for examples: ellipsometry, surface plasmon resonance, surface enhanced Raman spectroscopy, scanning electron microscopy (SEM) and more recently atomic force microscopy (AFM). The last technique appears to be ideal for the direct study of adsorptive processes. It generates a real-space topographic image of a surface with high lateral and vertical resolutions. This technique is employed in the present study to investigate the adsorptive behaviour of horse hepatitis B antibody (anti-HBs), hepatitis B antigen (HBsAg), anti-thyroxine (anti-T4), and hepatitis C virus (HCVAg) on natural rubber (NR) latex film surface to assess its possible use as a substrate in immunodiagnosics. The adsorption of these biomaterials on the usual PP substrate was also carried out for comparison purposes and the adsorptive behaviour was further corroborated by SEM.

The modes of adsorption of these proteins on the two substrates were strikingly different. Adsorption on NR latex film surface appeared to display random nucleation over the surface resulting in clusters of aggregates of differing sizes. These clusters gave the appearance of being partially submerged into the latex film itself and less than half of the substrate surface was covered by these clusters. There is also a variation in cluster size of the adsorbed binder proteins, decreasing in the order of HBsAg > anti-HBs > anti-T4 which is in the same order as their molecular weights.

In general, the PP surface was more evenly coated by the above biomaterials, the coating appeared flat and thin giving the impression that denaturation could have occurred during adsorption. Nonetheless the adsorption appeared patchy and some bare substrate surface remained uncovered. The larger surface coverage of these immobilised binder proteins on the PP, in comparison to the NR latex film surface, was reflected in higher bindings found for serum antigen and antibodies using this substrate. Further variation in adsorption mode was noted among the various biomaterials on the same substrate. On PP surface, anti-HBs gave rather flat adsorbed thin layer of thread-like and dendrite-like features whereas anti-T4 produced both tiny globular structures and large star-shaped structure with extending fibrils that appeared to bear the mark of materials left behind by evaporation of some large drying droplets. As for HCVAg, relatively dense adsorption of bundles of elongated strands covering most of the PP substrate was seen.

The contrasting behaviour of the binder proteins on PP and on NR latex film surface could be attributed to the different hydrophobicity and the chemical characteristics of these surfaces. The interaction of binder proteins with different chemical natures with the same substrate surface further contributed to the diverse features of adsorbed protein shapes observed. Both the SEM and AFM techniques gave concurring results.

Novel Dip-Processed Natural Rubber Latex Film Containing Palm Oil

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ABSTRACT

The blending of palm oil-in-water emulsions with natural rubber (NR) latex to modify the vulcanisation process is a new development in NR latex technology. Previous investigation has shown that the pre-vulcanisation of NR latex film containing palm oil, with zinc dibutyl dithiocarbamate (ZDBC) as the accelerator, can be achieved faster than that with NR latex alone. The significance of this finding is that, the concentration of the vulcanising agents can be reduced and the process of making latex-dipped goods can be shortened considerably. Furthermore, thermal oxidative ageing of NR latex was slowed down in the presence of palm oil. When zinc dibenzyl dithiocarbamate (ZTC), a very slow accelerator, was used together with palm oil, pre-vulcanisation was almost absent. After post-vulcanisation, tensile strength of the film prepared was significantly higher than film without palm oil. ZTC does not produce nitrosatable amine intermediates which are carcinogenic. Its compound also has a longer storage life and can be kept up to two months at room temperature without adverse effect on tensile properties. In general, the modulus, the tensile strength and the elongation at break of the NR latex vulcanisates decreased with an increase in palm oil concentration. Thicker products could be made without sacrificing softness of NR latex film which usually could only be achieved with normal product thickness.

INTRODUCTION

Recent new development in environmental-friendly products has generated special interest in the potential use of vegetable oils such as palm oil in industrial processes and as additives. Both palm oil and natural rubber are important primary commodities of Malaysia and thus could provide considerable synergistic advantage if some combined usage can be achieved. Oil acts as a diluent in rubber products and a known application of mineral oil in the industry is the oil-extended styrene butadiene rubber. Oil-extended natural rubber has also been introduced and its effect on tyre properties was compared to those of oil-extended styrene butadiene rubber [1]. Depending on the type of mineral oil used, some are not biodegradable and adds to the increasing environmental pollution. An example is aromatic oil containing polycyclic hydrocarbons which are toxic to human and the environment [2].

Nevertheless, information on the use of mineral oils in NR latex is almost non-existent. The use of vegetable oil viz. rice bran oil in the compounding of styrene butadiene rubber was reported by Kuriakose and Rajendran [3]. It was found that rice bran oil can replace conventional oils used as processing aids in rubber compounding without affecting the vulcanisate properties. The effect of mineral oil as a diluent in NR latex vulcanisates was confirmed [4]. At various dosage of tellus oil, C10 (Shell), added in the form of an oil-in-water emulsion to NR latex compounds, decreasing modulus of NR latex vulcanisates was observed with increasing amount of oil.

This paper deals with the use of palm oil in the form of palm oil-in-water emulsion in modifying the process of crosslinking of NR latex by sulfur vulcanisation. It was observed that NR latex in the presence of palm oil droplets, under specific conditions, showed an increase in particle size. This was associated with the absorption of palm oil and subsequent swelling of the latex particles [5].

Even though this increase is not substantial, i.e. about 1.5 times, the possibility of such swollen latex particles to have a better efficiency in capturing vulcanising agents was seriously considered. Indeed, it was further proven that when palm oil emulsion was added to NR latex and allowed to incubate at the required temperature, prior to the addition of vulcanising agents, an increase in both modulus and tensile strength was observed for films (without heating) containing palm oil. Improved pre-vulcanisation of NR latex particles, which is essential for latex-dipped process was achieved using ZDBC as an accelerator. A certain degree of pre-vulcanisation is important to realise

INFLUENCE OF ALKALI SOLUBLE RESIN ON LATEX FILM MORPHOLOGY OF POLY(BUTYL METHACRYLATE) STUDIED BY AFM

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ABSTRACT

A series of mixture of monodisperse poly(butyl methacrylate) (PBMA) latex particles and alkali soluble resin (ASR) was prepared to investigate the effects of ASR on PBMA film structure and individual morphology of particles using the atomic force microscopy (AFM). It has been found that the more instances of disruption to regular packing of particles, such as more holes, cracking, dislocations in regular arrays, and domains of random arrangement of particles in film with addition of ASR into the PBMA latexes. In addition, the "dent" appeared on the latex particle surfaces and the number of particles with dent was increasing with ASR concentration, annealing temperature, and annealing time.

INTRODUCTION

Emulsion polymer latex is an important industrial product used for coatings, adhesives, thermoplastics. Film formation process from emulsion polymer latexes have been the subject of much attention theoretically and experimentally.^{1,2} It depends on the viscoelastic properties and on the morphology of the latex particles. This film process has been studied by non-radio fluorescence energy transfer attenuated total reflectance FT-IR, small angle neutron scattering (SANS), and freeze fracture and atomic force microscopes (AFM).^{3,4} Little is known, however, about the mechanism of the ASR as a polymeric emulsifier on latex film formation. It is well known that the amphiphilic polymers which consist of both hydrophobic and hydrophilic groups can stabilize polymer particles as the intermolecular and/or intramolecular hydrophobic interaction.^{5,6} Several patents have claimed the use of durable emulsion polymers prepared using these types of resins,⁷⁻¹¹ which has been applied to a variety of substrates such as floor tiles, countertops, wall and shower tiles and so forth.

In the present work, we report the first experiments which describe the influence of ASR on film formation and individual latex particle morphology with AFM.

EXPERIMENTAL

Materials and polymerization

Distilled water was used throughout. Butyl methacrylate (BMA) were purchased from Junsei Chemical Co. (Japan). They were purified by vacuum distillation and stored in a refrigerator. The initiator was potassium persulfate (KPS : Samchun Pure Chemical Ind., Ltd. (Korea)). The SAA, poly(styrene/alpha-methylstyrene/acrylic acid) [Mn : 4,300, Mw : 8,600, acid number : 190], obtained from Morton Inc(USA) was used as received. The other chemicals used were of reagent grade

The polymerization were performed in a double-wall 2 L glass reactor by emulsifier-free emulsion polymerization at 70 °C.

Latex Purification

All latex samples were purified by ion-exchange and serum replacement technique until conductivity and surface tension were < 10⁻¹ ohm⁻¹ cm⁻¹ and 72-73 mN m⁻¹, respectively. Under conditions of low salt, no ionic surfactant, and monodisperse particles, charge-stabilized latex particles undergo spontaneous ordering in water. This face-centered cubic (FCC) structure is preserved as the water evaporates.

Film Preparation

Films were prepared by pouring a few drops of the mixture of PBMA latex and resin solution onto a freshly cleaved mica surface (cut into squares of ca. 10 mm x 10 mm) and allowing the film to dry slowly at room temperature in a desiccator. The effects of aging at elevated temperatures were investigated by annealing in a convection oven, at temperatures of either 25, 60, 70, 90 °C for various lengths of time. After annealing, the samples were returned to a desiccator, in readiness for imaging by AFM.

Measurements

Particle Size and Distributions

The particle diameter and distribution of particles was determined by the particle size analyzer (Capillary Hydrodynamic Fractionation, CHDF-1100, Matec Applied Sciences)

Glass Transition Temperature

The glass transition temperature was analyzed by DSC (Polymer Laboratory, U.K) in nitrogen flowing atmosphere at heating rate of 10 °C/min.

Molecular Weight

The molecular weight was determined by gel permeation chromatography (GPC) in tetrahydrofuran solution and is based on polystyrene standards.

Atomic Force Microscope

All films were imaged with a Nanoscope III from Digital Instruments, Inc. The images were recorded with the piezoelectric scanner that has a lateral scan area of up to 12 x 12 μm². Image was recorded in the Tapping mode, under ambient conditions, in air. In this way, a three-dimensional image is produced by recording the z direction while scanning the sample in the x and y directions.

RESULTS AND DISCUSSION

Fig. 1 shows the three-dimensional images of PBMA films. The images of (1) and (2) are of the pure PBMA latexes, prepared at 70 °C. The surface structure of homopolymer films has a high degree of order, surface layer of latex particles is even with hexagonal packing of the latex. As the annealing time is increased, 'holes' formed by missing latex particles in the hexagonal arrays are observed within the layer. There are also sunken areas within the outermost top layer which is best interpreted as due to 'holes' in the layer below. These became apparent as a result of the softening of the latex particles at higher annealing temperature: the particle in the top layer sagged slightly into the 'hole' below upon softening on annealing. In contrast, when the SAA resin was added to PBMA homopolymer latex, the observed morphology is much different. The irregular packing of latex particle was observed and deviations from size mono-dispersity occurred.

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(1) Novel Crystallization Process in Dilute Ionic Colloids. After homogenizing a colloidal silica dispersion (volume fraction: 0.0183, particle radius: $0.053\mu\text{m}$, effective charge density: $0.25\mu\text{C}/\text{cm}^2$) by shaking, H. Yoshida (Polymer Phasing Project, ERATO, Japan Science and Technology Corporation, Seika, Kyoto 619-02) et al. carried out confocal laser scanning microscope (CLSM) observation in the internal region of the dispersions (up to $200\mu\text{m}$ from the coverslip surface) and found that space-filling bcc grains were first formed at $t < 40$ sec. Then disordered liquid-like regions were observed to develop inside the space-filling crystalline grains resulting in "cheese-with-holes-like" structures. Many small disordered regions were found at $t = 8$ min, but their average sizes increased while their number decreased with t . The disordered regions close to the grain-grain interfaces were extruded from the grains and formed the interstitial disordered region while those inside the grains formed spherical disordered regions. The USAXS profile at $t = 24$ hrs showed powder-like diffraction peaks due to the (110), (200), (211), (220) and (310) planes. The lattice constant was confirmed to be $0.376\mu\text{m}$ after $t = 8$ min. Although the USAXS study could not be carried out at $t < 40$ sec, we expect the spacing to be $0.408\mu\text{m}$ from the space-filling nature. Obviously a contraction took place between $t = 40$ sec and 8 min. An interpretation could be that, just after homogenization

($t \sim 0$), particles had kinetic energies larger than the potential minimum of the effective pair potential so that they formed a space-filling ordered structure according to the "seeming" repulsion-only mechanism and, as time passes, they lost the excess energy and were trapped in the potential minimum to form the non-space-filling structure. The transient space-filling structure in the early stage of crystallization could be observed by a fortunate combination of the experimental variables and was not inconsistent with our constant claim of the long-range attraction. (H. Yoshida et al., *Langmuir* in press.)

(2) Re-entrant Solid-Liquid Transition with Increasing Charge Number. Yamanaka (Polymer Phasing Project, ERATO, Japan Science and Technology Corporation, Sakyo, Kyoto 606) et al. examined the solid-liquid transition at 25°C in aqueous dispersions (volume fraction : 0.03) of two kinds of silica particles (radius: 0.06 and 0.05 μm) as a function of the analytical charge number (σ_a) by controlling the amount of sodium hydroxide to be added. The salt concentration (C_s) at the phase boundary increased first with increasing σ_a and, after passing a maximum, decreased. The USAXS measurements gave four orders of the Bragg diffraction at $q = 2.4 n \times 10^{-3} \text{ \AA}^{-1}$ (with n being an integer) in the solid region ($\sigma_a = 0.96 \mu\text{C}/\text{cm}^2$, $C_s = 10^{-5}\text{M}$), while those in the liquid region ($\sigma_a = 0.1 \mu\text{C}/\text{cm}^2$, $C_s = 10^{-5}\text{M}$) showed a broad peak on the top of the form factor due to an isolated sphere. It was concluded that the crystal had a bcc symmetry with a lattice constant of 0.376 μm , d_{110} of 0.266 μm , and the closest interparticle distance ($2D_{exp}$) of 0.326 μm . The same profile in the solid region was observed at multiple angles of 60° of rotation of the capillary around the capillary axis, indicating that the crystal was of a six-fold symmetry and the [111] direction was parallel to the capillary wall. (J. Yamanaka et al., *Prog. Coll. Interface Sci.* in press)

Recently, the 3D-phase diagram was experimentally determined as functions of C_s , σ_a and ϕ . In the ϕ range between 0.02 and 0.04, monotonic increase in σ_a at constant C_s caused

liquid-solid-liquid transition. A similar re-entrant transition was also observed for polymer latex particles at high charge densities. It is recalled that the Monte-Carlo simulation using the Sogami potential predicted the homogeneously ordered to inhomogeneously ordered and/or disordered (coexisting with voids) transition at high charge density, while the homogeneous to inhomogeneous transition could not be reproduced by the DLVO potential (B.V.R. Tata and N. Ise, *Phys. Rev. B* 54, 6050 (1996) and also see below). Yamanaka et al. furthermore demonstrated that such a re-entrant solid-liquid transition could not be accounted for in terms of Robins et al.'s treatment using the DLVO potential, which gave a satisfactory agreement with experiments only at very small σ_a . (J.Yamanaka et al. in preparation)

(3)Monte-Carlo Study of Structural Ordering in Charged Colloids Using Long-Range Attractive Interaction. Tata (Visiting Scientist, Rengo Co., Ltd. Osaka 553: Permanent Address: Indira Gandhi Centre for Atomic Research, Kalpakkam, TN, India) and Ise further performed a detailed Monte-Carlo simulation for aqueous charged colloidal dispersions using the Sogami potential $U_s(r)$ and the DLVO potential $U_d(r)$ over four orders of magnitude of particle volume fractions (ϕ) under salt-free as well as added salt conditions. The computed pair correlation function $g(r)$ showed a fcc crystalline order at high ϕ 's, which is found to transform to a bcc crystalline order upon lowering of ϕ . The crystalline order is found to melt into a liquid-like order upon addition of salt. Earlier $U_d(r)$ was claimed to be responsible for the formation of bcc, fcc and the associated order-disorder transitions. It is now clear that $U_s(r)$ also explained equally well such phenomena and the simulation results were shown to be in close agreement with experiments. The simulations in the dilute regime reproduced vapor-liquid transition upon variation of ϕ and also the coexistence of ordered and disordered regions with voids upon variation of the particle

charges. It should be remarked that the void structure could not be reproduced by $U_d(r)$. At very low volume fractions, $g(r)$ showed only a single peak and was found to be independent of ϕ as was recently reported. Further discussion was given on recent direct measurements of the pair potential (B. V. R. Tata and N. Ise, in preparation.)

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Paper presented at the 8th RC1 User Forum Europe, held in Lugano, Switzerland, November 2-6, 1997.

A LOOK AT THE KINETICS OF METHYL METHACRYLATE POLYMERIZATION

P. E. Gloor, R. J. Warner, S. Mohammed, S. Blechinger, K. E. Sorenson and M. A. Villalobos

ABSTRACT

Polymers of methyl methacrylate are industrially important, having a wide range of applications from Plexiglas to paints. These polymers are made using bulk, solution and emulsion free radical polymerization processes

The kinetics of methyl methacrylate (MMA) polymerization has been studied for sometime. MMA polymerization is interesting because of the large auto acceleration in rate observed as the conversion increases and because of limiting conversion as the reaction mixture solidifies into a glass. Many authors have tried to, mathematically, model the rate of polymerization, testing the models against the conversion versus time data. These models seem to adequately represent the conversion history, however, they can give very different rate of polymerization versus conversion (or time) profiles. The rate of polymerization is more difficult to determine from conversion versus time data because it requires differentiation of a limited set of discrete data. The rate of reaction is often used for reactor design, so these model differences have industrial importance.

In this study, we determine the rate of polymerization directly using reaction calorimetry (Mettler - Toledo RC1) to measure the heat flow. Suspension polymerization techniques are used to polymerize the monomer and maintain adequate viscosity and heat transferr. These data are then compared to some of the mathematical models found in the literature.

CONTRIBUTION FROM DSM RESEARCH TO THE INTERNATIONAL POLYMER COLLOIDS GROUP NEWLETTER

Appeared in *Macromolecules* **1998**, 31, 1621-1626:

Intermolecular Interactions between Dendrimer Molecules in Solution Studied by Small-Angle Neutron Scattering

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ABSTRACT: Small-angle neutron scattering has been applied for structural investigations of amine-terminated poly(propylene imine) dendrimer (Astramol™) solutions in D₂O as a function of concentration and acidity. The forward scattering, $d\Sigma/d\Omega(Q=0)$, decreases progressively by increasing dendrimer concentration due to interdendrimer interference, giving rise to a well-defined interference peak. Upon increasing dendrimer concentration, a shift is observed in the peak position, Q_{\max} , with the empirical scaling relation $Q_{\max} \sim \phi^{0.55 \pm 0.05}$, which is significantly larger than that of a simple packing argument $Q_{\max} \sim \phi^{1/3}$. At high Q values, all data sets collapse to a single curve, indicating that the internal structure of the dendrimers are unaffected by interactions between neighboring molecules. Upon addition of acid, the dendrimers become charged, giving rise to a pronounced interference peak. These Coulomb interactions can be screened by addition of either excess acid or salts.

Appeared in *Macromolecules* **1998**, *31*, 456-461:

The Molecular Characteristics of Poly(propyleneimine) Dendrimers as Studied with Small-Angle Neutron Scattering, Viscosimetry, and Molecular Dynamics

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ABSTRACT: The molecular characteristics of the first five generations of poly(propyleneimine) dendrimers with two different types of end groups have been investigated using small-angle neutron scattering (SANS), viscosimetry, and molecular dynamics simulations. The dimension of the poly(propyleneimine) dendrimers, as measured by both SANS and viscosimetry, increases linearly with the generation number and roughly as $M^{1/3}$, where M is the molar mass of the dendrimer. This relationship proves to be independent of the character of the end group and the solvent used and is indicative of a compact (space-filling) structure with a fractal dimensionality of approximately 3. The distinct maximum in the Kratky representation of the scattering data and the observed relation (i.e. $R_h \cong \sqrt{5/3}R_g$) between the hydrodynamic radius R_h and the radius of gyration R_g are consistent with such a structure. Molecular dynamics simulations for two different solvent qualities, are in good accordance with the acquired experimental results. The probability distributions of the amine end groups, based on these simulations, exhibit a substantial degree of backfolding. The corresponding radial density distributions show a constant density plateau and a monotonic decrease of the density toward the exterior of the molecule. The Above results indicate that the poly(propyleneimine) dendrimers can be considered as flexible molecules with a relatively homogeneous radial density distribution. This view clearly deviates from both the dense shell and dense core models.

Accepted for publication in *Macromolecules* 1998:

Polyelectrolyte Behavior of Astramol™ poly(propyleneimine) dendrimers.

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M.F. Zansochova*, J.G.H. Joosten**, J. Brackman**

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ABSTRACT: Polyelectrolyte behavior of Astramol™ poly(propyleneimine) dendrimers of five generations, DAB-*dendr*-(NH₂)_x (where x is equal to 4,8,16,32 or 64) was studied by means of potentiometric titration in salt-free water solutions and also in the presence of a shielding low molecular electrolyte (NaCl). In addition to x outer primary amine groups the dendrimer molecule contains x-2 inner tertiary amine groups. It was found that in the case of three lower generation dendrimers the pH intervals of protonation of primary and tertiary amine groups can be discriminated.

However, they are considerably overlapped in the case of the higher generations because of a strong electrostatic interaction between the charged units within the dendrimer structure. The extent of such overlapping decreases somewhat in the presence of a shielding simple salt.

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

Preparation of Small Sized Carboxylate Latexes by Emulsion Polymerization Using Alkali-Soluble Random Copolymer

- DY Lee and JH Kim

Alkali-soluble random copolymer (ASR), poly(styrene/alpha-methyl styrene/acrylic acid) [Mn: 4,300, acid number: 190], was used as a polymeric emulsifier in the emulsion polymerization of styrene and methyl methacrylate, respectively. ASR containing a large number of carboxyl groups could form aggregates like micelles and the solubilization ability of the aggregates was dependent on the neutralization degree of ASR. The polystyrene (PS) latexes prepared using ASR showed the small particle size (ca. 40 nm) and 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. The thin layer chromatography/flame ionization detector (TLC/FID) analysis confirmed that the grafting reaction of PS to ASR occurred during emulsion polymerization. The potentials of final latexes showed high values due to ASR which was adsorbed and grafted on the surface of the latex particle.

- Accepted and published soon, J. Appl. Polym. Sci.(1998)

Kinetics of Latex Film Formation of PBMA Latex in the Presence of Alkali Soluble Resin Using Atomic Force Microscopy - YJ PARK, MC KHEW, CC HO, and JH KIM

The effect of alkali soluble resin (ASR), poly(ethylene-co-acrylic acid), post-added to emulsifier-free monodisperse poly(butyl methacrylate) (PBMA) latexes on the kinetics of film formation was investigated using atomic force microscopy (AFM). Corrugation height of latex particles in films was monitored at various annealing temperatures as a function of annealing time. Enhanced polymer diffusion was found in latex film containing ASR regardless of annealing temperature. With increasing annealing temperature, much higher rate of polymer diffusion was found in latex film containing ASR. These results can be interpreted that the

low molecular weight and low Tg EAA resin adsorbed at the particle surface is more susceptible to diffusion than that of the PBMA in the film formation stage, thus it enhances the mobility of PBMA polymer.

- Accepted, *Colloid Polym. Sci.* (1998)

Effects of Carboxyl Groups Dissociation and Dielectric Constant on Particle Size of Polyurethane Dispersions - SH SON, HJ LEE, and JH KIM

Aqueous polyurethane (PU) dispersions were prepared by pre-polymer mixing and neutralization emulsification method. PU dispersions were electrostatically stabilized with carboxyl groups incorporated into their particles, which are neutralized by triethylamine (TEA). The reaction parameters were molecular weight of polyol, amount of chain extender, TEA/dimethylolpropionic acid(DMPA) mole ratio, and the dielectric constant of the dispersion medium. The average particle sizes ranged between 27 and 415 nm. Due to an enlargement of the stabilization site, the particle size decreased as the concentration of carboxyl groups and the degree of neutralization increased.

- Accepted, *Colloid & Surfaces A.* (1998)

Selected Recent Journal Publications

1. Effects of Carboxyl Group and Dielectric Constant on Particle Size of Polyurethane Dispersions - SH SON and JH KIM, *Colloid and Surfaces A*, 133(3), 295 (1998).
2. Simulation of Secondary Particle Formation in Seeded Emulsion Polymerization – Effect of Surface Charge Density of Seed Particle - IW CHEONG and JH KIM, *Macromol. Theory Simul.*, 7, 49 (1998).
3. Effects of Interfacial Chain Structure on Toughening Behavior in Rubber Modified Poly(methyl methacrylate) – HJ HA, YJ PARK, JH AN, and JH KIM, *Polymer Int.*, 44, 490 (1997).

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 R/F Emulsion Gel Using Supercritical Fluid.
4. Kinetics Study on Modification of Polyurethane Dispersion.
5. Synthesis and Characterization of Structured IPN Latexes with Damping Properties.

Leiden Colloid and Interface Science Group

Acid-base properties of poly(propylene imine) dendrimers

RC vanDuijvenbode, M Borkovec, GJM Koper

Potentiometric titration experiments of poly(propylene imine) dendrimers (up to the fifth generation) were carried out at salt concentrations of 0.1, 0.5 and 1.0 M KCl and NaCl. The experiments were performed at two different locations on different instruments and were converted to titration curves using two different methods, resulting in a consistent experimental data set for the dendrimers measured. The titration curves feature two distinct steps around pH 6 and 10 with an intermediate plateau at 2/3 of the total ionizable groups. This protonation pattern reflects short-ranged repulsive interactions between ionizable sites and can be modeled using an Ising model with nearest-neighbour pair interactions. The intermediate plateau results from the stability of an onion-like structure where all odd shells of the dendrimer are protonated, while the even ones remain deprotonated. The Ising model permits a quantitative analysis of the titration curves. For larger dendrimers, this Ising approach is shown to be superior to the classical analysis in terms of successive protonation equilibria.

To appear in POLYMER

Kinetics of particle adsorption in stagnation point flow studied by optical reflectometry

MR Böhmer, EA van der Zeeuw, GJM Koper

The kinetics of adsorption of nano-sized silica particles on a polymer pretreated surface were followed in situ by using optical reflectometry in a stagnation point flow setup. Conversion of the reflectometric signal to the surface coverage could be performed using a homogeneous slab model which was verified by determining the particle density on SEM pictures taken in the stagnation point and by comparison with a model which includes the particulate nature of the layer explicitly. The effects of salt concentration on the plateau adsorbed amounts for all particle sizes can be described with an effective hard sphere concept. Although initial slopes and plateau values are in reasonable agreement with a random sequential adsorption model, this model does not accurately describe the evolution of the surface coverage as a function of time in a stagnation point flow system.

To appear in J Colloid Interf Sci

Protonation mechanism of poly(propylene imine) dendrimers and some associated oligo amines

GJM Koper, MHP van Genderen, C Elissen - Roman, MWPL Baars, EW Meijer, M Borkovec

The protonation behavior of poly(propylene imine) dendrimers and some related oligo amines has been measured using natural abundance N-15-NMR. The chemical shifts of the different shells of nitrogen nuclei as a function of pH have been directly interpreted as the degree of protonation for that shell. The thus obtained protonation behavior is described systematically using the Ising model which only requires values for the intrinsic protonation constants and for the pair interaction free energies between the different nitrogen nuclei. This subsequently leads to a quantitative description of the titration curves of the individual shells and to a rationalization of the microscopic and macroscopic equilibrium constants for these molecules.

Appeared in JACS 1997, 119, 6512-6521

On the difference in ionization properties between planar interfaces and linear polyelectrolytes

M Borkovec, J Daicic, and GJM Koper

Ionizable planar interfaces and linear polyelectrolytes show markedly different proton-binding behavior. Planar interfaces protonate in a single broad step, whereas polyelectrolytes mostly undergo a two-step protonation. Such contrasting behavior is explained using a discrete-charge Ising model. This model is based on an approximation of the ionizable groups by point charges that are treated within a linearized Poisson-Boltzmann approximation. The underlying reason as to why planar interfaces exhibit mean-field-like behavior, whereas linear polyelectrolytes usually do not, is related to the range of the site-site interaction potential. For a planar interface, this interaction potential is much more long ranged if compared with that of the cylindrical geometry as appropriate to a linear polyelectrolyte. The model results are in semi-quantitative agreement with experimental data for fatty-acid monolayers, water-oxide interfaces, and various linear polyelectrolytes.

Appeared in PNAS 1997, 94, 3499-3503

CONTRIBUTIONS TO THE INTERNATIONAL POLYMER COLLOIDS GROUP
FROM EMULSION POLYMERS R&D, THE DOW CHEMICAL COMPANY

Do Ik Lee

THE CRITICAL PIGMENT VOLUME CONCENTRATION CONCEPT FOR PAPER
COATINGS:

I. MODEL COATING SYSTEMS USING PLASTIC PIGMENTS AND LATEX BINDERS
FOR PAPER COATING APPLICATIONS*

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

The immobilization and consolidation of the model coatings based on the plastic pigment and latex binder of known particle sizes were theoretically studied in terms of the dense random packing of binary spheres and varying extent of latex film shrinkage. The porosity of the model coatings was calculated based on three proposed latex shrinkage models: Maximum, Minimum, and Linearly Decreasing Latex Shrinkage. The increasing extent of latex shrinkage was calculated up to the critical pigment volume concentration (CPVC) as a function of plastic pigment volume fractions, and the maximum latex shrinkage was estimated from the CPVC. Also, the number of pores and the average equivalent spherical pore diameters were calculated based on those proposed models. The opacity and gloss of the model coatings on polyester films were measured and their porosity was also determined by a simple coat weight-thickness method. As expected, various coating structure-property-composition relationships, such as opacity, gloss, porosity, etc., were shown to exhibit sharp transitions near the CPVC. The CPVC values determined by the opacity, gloss, and porosity vs. PVC relationships, respectively, agreed very well with each other. Especially, the CPVC's determined by the opacity and porosity vs. PVC curves were identical. The comparison between the theoretically calculated and experimental porosity values showed that the intermediate value between the maximum and minimum latex shrinkage would best fit the experimental porosity data. The effect of plastic pigment particle size on the optical properties and porosity of model coatings was also studied and it was observed that the coating opacity and porosity increased with increasing plastic pigment particle size, but the gloss decreased. The ink gloss of the uncalendered model coatings applied onto commercial sheet offset coated papers was shown to be affected by both the coating gloss and porosity: the higher the coating gloss, the higher the ink gloss, but the higher the coating porosity, the lower the ink gloss. Their printability was also studied in terms of the number of passes-to-fail and the rate of ink setting as a function of both plastic pigment volume fractions and plastic pigment particle sizes. A minimum crack-free temperature (MCFT) of latex-bound coatings was proposed to better predict the behaviors of latexes as coating binders. The wet state of model coating dispersions, the surfaces of consolidated model coatings, and their internal structure were examined by both electron and atomic force microscopy, and their micrographs were found to be consistent with our immobilization and consolidation models.

* *Presented at the 1998 TAPPI Coating Conference in May 3-6, 1998 in New Orleans.*

Dr. Peter A. Lovell

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UK Polymer Colloids Forum

The booklet of profiles of all UK academics who are active in the field of Polymer Colloids that I mentioned in the previous newsletter was published late last year. Each profile has full contact information and comprises a one-page overview of the research interests, expertise and facilities available to the academic in the form of a bulleted list. I plan to send all IPCG members a copy of the booklet this Summer.

Recent Papers**"Chain Transfer to Polymer in Free-Radical Solution Polymerization of n-Butyl Acrylate Studied by NMR Spectroscopy"**

N.M. Ahmad, F. Heatley and P.A. Lovell, *Macromolecules*, **31**, 2822-2827 (1998)

Abstract: The effects of the initial monomer concentration, $[M]_0$, and % conversion on the extent of chain transfer to polymer in free-radical solution polymerization of n-butyl acrylate has been studied. The polymerizations were carried out in cyclohexane at 70 °C using 0.1 % (w/w) 2,2'-azobis-(2-cyanopropane) as initiator and the mol% branched repeat units (mol% branches) in the poly(n-butyl acrylate) was determined from unique resonances of branch-point carbons in the ^{13}C NMR spectra. At $[M]_0 > 10$ % (w/w) the mol% branches is independent of $[M]_0$ and increases from 0.8 to ~2.2 % as conversion increases from 35 to ~95 %. However, for more dilute solutions, with $[M]_0 \leq 10$ % (w/w), the mol% branches increases as $[M]_0$ decreases and is higher than at equivalent conversions for the more concentrated solution polymerizations, e.g. at ~25 % conversion the mol% branches increases from 2.7 % for $[M]_0 = 10$ % (w/w) to 5.9 % for $[M]_0 = 3$ % (w/w). These observations are explained in terms of the ratio of the concentrations of polymer repeat units and monomer in the vicinity of the propagating chain end. In more concentrated solutions, intermolecular chain transfer to polymer dominates because, at all except the lowest % conversions, the overall polymer repeat unit concentration is sufficient for overlap of individual polymer coils. However, in the dilute solutions the overall polymer repeat unit concentration is too low for overlap of individual polymer coils and intramolecular chain transfer to polymer dominates. Under these conditions, the local polymer repeat unit concentration within the isolated propagating chains is defined by the chain statistics and so is approximately constant, whereas the monomer is distributed uniformly throughout the solution. Thus, for dilute solutions, as $[M]_0$ decreases, the probability of chain transfer to polymer (and hence the mol% branches) increases.

"Chain Transfer to Polymer in Free-Radical Bulk and Emulsion Polymerization of Vinyl Acetate Studied by NMR Spectroscopy"

D. Britton, F. Heatley and P.A. Lovell, *Macromolecules*, 31, 2828-2837 (1998)

Abstract: Chain transfer to polymer in free-radical bulk and emulsion polymerization of vinyl acetate has been studied using ^{13}C NMR spectroscopy. The poly(vinyl acetate) (PVAc) spectra have been fully interpreted in terms of structural features arising from (i) normal and inverted repeat unit placements, (ii) chain transfer to polymer and (iii), in the case of emulsion polymerization, hydrolysis of acetate side-groups. Although evidence was obtained for chain transfer to polymer via H-abstraction from both backbone tertiary C-H bonds and methyl side-groups, the latter make the dominant contribution. The spectral assignments facilitated calculation of the mol% branches and the mol% of inverted repeat units in the PVAc samples produced, the latter quantity taking values of 1.44 ± 0.24 mol% independent of conversion in the emulsion polymerizations. The absence of an initiator effect in the bulk polymerizations shows that the propagating PVAc chain radicals are the principal hydrogen atom abstractors. In both bulk and emulsion polymerization, the mol% branches increased steadily with overall conversion. However, because the emulsion polymerizations proceed almost exclusively within the latex particles and at high instantaneous conversions, the levels of branching in the PVAc produced (final levels = 0.61-0.75 mol%) were much higher than in the PVAc produced by bulk polymerization (final levels = 0.13-0.23 mol%). Increasing the temperature of emulsion polymerization from 60 to 70 °C led to an increase in the mol% branches but had no measurable effect on the mol% of inverted repeat units.

Submitted to J. Colloid Interface Sci.

Contributions of Hans
Lyklema to the IPCG Newsletter
May 1998

Title:

Streaming Potentials and Conductivities of Latex Plugs in Indifferent Electrolytes

Authors:

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Address:

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Dreijenplein 6, 6703 HB Wageningen, The Netherlands.

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ABSTRACT. The low-frequency permittivity and the conductivity increments of a well-characterised polystyrene sulphate latex with constant surface charge density were measured in KCl electrolyte solutions. The ionic strength was varied in the range 0.4-6 mM. The data could be explained with one absolute surface-conductivity parameter over the complete concentration range. The titratable surface charge density correlates well with the surface conductivity, the ions in the double layer having the bulk mobility. The results are in good agreement with static conductivities of plugs composed of the same particles obtained in a previous study (1). The electrokinetic charge obtained from streaming potentials (1) in that study is significantly lower, confirming the presence of conduction behind the shear plane.

In order to interpret the conductivity data, simple analytical expressions have been derived for the frequency-dependent complex conductivity of a dilute dispersion of spherical particles with relatively thin double layers ($\kappa a \gg 1$ where a is the particle radius and κ^{-1} the Debye screening length). The expressions are restricted to binary suspending electrolytes. However, no restrictions on the ion mobilities and ion valencies are made. Our results agree well with the numerical results of the dielectric model of Mangelsdorf and White (2,3) and reduce to O'Brien's static conductivity results (4) in the limit of low frequencies.

KEYWORDS:

Low-frequency dielectric dispersion, polystyrene latex, surface conduction, electrokinetics.

original figures

Submitted to J. Colloid Interface Sci.

Title:

Low-Frequency Dielectric Response of Polystyrene Latex Dispersions

Authors:

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Abstract:

Streaming potential and conductivity measurements were performed on porous plugs in a number of indifferent electrolytes. The plugs were made of monodisperse spherical polystyrene sulphate latex with fixed surface charge density. The observed surface conductivity could be interpreted with the classical Bikerman expression corrected for conduction behind the shear plane. It was shown that electroosmosis positively, and the depletion of co-ions in the double layer negatively contribute to the surface conductivity. It was further demonstrated that a significant part of the conduction is located behind the slip plane. The ion mobility of the indifferent counterions behind as well as beyond the shear plane is close to the bulk mobility. In the correct determination of ζ -potentials in the low electrolyte concentration range, it is necessary to take surface conduction behind the plane of shear into account. By doing so, the maximum in the curve of the ζ -potential versus electrolyte concentration disappears.

Keywords:

polystyrene sulphate latex, porous plug, streaming potential, conductivity, surface conduction, ζ -potential, indifferent electrolyte.

Contribution to Polymer Colloids Group Newsletter

by

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News on Polymer Colloids in Japan:

The 10th Polymeric Microsphere Symposium will be held in Fukui in November 11-13, 1998. Those who are interested in presenting a paper (in English) in this symposium, please write Professor Nomura by July 17, 1998. Financial support will be considered for the speakers from abroad.

Recent Research Activity on Polymer Colloids in Fukui University:

(1) A New Kinetic Interpretation of Styrene Microemulsion Polymerization

M. Nomura, and K. Suzuki, Department of Materials Science and Engineering, Fukui University, Fukui, Japan, *Macromol. Chem. Phys.*, **198**, 3025-3039 (1997)

Synopsis: The polymerizations of styrene initiated by potassium persulfate were conducted at 50°C in oil-in-water microemulsions made with sodium lauryl sulfate and 1-pentanol as emulsifier and cosurfactant, respectively. Based on the experimental findings that both particle size and molecular weight of polymers are almost independent of styrene conversion and the initial initiator concentration, a kinetic picture of microemulsion polymerization of styrene is proposed, which assumes that (1) particle nucleation occurs in monomer-swollen micelles and almost all the radicals in the water phase enter the monomer-swollen micelles and finally initiate polymerization therein (2) with negligible radical termination in the water phase and (3) with negligible radical entry into the preformed polymer particles, and accordingly, (4) all chain-stopping events in the active polymer particles are the chain transfer reaction to monomer. Based on this kinetic picture, a simple mathematical kinetic model is proposed. It is demonstrated by comparing the experimental data with the model predictions that the proposed model can explain fairly well the progress of styrene microemulsion polymerization.

(2) Effect of the Number of Seed Polymer Particles on the Kinetic Behavior of the Seeded Emulsion Copolymerization of Styrene and Acrylamide

M. Nomura, H. Ichikawa, K. Fujita and T. Okaya, Department of Materials Science and Engineering, Fukui University, Fukui, Japan. *J. Polym. Sci.: Part A: Polym. Chem.*, **35**, 2689-2695 (1997)

Synopsis: The seeded emulsion copolymerizations of styrene and acrylamide were carried out at 50°C using polystyrene latex particles as seed and potassium persulfate as initiator, respectively. It was found that the change in the number of seed particles initially charged causes a drastic change in the kinetic behavior of this seeded emulsion copolymerization system: when the number of seed particles initially charged was less than a certain critical value, both styrene and acrylamide started polymerization from the beginning of the reaction. However, when the number of seed particles was higher than this critical value, an apparent induction period suddenly emerged only for acrylamide polymerization, that is, acrylamide did not start polymerization until the styrene conversion exceeded around 75%, while the styrene polymerization started and continued very smoothly from the beginning of the reaction.

(3) Molecular Weight Distribution in Nonlinear Emulsion Polymerization

H. Tobita, Department of Materials Science and Engineering, Fukui University, Fukui, Japan. *J. Polym. Sci.: Polym. Phys.*, **35**, 1515-1532 (1997)

M. Okubo, T. Hosotani, T. Yamashita, J. Izumi

Influence of the swelling stage of seed polymer particles with monomer on the morphology of micron-sized monodispersed composite polymer particles produced by seeded polymerization utilizing the dynamic swelling method

Colloid Polym. Sci., **275**, 888-892 (1997)

Micron-sized monodispersed polystyrene (PS)/poly(n-butyl methacrylate) (PBMA) composite particles (PS/PBMA=2/1 by weight) having a heterogeneous structure in which many fine PBMA domains dispersed in a PS matrix near the particle surface were produced by seeded polymerization of n-butyl methacrylate (BMA) of which almost all had been absorbed by 1.8 μm -sized monodispersed PS seed particles utilizing the dynamic swelling method. The morphology was varied by changing the PS/BMA ratio and polymerization temperature. It was concluded that the swelling state of 2 μm -sized BMA-swollen PS particles in the seeded polymerization process is one of the important factors to control the morphology of the composite particles.

M. Okubo, N. Fukami, A. Ito

Effect of molecular weight on the preparation of nanoparticles by the particle dissolution method from submicron-sized ionized styrene-methacrylic acid copolymer particles in nonionic emulsifier solution

J. Appl. Polym. Sci., **66**, 1461-1464 (1997)

Styrene-methacrylic acid copolymer (P(S-MAA)) (92/8, molar ratio) nanoparticles were prepared by a dissolution of submicron-sized P(S-MAA) particles having various molecular weights in a polyoxyethylene nonylphenylether nonionic emulsifier aqueous solution at pH 13.0 and above 90°C. The latter particles were produced by emulsion copolymerization in the presence of various concentrations of n-octyl mercaptan. The effect of molecular weight on the dissolution behavior was examined at various conditions and using various kinds of the nonionic emulsifier. It was clarified that a decrease in the molecular weight led to the production of the nanoparticles at mild treatment conditions.

M. Okubo, H. Minami

Formation mechanism of micron-sized monodispersed polymer particles having a hollow structure

Colloid Polym. Sci., **275**, 992-997 (1997)

Recently, the authors reported that micron-sized monodispersed cross-linked polymer particles having single hollow in the inside were produced by the seeded polymerization for the dispersion of (toluene/divinylbenzene)-swollen polystyrene (PS) particles prepared utilizing the dynamic swelling method which the authors had proposed. In this article, the particles at various conversions of the seeded polymerization were observed with an optical microscope in detail. From the obtained results, the formation mechanism of the hollow structure was suggested as follows. As the seeded polymerization proceeds, polydivinylbenzene (PDVB) molecules precipitated in the swollen particle are trapped near the interface and gradually piled at the inner surface, which results in cross-linked PDVB shell. PS which dissolve in the swollen particles are repelled gradually to the inside. After the completion of the polymerization, toluene in the hollow evaporates by drying, and PS clings to the inner wall of the shell uniformly.

M. Okubo, T. Yamashita

Morphology of micron-sized monodispersed composite polymer particles produced by seeded polymerization for the dispersion of highly monomer-swollen polymer particles

Colloid Polym. Sci., **276**, 103-108 (1998)

Monodispersed polystyrene (PS)/poly(*n*-butyl methacrylate) (PBMA) composite particles having 9.4 μm in diameter were produced by seeded polymerization for the dispersion of highly *n*-butyl methacrylate (BMA)-swollen PS particles, and their morphologies were examined. The highly BMA-swollen PS particles (about 150 times the weight of the PS seed particles) were prepared by mixing monodispersed 1.8 μm -sized PS seed particles and 0.7 μm -sized BMA droplets prepared with an ultrasonic homogenizer in ethanol/water (1/2, w/w) medium at room temperature. After NaNO_2 aqueous solution as inhibitor was added in the dispersion, the seeded polymerization was carried out at 70°C. In an optical microscopic observation, one or two spherical high contrast regions which consisted mainly of PS were observed inside PS/PBMA composite particles. In the PS domain, there were many fine spherical PBMA domains. Such morphologies were based on the phase separation of PS and PBMA within the homogeneous swollen particles during the seeded polymerization.

M. Okubo, T. Masuda, T. Mukai

Synthesis of needle-like crystalline particles by chemical oxidative dispersion polymerization

Colloid Polym. Sci., **276**, 96-99 (1998)

Chemical-oxidative dispersion polymerization of 3,5-xylydine was carried out in an aqueous medium with ammonium persulfate as an oxidant and polyvinylalcohol as a stabilizer. The polymerization proceeded smoothly at room temperature, resulting in a stable polyxylydine (PXy) dispersion. The produced PXy particles had two types of shapes: needle-like and spherical. Results obtained by electron diffraction and X-ray diffraction measurements indicated that the PXy needle-like particles had a crystalline structure.

M. Okubo, T. Fujiwara, A. Yamaguchi

Morphology of anomalous polystyrene/polybutyl acrylate composite particles produced by seeded emulsion polymerization

Colloid Polym. Sci., **276** 186-189 (1998)

Recently, we found that "golf ball"-like polystyrene (PS)/polybutyl acrylate (PBA) composite particles could be produced by seeded emulsion polymerization of butyl acrylate (BA) with PS seed particles. In this article, the effects of the polymerization temperature, BA monomer concentration, and the presence of 1-octanol, which is a good solvent for PBA and a poor solvent for PS in the polymerization, on the morphology was studied.

M. Okubo, H. Ahmad

Enzymatic activity of trypsin physically immobilized on temperature-sensitive composite polymer particles

J. Polymer Science, Part A: Polymer Chemistry, **36**, 883-888 (1998)

Two types of temperature-sensitive composite polymer particles were prepared by seeded emulsion copolymerizations of dimethylaminoethyl methacrylate and ethylene glycol dimethacrylate with 0.14 μm -sized polystyrene and 0.26 μm -sized polymethylmethacrylate seed particles. To evaluate the usefulness as a carrier for biomolecules, the specific activities of trypsin adsorbed on these two composite polymer particles were measured at temperatures

above and below each lower critical solution temperature (LCST). In both cases, adsorbed trypsin retained its enzymatic activity during repeated adsorption/desorption measurements

M. Okubo, Y. Lu

Estimation of surface morphology of composite polymer particles prepared by the stepwise heterocoagulation method with ζ -potential measurement

Colloid Polym. Sci., **276**, 282-285 (1998)

Core-shell composite polymer particle was prepared by the stepwise heterocoagulation of cationic small polymer particles (SPs) onto an anionic large polymer particle (LP), following heat treatment at temperatures which were higher than glass transition temperature ($T_g = 18^\circ\text{C}$) of SP. At pH 9 the zeta-potential of the heterocoagulated particle (HP) was negative, but it changed to positive by the heat treatment and increased with the treatment time and finally attained to that of SP. The treatment time to attain the zeta-potential of SP became short by elevating the treatment temperature. This indicates that during the heat treatment, SP continued to melt on the surface of LP and finally formed a continuous shell.

M.Okubo, Y. Lu

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

J. Appl. Polym. Sci., in press

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.

Contribution to the IPCG Newsletter May 1, 1998

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Main activity of our group is 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. This May and July the microgravity experiments on the rotational diffusion of anisotropic shaped colloids of tungstic acid and crystallization kinetics of colloidal alloys will be made using dropping and aircraft methods. Absorption and/or adsorption phenomena 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(1997-)

(1)"Structural and Dynamic Properties in the Complex Fluids of Colloidal Crystals, Liquids and Gases", T. Okubo and K.Kiryama, *J.Mol.Liquids*, 72, 347-364(1997).

Static(SLS) and dynamic light-scattering(DLS) measurements are made for colloidal-crystals, -liquids and -gases of silica spheres, 110 nm in diameter, which are typical examples of the complex fluids. Very sharp peaks are observed in the light-scattering curves. At the peak scattering vectors in the scattering intensity(I), very small values of the effective diffusion coefficient(D_{eff}) are evaluated. Product of I and D_{eff} is roughly constant for the colloidal crystals, liquids and gases over the scattering angles measured. The structure factor, $S(q)$ are evaluated from the $I(q)$ observed and the particle structure factor, $P(q)$. The nearest-neighbour interparticle distances of colloidal crystals and liquids estimated from the peaks in the $S(q)$ curves, l_{obs} agree excellently with the effective diameters of spheres(d_{eff}) including the electrical double layers in the effective hard-sphere model and also with the mean intersphere distances, l_0 calculated from the sphere concentration($l_{obs} \approx d_{eff} \approx l_0$). Three and two dynamic processes have been extracted separately from time profiles of autocorrelation function of colloidal crystals and liquids, respectively from the non-negative least square analysis. Hydrodynamic diameters of spheres in the crystal-like and liquid-like suspensions can not be evaluated from DLS measurements. Decay curves of colloidal gases are characterized by a single translational diffusion coefficient. The latter is always lower than the calculation from the Stokes-Einstein equation using true diameter of spheres and increases as ionic concentration increases. These experimental results emphasize the importance of the expanded electrical double layers and the electrostatic intersphere repulsion on the structural and dynamic properties of the colloidal crystals, liquids and gases.

(2) "Kinetic Study on the Colloidal Crystallization of Silica Spheres in the Highly Diluted and Exhaustively Deionized Suspensions As Studied by the Light-scattering and Reflection Spectroscopy", T.Okubo, S.Okada and A.Tsuchida, *J.Colloid Interface Sci.*, 189, 337-347(1997).

Static(SLS)- and dynamic light scattering(DLS) measurements and the reflection spectroscopy are made for the kinetic analyses of the growing processes of colloidal crystals of silica spheres(103 nm and 110 nm in diameter) in the highly diluted and exhaustively deionized aqueous suspensions. Changes in the SLS curves demonstrate that there exists an induction period in the nucleation process, which is prolonged with decreasing sphere concentration. Induction periods observed from DLS measurements are from 1 min to 21 min, and also increase as sphere concentration decreases. The diffusion coefficients of colloidal spheres in the super-saturated liquids and crystal-like structures are estimated to be $1 \times 10^{-12} \text{ m}^2/\text{s}$ and $5 \text{ \AA} \cdot 10 \times 10^{-12} \text{ m}^2/\text{s}$, respectively, which are smaller and larger than the diffusion coefficient of the independent sphere evaluated using Stokes-Einstein equation, $4.36 \times 10^{-12} \text{ m}^2/\text{s}$. Nucleation rates are $3.5 \times 10^5 \text{ s}^{-1}$ to $8.1 \times 10^7 \text{ s}^{-1}$ at $\phi=0.0006$ to 0.001 from the DLS and reflection spectroscopy. Crystal growing process is beautifully explained by the classical diffusion theory of crystallization, though the restricted diffusion of the reacting spheres like as the fused metal systems should be taken into account. Crystal growth rates range from 2.9 \mu m/s to 20.7 \mu m/s , and increase substantially as the sphere concentration increases. The importance of the electrostatic intersphere repulsion through the electrical double layers and the cooperative fluctuation of colloidal spheres in the crystallization processes is supported strongly.

(3) "Kinetic Analyses of the Colloidal Crystallization of Silica Spheres As Studied by the Reflection Spectroscopy", T.Okubo and S.Okada, *J.Colloid Interface Sci.*, 192, 490-496(1997).

Reflection spectroscopy is made for the kinetic analyses of the nucleation and growth processes of colloidal crystals of silica spheres(110 nm in diameter) in the exhaustively deionized aqueous suspensions. Sphere concentrations range from 0.001 to 0.0025 in volume fraction(ϕ) for the nucleation and 0.0014 to 0.0036 for the crystallization process, respectively. Induction periods are from 1 to 500 seconds, and prolonged with decreasing sphere concentration. Nucleation rates are 10^{-3} to $10^3 \text{ \mu m}^{-3}\text{s}^{-1}$, and increase sharply as sphere concentration increases. The crystallization process has been observed from the sharpening and the increase of intensity in the reflection peaks for the suspension in a test tube, which stands still after being inverted. Crystal growth rates, v range from 2 to 15 \mu m/s , and decrease linearly as the reciprocal sphere concentration increases. Crystal growth rates represented by the number of the unit cells, u also increase as ϕ increases, ranging from 2 to 23 no. of unit cells/s. The importance of the electrostatic intersphere repulsion through the electrical double layers and the cooperative fluctuation of colloidal spheres in the crystallization processes is supported.

(4) "Kinetic Analyses of the Colloidal Crystallization in Alcoholic Organic Solvents and Their Aqueous Mixtures As Studied by Reflection Spectroscopy", T.Okubo and S.Okada, *J.Colloid Interface Sci.*, in press.

Reflection spectroscopy is made for the kinetic analyses of the nucleation and growth process 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 $\text{mm}^{-3}\text{s}^{-1}$ 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 $\mu\text{m/s}$ 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 repulsion through the electrical double layers and the cooperative and synchronized fluctuation of colloidal spheres in the crystallization processes is supported.

(5) "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.

(6) "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.

(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 acoustic 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 explained by the symmetric structure of the shear waves.

(9) "Electro-optic Properties of Colloidal Crystals As Studied by Reflection Spectroscopy", T.Okubo, A.Tsuchida, T.Tanahashi and A.Iwata, *J.Colloid Interface Sci.*, in press.

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 including expanded electrical double layers in the crystal lattice will be one of the main causes for the electro-optic nature of the crystals.

(10) "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 colloidal crystals. Three and two dynamic processes are extracted separately from time profiles of autocorrelation function of colloidal 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 demonstrates their relation to undamped shear waves of the crystal lattice.

(11) "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 electro-optic properties of colloidal suspensions are reviewed. Contents are Introduction, Electro-optic effects in suspensions of spherical particles, Electro-optic effects in suspensions of anisometric particles and References.

(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 rates 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, *J.Colloid Interface Sci.*, in press.

Kinetic analyses of the formation reaction of colloidal silica spheres, which are synthesized from ethyl silicate (EtSi), ammonia (NH₃) 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. t_i increases as the concentrations of NH₃, EtSi and/or H₂O 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 horizontal 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, NH₃ and/or H₂O 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, *J.Colloid Interface Sci.*, in press.

Polymerization reactions of colloidal silica spheres via the hydrolysis and dehydration processes of tetraethyl 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)"Recent Advances in the Kinetic and Dynamic Properties of Colloidal Crystals", T.Okubo, *Current Topics of Colloid Interface Sci.*, 1, 169-193(1997).

Recent works mainly in our laboratory on the kinetic study of the colloidal crystallization, structural and dynamic properties and the electro-optic effects of colloidal crystals have been reviewed. Crystal structure and the giant size of single crystals are formed in the diluted and highly deionized suspensions of colloidal spheres. Nucleation and crystal growing processes in colloidal crystallization are studied using the techniques of static and dynamic light-scattering and the reflection spectroscopy. Importance of the intersphere repulsion and the synchronous fluctuation are supported in the crystallization processes. Retardation in the nucleation and growing rates is observed from the micro-gravity experiments using parabolic flights of an air-craft. Dynamic character of colloidal crystals, liquids, and gases are discussed from the dynamic light-scattering data. One, two and three dynamic modes are observed for colloidal crystals, liquids and gases, respectively. Furthermore, electro-optic properties such as modulation effects(phase delay, harmonics, transformation in wave forms, etc.) and acoustic shear waves have been clarified for the colloidal crystals.

(16)"Surface Tension of Biological Polyelectrolyte Solutions", T.Okubo and K.Kobayashi, *J.Colloid Interface Sci.*, in press.

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.

Effect of PEO molecular weight on the flocculation and resultant floc properties of polymer-induced PCC flocs

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The tensile strength of precipitated calcium carbonate flocs, formed with the PEO cofactor flocculation system, was measured as a function of PEO molecular weight together with two types of cofactor, a commercial sulfone containing phenolic resin and a linear copolymer of vinyl phenol and sodium acrylate. The floc tensile strength ranged from 10 to 130 nN when PEO molecular weight was increased from 2 to 8 million. The two types of cofactors gave approximately the same range of tensile strengths, however, the elongation at break was about 800% for the vinyl phenol-based cofactor whereas the commercial cofactor gave only about 300% elongation. It was postulated that elongation is an important predictor of floc survivability in turbulent flow.

The influence of phenolic cofactors on the properties of calcium carbonate flocs formed with PEO

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The tensile strength of flocs formed from the flocculation of precipitated calcium carbonate (PCC) by the addition of cofactor (poly(vinyl phenol-co-sodium acrylate)) followed by PEO was measured as a function of the cofactor/PEO mass ratio. The maximum floc strength corresponded to a cofactor/PEO ratio of 2~3. Two modes of floc rupture were observed. Weak flocs tended to give "stretchy" behavior in which the flocs extended under tension leaving a long thin polymer tether with single embedded PCC particles. Strong flocs showed a "tough" mode in which elongation at rupture was low. Stretchy flocs gave distances between neighboring embedded PCC particles in the tethers as great as 30 μm indicating that many PEO chains are involved in the bridges or tethers between two particles. We speculate that

these PEO assemblies originate from the mechanical entanglement of the very long PEO chains supplemented with PEO-to-PEO binding from the small cofactor molecules.

On the role of hydrophobic particles and surfactants in defoaming

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The role of hydrophobic particles in mineral oil-based defoamers was investigated by fluorescence labeling and microscopy. Defoamer emulsion droplets in water adhere to the air/water interface to become lenses that nucleate bubble coalescence. Fluorescent labels were covalently bonded to silica and confocal laser scanning microscopy showed that the hydrophobic silica particles concentrate in the oil/water interface near the three phase contact line. Furthermore, surfactants added to defoamers to facilitate emulsification are required for the transport of the silica to the water/oil interface. Removal of excess silicone oil from the emulsification process lowered defoamer performance suggesting that very small amounts of free silicone oil have a role in the defoaming mechanism.

The transport of latexes and wood pulp fibres through aqueous foams

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Abstract

The possibility of washing pulp fibres from a flotation froth was evaluated by creating a steady-state froth column 55 or 65 cm deep in which foam formation balanced foam collapse. Dilute pulp and wash water were sprayed on the top of the froth and the break through of fibres into the liquid area below the froth was measured. The results showed that it was possible to increase pulp yield in deinking flotation by washing the froth. Laboratory flotation runs demonstrated that a minimum wash water flux was required to keep fibres out of the froth. A mechanism for washing fibres from relatively dry froths is proposed.

**Contribution to IPCG Newsletter From Laboratoire de Chimie des
Procédés de Polymérisation
(LCPP-CNRS)
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(submitted by A. Guyot and C. Pichot)

Methacrylic Maleic Bifunctional Stabilizer in Emulsion Polymerization

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ABSTRACT

A new type of reactive surfactant, containing both a methacrylic and a maleic group, was prepared and engaged in batch and seeded emulsion polymerization of styrene and styrene-butyl acrylate. The stability of core - shell latexes versus electrolytes has been studied.

Hemiesters and Hemiamides of Maleic and Succinic Acid : Synthesis and Application of Surfactants in Emulsion Polymerization with Styrene and Butyl Acrylate

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ABSTRACT

Hemiesters and hemiamides of maleic acid with different length of hydrophobic alkyl chain ($R=C_8H_{17}$, $C_{10}H_{21}$, $C_{12}H_{25}$, $C_{16}H_{33}$) have been synthesized and used in the emulsion polymerization of styrene and butyl acrylate. The same polymerization experiments have been carried out using nonreactive surfactants with analogue structure. The chemical structure of surfactants has been confirmed by 1H NMR. Melting point and critical micelle concentration (CMC) for synthesized surfactants were measured. All investigated surfactants are providing good stability of styrene/butyl acrylate latices. As a reference, styrene/butyl acrylate latex prepared with SDS is used.

The amount of surfactant grafted on the particles of the final latex has been estimated by conductimetric titration. 33-68% of surfactant used in emulsion polymerization were found onto the surface of latex particles. Electrolyte addition and freeze/thaw cycle cause flocculation of latices. Glass transition temperatures for polymers have been found between 13-22°C.

Cationic and Zwitterionic Polymerizable Surfactants - Quaternary Ammonium Dialkyl Maleates : Part I. Synthesis and Characterization

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ABSTRACT

Cationic and zwitterionic reactive dialkyl maleates with different hydrophobic chain length ($R = C_{10}H_{21}, C_{12}H_{25}, C_{16}H_{33}, C_{18}H_{37}$) and some similar surfactants without C=C double bond were synthesized with an aim to use them as stabilizers in the batch and seeded emulsion copolymerization of styrene and butyl acrylate (Part II). Surfactants are obtained in three step synthesis, starting from ring opening of maleic anhydride, followed by O-alkylation with amino alkyl compound and finished by quaternarization of amino group in the hydrophilic part of the molecule. The chemical structure of surfactants was confirmed by 1H NMR. Melting points and critical micelle concentrations (CMC) of the synthesized surfactants were measured. The specific area per molecule at the air / water interface was calculated for most of the surfactants. The adsorption of the surfactant on the polystyrene (PS) and PS/polybutyl acrylate (PBA) copolymer was also measured and the specific area occupied by surfactant molecule was calculated in one example.

Cationic and Zwitterionic Polymerizable Surfactants - Quaternary Ammonium Dialkyl Maleates : Part II. Emulsion Polymerization of Styrene and Butyl Acrylate

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ABSTRACT

Polymerizable cationic and zwitterionic dialkyl maleates with different hydrophobic chain length ($R = C_{10}H_{21}, C_{12}H_{25}, C_{16}H_{33}, C_{18}H_{37}$) and different counter ions (I, Br, HSO_4) for the cationic hydrophilic part, as well as some similar surfactants dialkyl succinates were used in batch and seeded emulsion polymerization of styrene and butyl acrylate. All examined surfactants, when used in emulsion polymerization, were providing good stability of styrene/butyl acrylate latices. A styrene/butyl acrylate latex prepared with sodium dodecyl sulfate (SDS) was used as a reference. Some stability tests for latices were performed and the glass transition temperatures, as well as the molecular weights of the obtained polymers were measured. Finally, films from two zwitterionic latices were formed, and mechanical traction tests were performed and the water absorption was measured.

**A combined hardware/software sensing approach
for on-line control of emulsion polymerisation processes**

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In the present work, a new strategy for the on-line determination of information concerning a free radical polymerisation (overall and individual monomer conversions, and the product of the number of radicals per particle multiplied by the number of particles) is presented. It is based on the construction of a non-linear observer that uses information obtained via a new adaptive inferential calorimetric measurement scheme. The results, presented for the case of the emulsion copolymerisation of methyl methacrylate (MMA) and vinyl acetate (VAc), show that with only a rough model of the physical process, it is possible to obtain reliable estimates of the evolution of the polymerisation reaction.

Partitioning of styrene, butyl acrylate and methacrylic acid in emulsion systems

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The partitioning behaviour of styrene, butyl acrylate and methacrylic acid was studied from an experimental and theoretical point of view. Under conditions representative of typical emulsion polymerisations, it was found that the partition coefficients of styrene and butyl acrylate depended to a large extent on temperature, but not on pH, nor on the relative concentrations of organic material in the system. On the other hand, the value of partition coefficient for methacrylic acid (MAA) was a very strong function of pH, decreasing rapidly as the pH is increased from 2 to 6. Beyond this limit no MAA is found in the organic phase. Furthermore, k_M of MAA was observed to be a very weak function of the fraction of organic material in the system and of the temperature. In order to model the partitioning behaviour of MAA in the ternary system it is necessary to allow for the possibility of significant dimerisation in the organic phase.

Preparation of Poly(N-isopropylmethacrylamide) Latexes Kinetic studies and Characterization

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(submitted J Polym. Sci.)

ABSTRACT: Thermosensitive poly[N-isopropylmethacrylamide] latexes have been synthesized using N-isopropylmethacrylamide (NIPMAM) as a main monomer, methylene bisacrylamide (MBA) as a cross-linker and potassium persulfate (KPS) as the initiator. Polymerizations kinetics were first investigated upon studying both the influence of crosslinker (MBA) and initiator (KPS) concentration and temperature effect on the the conversion, the particle size and water soluble polymer (WPS) formation as a function of time. Particle size analysis by Scanning Electronic Microscopy (SEM) showed that short nucleation step afforded the formation of monodisperse latexes. In addition, it was found a strong dependence of WPS on MBA and KPS concentration. Comparison of particle size by SEM and quasiaelastic scattering clearly evidenced the dramatic effect of temperature on particle size. Moreover, highly monodisperse particles allowed to produce an orderly array observed. Finally, low critical solubility temperature of latexes (LCST) were determined and their variation were indicative of the formulation recipe.

Electrokinetic properties and Colloidal stability of Cationic amino-containing N-isopropylacrylamide-styrene copolymer particles bearing different shell structures

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(Submitted to Langmuir)

ABSTRACT

The electrokinetic properties and colloidal stability behavior of styrene/N-isopropylacrylamide and styrene/N-isopropylacrylamide-co-aminoethylmethacrylate core-shell latexes were investigated. The electrophoretic mobility was first measured as a function of pH, temperature and ionic strength. On the basis of the results obtained for the electrokinetic measurement a charge distribution model (volume charge distribution) was proposed to help the suggested interpretation. By using the Eversole's and Bordman's equation, the shear plane positions were estimated as a function of ionic strength and good correlation was found between the calculated values and the values obtained from the QELS measurement. The colloidal stability of those core-shell latexes was examined above and below the LCST (~32°C). Below the LCST, stabilization was mainly attributed to the combination of both electrostatic and steric stability. Whereas, above the LCST, only the electrostatic stability was the driving parameter. In addition, an apparent Hamaker constant of the core-shell latex was experimentally determined above the LCST.

Synthesis and Characterization of Surface-cyanofunctionalized Poly(N-isopropylacrylamide) latexes

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(Submitted to Colloid & Polymer Science)

ABSTRACT

A series of poly(N-isopropylacrylamide) (P[NIPAM]) latexes with different contents of cyano groups were successfully prepared by either seeded or shot-growth polymerizations of an aqueous solution containing acrylonitrile (AN) onto a seed P[NIPAM] latex, respectively and further characterized by FT-IR, ¹H-NMR, elemental analysis, as well as by quasielastic light scattering (QELS) and scanning electron microscopy (SEM). All prepared surface-cyanofunctionalized P[NIPAM] latexes exhibited the same range of lower critical solution temperature (LCST) as a pure P[NIPAM] latex. The shot polymerization process proved more efficient at yielding cyano derivatized latexes than the seeded polymerization technique. The amount of incorporated cyano groups onto the particles was determined with a good correlation both by ¹H-NMR and elemental analysis. The higher the amount of initially introduced AN monomer in the reaction mixture, the more cyano groups were incorporated onto the particles. The surface of the particles with high content of cyano groups appeared quite rough by SEM in comparison with that of the pure P[NIPAM] particles.

Cationic amino-containing N-isopropylacrylamide-styrene copolymer particles: 2-Surface and Colloidal Characteristics

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(Submitted to Colloid & Polymer Science)

ABSTRACT : In a previous paper [1], the synthesis of various polystyrene-poly[NIPAM] core-shell latexes bearing cationic amidino and/or amino charges has been described. Several colloidal properties of these cationic latexes have been characterized such as: particle size, surface charge density, electrophoretic mobility and finally colloidal stability. Due to the poly[NIPAM]-rich layer in the shell, it was found that temperature played a significant role on all these properties, a LCST around 33°C being exhibited. In addition, ionic strength was also found to affect the colloidal behavior of these latexes, the largest effect being observed with latexes having both amidino and amino surface charges. The critical coagulation concentrations (CCC) of the various latexes above and below the LCST were determined, highlighting the contribution of electrostatic and steric repulsive forces to the stability of these particles.

Multiple conformations of oligonucleotides covalently grafted on latex nanospheres as evidenced by time-resolved energy fluorescence experiments

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In a previous newsletter (IPCG Newsletter, March 96), the effect of pH and salt concentration on the conformation of single strand DNA fragments (oligonucleotides, ODN) covalently bound to the surface of polystyrene latex microspheres was studied by steady-state fluorescence energy transfer. Results showed that ODN tend to adopt an expanded conformation upon increasing pH or salt concentration. However, these experiments only revealed general tendencies and could not give a detailed picture of the situation, i.e., if all ODN have exactly the same conformation on the surface of one latex particle, or, if several populations of ODN corresponding to different conformations may coexist. Some months ago, a picosecond time-resolved fluorescence study of the same system was carried out, which confirmed the influence of pH and salt concentration and gave an insight into the above question.

For example, at the slightly acidic pH of 6, total contribution of the quenched lifetimes, 0.2 ns (quenching by acceptor) and 2 ns (quenching by polystyrene rings), is 83 %, whereas contribution of the free lifetime, 3.9 ns, is 17 % : ODN are mainly (but not all) adsorbed on the latex surface, but 17 % are fully expanded in the aqueous phase. When pH increases to 10, contribution of the quenched lifetimes, decreases to 40 % [0.2 ns (6 %), 1 ns (13 %) and 2 ns (21 %)] whereas contribution of the free lifetime, reaches 60 %. In this latter experimental conditions, ODN are mainly fully expanded in the aqueous phase ; however, some remain close to the latex particle and another population is still adsorbed on the surface.

Consequently, the simultaneous presence of different ODN conformations on the latex surface could be evidenced by these time-resolved fluorescence experiments.

Recent Papers:

The effect of Triton X-405 on the adsorption and desorption of single-stranded DNA fragments onto positively charged latex particles, F. Ganachaud, A. Elaïssari, C. Pichot, *Langmuir*, 13, 7021-7029, (1997)

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Surface characterization of amine-containing latexes by charge titration and contact angle measurements, F. Ganachaud, B. Bouali, L. Véron, P. Lanteri, A. Elaïssari, C. Pichot, *Colloids and Surfaces*, in press, 1998

Gérard RIESS

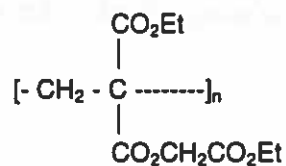
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End 1997 and beginning 1998, 5 PhD students working on block copolymers and colloidal systems submitted their thesis.

Eric FILLOD has synthesized homologous series of acrylic block copolymers having either a PAA block or a poly(2 vinylpyridine) block. He examined the micellization of these block copolymers in organic medium and their adsorption behavior on carbon black.

Olivier LAMBERT has developed the synthesis techniques of amphiphilic triarm star copolymers based on PS, PMMA and PEO. Their micellization behavior in aqueous medium was studied (see IPCG 28 [1] October 1997).

Virginie LARRAS was interested in the preparation of nano- and microspheres based on poly(methylene malonate) of the following structure :



These polymers with 3 ester groups per monomer unit are biocompatible and biodegradable.

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

Pierre HOERNER has examined the stabilization with various block copolymers of polymeric emulsions having a rubber solution as a continuous phase and polyethylenglycol as a dispersed phase. After evaporation of the solvent of the rubber solution, these type of emulsions lead to elastomer films containing liquid droplet of adjustable size (European Patent Appl. N° 95 904 590).

Synthesis of acrylic and styrenic latexes in the presence of non-ionic polymeric surfactants

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We have previously shown [1-4] that polystyrene-poly(ethylene oxide) PS-PEO di- and triblock copolymers exhibit unique properties in emulsion polymerization, owing to their low critical micelle concentration (CMC), their lower diffusion coefficient with respect to classical surfactants and the stability of their micelles. In addition, these polymeric surfactants have the ability to promote the anchoring of the surfactant on the latex particle. This preliminary work with PS-PEO block copolymers has also shown that for a serie of different monomers at fixed reaction conditions, the particle size of the latex decreases, in the following order : butadiene (Bu), styrene (S), butyl acrylate (BA), methyl methacrylate (MMA), which is that of increasing polarity of the monomer. An additional effect is concerned with the compatibility or miscibility between the hydrophobic PS sequence of the copolymer and the polymer formed in the latex particle : the PS sequence is miscible with a PS latex, but is mostly non-miscible with PBA or PMMA.

In continuation of this work we have examined the emulsion polymerization of styrene (S), MMA and BA, as well as of binary systems S-BA and MMA-BA, by using a PMMA-PEO diblock copolymer as surfactant.

EXPERIMENTAL

The PMMA-PEO block copolymer provided by GOLDSCHMIDT (sample ME 10-30) has a PMMA block of $M_n = 1000$ and a PEO block of $M_n = 3000$.

The latexes were prepared by batch emulsion polymerization, following the classical procedures, e.g. purified monomers, degassed distilled water, nitrogen blanket,...

The typical recipe of polymerization is the following : 500 mL water, 110 g monomer, 2.5 to 10 wt % copolymer with respect to the monomer, 2.2 g of potassium persulfate, a temperature of 60°C. The

reaction times are ranging from 3 to 20 hours depending on the monomer system in order to reach almost complete conversion.

The particle size is determined by DLS. From the solid content and the particle size it is possible to calculate the number of particles per cm^3 of the final latex.

RESULTS AND DISCUSSION

At first, it was of interest to check the particle size and the particle surface generated as a function of surfactant concentration for the homopolymerization of styrene, MMA and BA. These values are given in Table 1.

TABLE 1 : Particle size and surface generated as a function of PMMA-PEO block copolymer concentration (in wt % with respect to monomer) for MMA, BA and styrene homopolymer systems.

		2.5 %	5 %	7.5 %	10 %	15 %	β
MMA	R_w nm	(102 ± 2)	100 ± 2	86 ± 1	55 ± 1	/	2.59 ± 0.09
	$S \cdot 10^{-3} \text{ cm}^2/\text{g}$	(54.9)	56.5	65.1	102.6		
BA	R_w nm	248 ± 9	127 ± 2	95 ± 3	73 ± 2	51	2.76 ± 0.12
	$S \cdot 10^{-3} \text{ cm}^2/\text{g}$	23.2	46.6	63.5	82.4	120.0	
Styrene	R_w nm	(105 ± 3)	141 ± 1	108 ± 4	83 ± 2	/	2.75 ± 0.02
	$S \cdot 10^{-3} \text{ cm}^2/\text{g}$	(58.2)	45.0	57.2	75.3		

The particle size R_w is given as the weight average of the hydrodynamic radius determined by DLS
 () values in bracket mean that partial flocculation occurred during synthesis
 S total particle surface generated by the given amount of block copolymer.

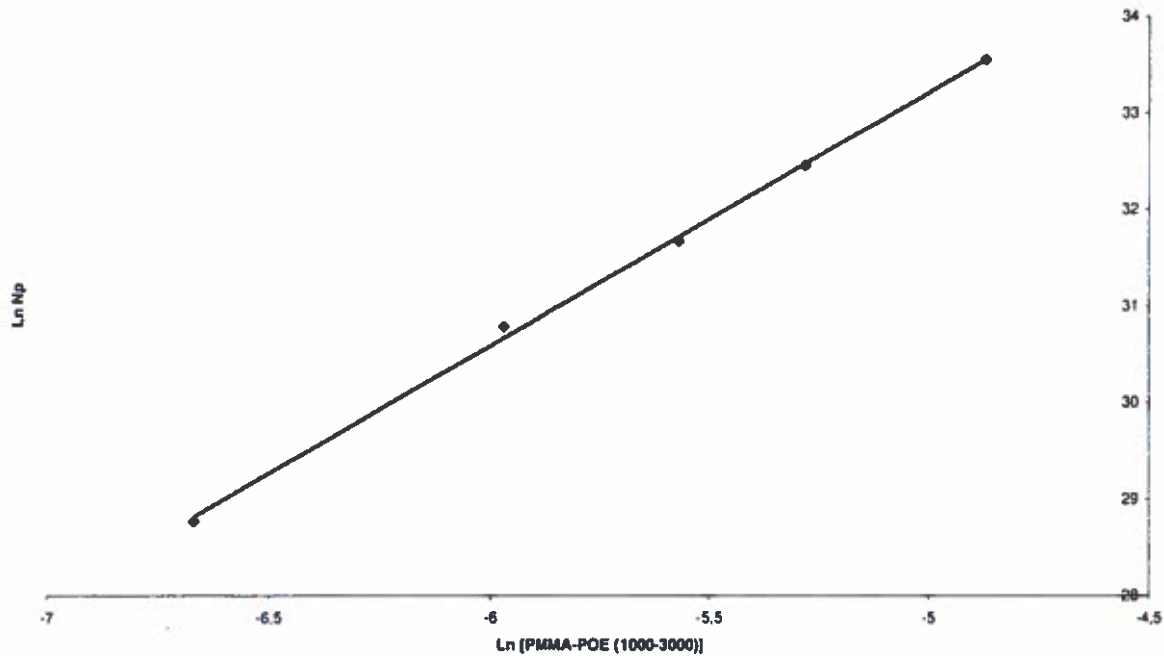
From this table one can notice that :

- the particle size decreases and therefore the particle surface generated by the block copolymer increases as expected with increasing concentrations of surfactant
- at a given surfactant concentration the particle size decreases in the following order : styrene (S), BA, MMA as previously established

- at low surfactant concentration (2.5 % with respect to monomer) some flocculation for the PMMA and PS latexes occurs, whereas the PBA latex is already stable at this surfactant concentration.

A plot of the number of particles N_p versus the surfactant concentration is given in Fig. 1 for the PBA latexes.

Fig 1: Number of particles N_p versus the surfactant concentration for the PBA latexes



From the classical relationship

$$N_p \sim [\text{surfactant}]^\beta$$

one can calculate the exponent β which is respectively 2.76 ± 0.02 for styrene and 2.59 ± 0.09 for MMA.

These values, which are typical for polymeric surfactants as previously shown (1-4), are much higher than that of 0.6 usually found for classical surfactants like SDS.

In extension to this study, we examined the emulsion copolymerisation of styrene-BA and of MMA-BA under the same experimental conditions as for the previous homopolymerizations.

The particle sizes of the latexes and the surface generated as a function of the surfactant concentration are given in Table 2.

TABLE 2 : Particle size and surface generated as a function of PMMA-PEO block copolymer concentration (in wt % with respect to monomer) for MMA + BA and BA + styrene copolymerization.

		2.5 %	5 %	7.5 %	10 %	β
MMA-BA 48 % - 52 %	R_w nm	190 ± 3	114 ± 1	90 ± 1	56 ± 1	2.66 ± 0.06
	$S \cdot 10^{-3} \text{ cm}^2/\text{g}$	26.8	49.0	63.1	104	
MMA-BA 30 % - 70 %	R_w nm	167 ± 2	110 ± 3	91 ± 3	58 ± 3	2.29 ± 0.09
	$S \cdot 10^{-3} \text{ cm}^2/\text{g}$	31.5	51.7	63.5	103	
BA-Styrene 52 % - 48 %	R_w nm	188 ± 9	121 ± 3	91 ± 2	77 ± 3	2.17 ± 0.07
	$S \cdot 10^{-3} \text{ cm}^2/\text{g}$	28.7	45.0	66.9	80.5	
BA-Styrene 64 % - 36 %	R_w nm	15 ± 4	126 ± 2	97 ± 2	74 ± 2	1.88 ± 0.13
	$S \cdot 10^{-3} \text{ cm}^2/\text{g}$	34.2	45.9	62.7	83.3	

For a given surfactant concentration (e.g. 10 wt %), one can notice that the styrene-BA system has essentially the behavior of a BA homopolymerization, whereas the MMA-BA behaves almost like a MMA homopolymerization.

The coefficient β for these systems which can be calculated from the relationship

$$N_p \sim [\text{surfactant}]^\beta$$

are also given in Table 2. It appears that the β value for the copolymerization MMA-BA (48:52) is similar to that of pure MMA whereas the other values are slightly lower than for the corresponding homopolymerizations.

Work is in progress to confirm this behavior with other block copolymers such as PS-PEO.

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Tailored modification of quartz surfaces by covalent immobilization of small molecules (γ -aminopropyltriethoxysilane), monodisperse macromolecules (dendrimers), and poly(styrene/acrolein/divinylbenzene) microspheres with narrow diameter distribution

**Paper submitted to Colloid and Polymer Science
will be available also on the IPCG website (sent to R.M.Fitch)**

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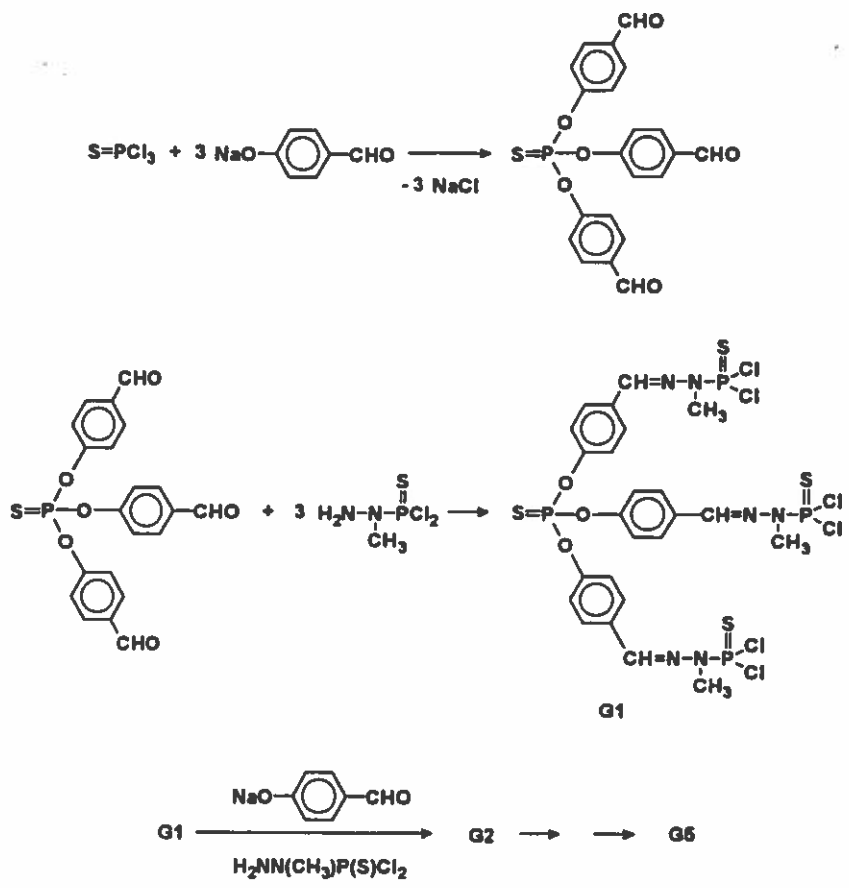
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Summary

Quartz plates were modified by consecutive immobilization of γ -aminopropyltriethoxysilane (APTS), phosphorus containing dendrimers with aldehyde groups (generation 5 - G5, c.f. Scheme 1), Starburst PAMAM dendrimers generation 4 (PAMAM), and poly(styrene-acrolein-divinylbenzene) microspheres (P(SAD)). In this way surfaces with heterogeneity on molecular, macromolecular, and microscopic level, which were equipped with functional amino or aldehyde groups, were obtained. Surface layers were characterized by X-ray photoelectron spectroscopy (XPS) and by contact angle measurements. Analysis of XPS spectra revealed that thickness of the layer of G5 on SiO₂-APTS substrate was 3.7 nm, i.e. was typical for macromolecular dimensions. The average thickness of the layer of PAMAM dendrimers on SiO₂-APTS-G5 was found to be equal 0.35 nm and 0.29 nm,

depending whether calculations were based on attenuation of the intensity of the signal Si2p or P2p, respectively. This thickness was unreasonably low for a monolayer of PAMAM dendrimers and indicated that surface of the SiO₂-APTS-G5 substrate was covered with these macromolecules incompletely. XPS method was used also for determination of the degree of coverage of the surface of SiO₂-APTS-G5-PAMAM plate with P(SAD) microspheres, which being equal 0.60 approached the maximal theoretically possible value (0.62) for microspheres attached chaotically and irreversibly to the surface in an arrangement one microsphere thick. Subsequent coverage of SiO₂-APTS-G5-PAMAM-P(SAD) substrate with PAMAM dendrimers resulted in formation of PAMAM adlayer 3.2 nm thick, close to molecular dimensions of these dendrimers. Contact angle measurements revealed considerable differences in hydrophobicity of surfaces of quartz plates, depending on their modification. Hydrophobicity increased in the order SiO₂ < SiO₂-APTS-G5-PAMAM < SiO₂-APTS SiO₂-APTS-G5 < SiO₂-APTS-G5-PAMAM-P(SAD).

Keywords: *quartz, dendrimers, microspheres, XPS, wettability.*



Scheme 1

POLYACROLEIN CONTAINING MICROSPHERES: SYNTHESIS, PROPERTIES, AND POSSIBLE MEDICAL APPLICATIONS

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Review (60 pages, 55 figures, 6 tables, and 116 references) will be
published soon
in *Prog. Polym. Sci.* Vol. 21

Summary

Polymeric microspheres are used in medical diagnostics, therapy, and as supports of enzymes and other proteins in biotechnology. These particles have also found application in fundamental studies in life-sciences as useful tools for separation of living cells and subcellular fragments. This article presents comprehensive information on polyacrolein containing microspheres suitable for medical applications. Various synthetic procedures (radical, anionic, and red-ox polymerizations) are described, leading to polyacrolein microspheres, microspheres made of polyacrolein and other polymers, and copolymer microspheres containing polyacrolein segments. These particles can be obtained in the range of diameters from Cca 50 nm to a few micrometers, often with very narrow diameter distribution. Depending on the particular synthetic routes, it is possible to obtain microspheres with a uniform structures, core-shell, and raspberry morphologies. In this review, methods used for the characterization of the chemical structure of the surface layer of microspheres, in particular methods used for determination of reactive (aldehyde) groups are also discussed. Results of studies on the immobilization of proteins onto polyacrolein containing microspheres, including relations between the mode of protein binding (covalent immobilization and physical adsorption) and the fraction of polyacrolein in surface layer of microspheres are reviewed. Methods allowing one to obtain protein-microsphere systems in which the attached proteins retain a substantial part of their biological activity are described. Polyacrolein containing microspheres, after attachment of selected antibodies, can be used as reagents in diagnostic tests. There are examples of using these particles for

fabrication of new materials for hemoperfusion columns and for formation of two-dimensional particle assemblies on surfaces of polyethylene, quartz, and glass which are potentially useful for fabrication of biosensors.

Keywords: polyacrolein, microspheres, core-shell microspheres, raspberry microspheres, fluorescent microspheres, two-dimensional assemblies of microspheres, structure of surface layer, adsorption of proteins, covalent immobilization of proteins, protein denaturation, biological activity of immobilized proteins, diagnostic tests, hemoperfusion

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BIODEGRADABLE POLY(L,L-LACTIDE) MICROSPHERES. PARTICLES FROM EARLIER SYNTHESIZED POLYMERS AND BY RING-OPENING POLYMERIZATION OF L,L-LACTIDE

(Will be presented at the ACS-98 Fall Meeting in Boston and published in

ACS Polym. Prepr. Vol. 39(2))

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Introduction

Many types of polymeric microspheres made of biodegradable polymers were investigated as potential carriers of drugs and other bioactive compounds. Some of the microsphere-drug systems found practical applications. Set of the key parameters characterizing microspheres for drug delivery comprises the chemical composition of polymeric materials in particles, its supramolecular structure and morphology, the chemical composition and morphology of surface layer of microspheres and their size. In several instances the latter parameter is of the primary importance. For example, in a number of papers published recently (c.f. Ref.1) it was established that microspheres with diameters (D) larger than $10 \mu\text{m}$ are too large to pass through the capillary blood vessels of many organs, those with $5 \mu\text{m} < D < 10 \mu\text{m}$ are captured in lungs, whereas microspheres with $D < 5 \mu\text{m}$ are efficiently captured by the mononuclear phagocyte system. It was found also that particles with $1 \mu\text{m} < D < 3 \mu\text{m}$ are captured effectively in spleen, with diameters $0.1 \mu\text{m} < D < 1 \mu\text{m}$ in liver, and particles with $D < 0.1 \mu\text{m}$ are captured predominantly in bone marrow. Thus, the control of particle diameters and diameter distribution is essential for their applications.

Polymeric microspheres composed of biodegradable polymers are usually made, using earlier synthesized polymers, by any of the methods which fall into one of the main three categories (A) polymer phase separation, (B) solvent evaporation and solvent extraction, and (C) spray-drying method (2). We developed a method allowing to synthesize biodegradable polyester microspheres directly during ring-opening polymerization of ϵ -caprolactone (CL) and lactides (Lc) (3 - 5). Diameters of microspheres produced from earlier synthesized polymers exceed $10 \mu\text{m}$ and their diameter distribution is broad. Microspheres synthesized by ring-opening polymerizations of CL and Lc have diameters usually smaller than $3 \mu\text{m}$ and values of their polydispersity parameters (D_w / D_n) are lower than 1.1. In this paper we present the new method suitable for synthesis of poly(Lc) microspheres with $D_n > 5 \mu\text{m}$ by ring-opening polymerization and compare diameters distribution of these microspheres with diameter distribution for microspheres obtained from the earlier synthesized polymers.

Experimental

Poly(L,L-Lc) microspheres were obtained from earlier synthesized polymer (in the solution polymerization of L,L- isomer of Lc initiated with tin(II) 2-ethylhexanoate, according to description in Ref 6) by solvent evaporation from the oil-in-water emulsion and/or by solvent extraction from the oil-in-oil emulsions of polymer solutions, as well as by ring-opening polymerization of L,L-Lc. For preparation of microspheres from polymer we used poly(L,L-Lc) with $M_n = 9300$ and $M_w / M_n = 1.06$.

Poly(L,L-Lc) Microspheres by Solvent Evaporation. In typical experiment 6.6 g of poly(L,L-Lc) was dissolved in 6.6 ml CH_2Cl_2 . This solution was added to 150 ml water solution of poly(vinyl alcohol) (1% wt/v) and stirred (170 rev/min) at room temperature for 30 min. At these conditions CH_2Cl_2 slowly evaporated. Finally, microspheres were isolated by sedimentation.

Poly(L,L-Lc) Microspheres by Solvent Extraction. Microspheres were prepared by dissolving poly(L,L-Lc) (1 g) in 10 ml of ϵ -caprolactone. This solution was dispersed by sonication and/or by mixing in 50 ml of Span 85 (3% wt/v) in heptane and introduced into isopropanol with 5% wt/v of PVP.

Poly(L,L-Lc) Microspheres by Ring-Opening Polymerization of L,L-Lc. Polymerizations of L,L-Lc were carried out in 1,4-dioxane:heptane mixed solvent (1:4 v/v) in the presence of poly(dodecyl acrylate)-g-poly(ϵ -caprolactone) (poly(DA-CL)) used as a surfactant. Polymerizations were initiated with tin(II) 2-ethylhexanoate. Descriptions of synthesis of surfactant and of the polymerizations leading to formation of microspheres are given in our earlier papers (cf. Ref. 3 and 4). Polymerizations with a stepwise monomer addition were carried out with concentration of poly(DA-CL) equal 1.67 g/l, initial monomer concentration $[\text{L,L-Lc}]_0 = 3.50 \cdot 10^{-1} \text{ mol/l}$, and $[\text{tin(II) 2-ethylhexanoate}]_0 = 5.70 \cdot 10^{-3} \text{ mol/l}$. Polymerization temperature was 95°C . After predetermined time periods samples of reaction mixture were taken for analysis and new portions of monomer were added.

Characterization of Microspheres. Diameters of microspheres were determined from microphotographs registered using scanning electron microscope (JEOL 35C). Molecular weight of poly(L,L-Lc) was determined by GPC calibrated using poly(ϵ -caprolactone) samples with narrow polydispersity.

Results and Discussion

Diameters and Diameter Distributions of Microspheres. Distributions of diameters of poly(L,L-Lc) microspheres obtained by solvent evaporation and solvent extraction methods, and by the ring opening polymerization are shown in Figure 1.

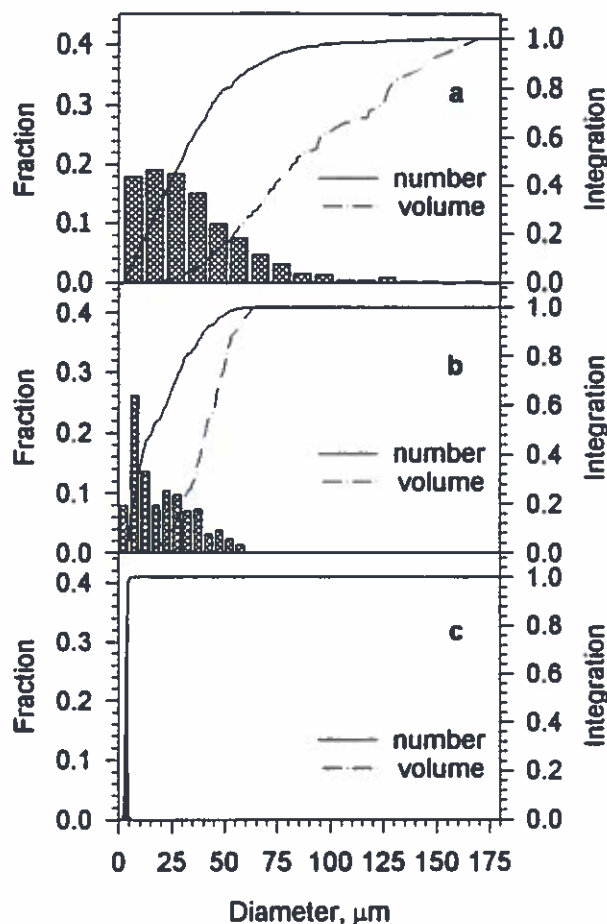


Figure 1 Diameter distributions of poly(L,L-Lc) microspheres obtained by (a) solvent evaporation, (b) solvent extraction method, and (c) by ring-opening polymerization with $[\text{L,L-Lc}]_0 = 2.77 \cdot 10^{-1} \text{ mol/l}$, $[\text{tin(II) 2-ethylhexanoate}]_0 = 4.9 \cdot 10^{-3} \text{ mol/l}$, $[\text{poly(DA-CL)}] = 1.6 \text{ g/l}$ (poly(DA-CL) with $M_n(\text{CL}) / M_w(\text{poly(DA-CL})) = 0.18$)

Plots in Figure 1 indicate the substantial difference in diameters and diameter distributions of microspheres obtained by various methods. Solvent evaporation method yielded microspheres with $D_n = 34.4 \mu\text{m}$ and $D_w / D_n = 2.68$. Microspheres obtained by the solvent extraction method gave microspheres with $D_n = 20.0 \mu\text{m}$ and $D_w / D_n = 2.06$. Ring-opening polymerization yielded microspheres with the substantially lower diameters and diameter distributions ($D_n = 3.6 \mu\text{m}$ and $D_w / D_n = 1.07$). It is worth noting that molecular weight of poly(L,L-Lc) in all types of microspheres was similar ($M_n = 9300$ and $M_w / M_n = 1.06$ for microspheres by solvent evaporation and by solvent extraction methods and $M_n = 8360$ and $M_w / M_n = 1.06$ for microspheres by ring-opening polymerization). It was important to find whether changes in the conditions of mixing would affect diameter distribution of microspheres, allowing to obtain more uniform particles and whether by changing the conditions of polymerization it would be possible to obtain microspheres with diameters larger than $5 \mu\text{m}$.

Diameters of Microspheres Obtained by Solvent Extraction Method. Influence of Rate of Mixing and/or Power of Sonication. Dependence of diameters and of diameter distributions of microspheres produced with various rates of mixing and/or power of sonication of polymer solution in Span 85 is illustrated in Figure 2.

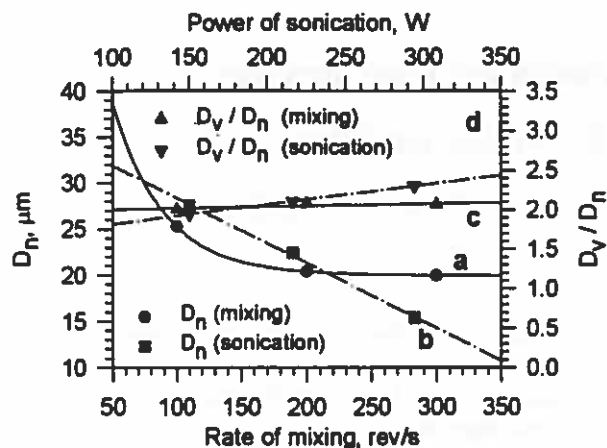


Figure 2 Dependence of diameters and diameter polydispersities on rate of mixing and on power of sonication.

Plots in Figure 2 indicate that the increasing rate of mixing results in decreasing values of D_n of microspheres which levels off at ca 20 μm. Diameter polydispersity parameter of these microspheres (D_v/D_n) is close to 2 and almost independent on the rate of mixing. When emulsions of polymer solution in Span 85 were obtained by sonication the increasing power of ultrasounds led to microspheres with smaller diameter, down to ca 15 μm, however, with the decreasing diameter of these microspheres the diameter polydispersity parameter increased from 1.95 to 2.30 when D_n decreased from 27.5 μm to 15.4 μm.

Diameters and Diameter Distributions of Poly(L,L-Lc) Microspheres Obtained by Ring-Opening Polymerization with the Stepwise Addition of Monomer. Diameter distributions of microspheres which were obtained after completion of the initial step of polymerization and after the first and second additions of new portions of monomer are illustrated in Figure 3. At the beginning of polymerization monomer concentration was equal $3.50 \cdot 10^{-1}$ mol/l. After 1.5 h a sample of the polymerizing mixture was taken for analysis (diameter distribution of these microspheres is shown in Figure 3a) and a new portion of L,L-Lc was added raising the overall concentration of monomer units in the mixture (unreacted monomer + L,L-Lc units in polymer) to $6.24 \cdot 10^{-1}$ mol/l. Than, 1.5 h later, the new sample of polymerizing mixture was withdrawn and analyzed (cf. Figure 3b) and a new amount of monomer was added raising the overall concentration of monomer units to $9.10 \cdot 10^{-1}$ mol/l. Subsequently, 1.5 h later polymerization was completed giving microspheres with diameter distribution shown in Figure 3c. Number average diameter of microspheres obtained after the first step of polymerization was equal $D_n = 3.97$ μm and $D_v/D_n = 1.09$; after the second step $D_n = 5.44$ μm and $D_v/D_n = 1.13$; after the third step $D_n = 6.36$ μm and $D_v/D_n = 1.20$. Thus, we noticed a substantial increase of the diameters of microspheres without significant broadening of the diameter polydispersity. This indicated that in the polymerization with the stepwise monomer addition a secondary nucleation of microspheres is absent. It is worth noting that due to the limited solubility of L,L-Lc it was impossible to carry on dispersion polymerization of L,L-Lc with the initial monomer concentration exceeding $4.0 \cdot 10^{-1}$ mol/l.

In our previous studies we found that during polymerization carried out at similar conditions the concentration of L,L-Lc remaining in solution (due to the reversibility of polymerization) is close to $1.4 \cdot 10^{-1}$ mol/l (4). Taking this into account we calculated from the mass balance that diameters of microspheres after the second and the third step of polymerization should increase from 3.97 μm to 5.24 μm and 6.12 μm, respectively, what agrees very well with values of D_n determined experimentally.

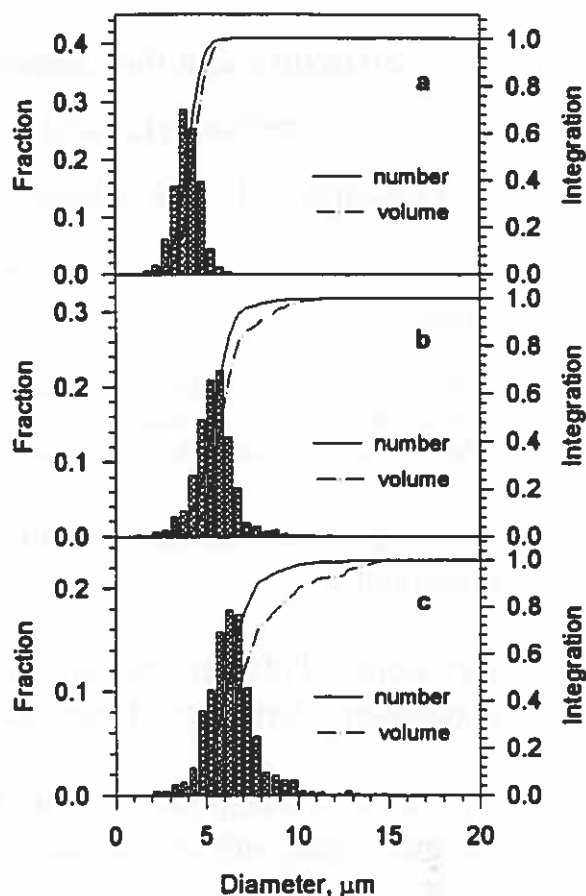


Figure 3 Diameter distributions of poly(L,L-Lc) microspheres i polymerization with the stepwise monomer addition after (a) first, (b) second and (c) third step of polymerization. Conditions of polymerization are describe in text.

Conclusions

Diameters of poly(L,L-Lc) microspheres obtained by solvent extractio polymer solutions are prepared (rate of mixing or power of ultrasounds i process of sonication) however, diameter distributions of these particles ar broad ($D_v/D_n > 2$). Direct synthesis of microspheres by ring-openin polymerization of L,L-Lc with the stepwise monomer addition allows to obtai microspheres with diameters controlled to ca 6 μm and with $D_v/D_n < 1.20$.

Acknowledgements

This work was supported by the KBN Grant 4 P05F 021 10.

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Structure and flow behaviour of crosslinked ethyl acrylate -

methacrylic acid copolymer dispersion particles

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Running head: Structure and flow behaviour of crosslinked acrylate dispersions

Key words: Polymer colloids, crosslinked ethyl acrylate - methacrylic acid copolymers, structure of particles, flow properties

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Summary

Changes in structure of dispersion particles of ethyl acrylate - methacrylic acid copolymers crosslinked (*N,N'*-methylenebisacrylamide) on alkali addition were investigated. Unlike dispersions of statistical ethyl acrylate-methacrylic acid copolymers, the particles of which disintegrate on alkalization, due probably to unintended crosslinking by chain transfer, particles of the studied dispersions had a more compact homogeneous structure. About 1 % of the crosslinking agent was sufficient to prevent the disintegration, while the flow properties of the dispersions were suitable for use as thickeners of polymer latex materials.

Submitted to Colloid & Polymer Science

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

Main activity of the group is 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. The work has been focused on copolymerization of monomers with different polarity in semi-continuous process as well as on the particle growth. Film-forming properties 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 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)**

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

**Butyl Acrylate/Styrene/HEMA copolymer latices.
(G. Baghaffar)**

**Butyl Acrylate/Styrene/methacryl amide copolymer latices -
copolymerization, particle formation, properties.**

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

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

**Emulsions of maleinized liquid telechelic polybutadienes for water-borne
paints.
(J. Fojtík - undergraduate)**

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International Polymer Colloids Group Newsletter

Spring 1998 Contribution

Polymer Research Group

University of New Hampshire

Durham, NH 03824 USA

Donald C. Sundberg

The following abstract on penetration characteristics of polymer radical and monomer into latex particles pertains to a paper that will be published in *Colloids and Surfaces* (1998).

Non-Equilibrium Particle Morphology Development in Seeded Emulsion Polymerization. I: Penetration of Monomer and Radicals As a Function of Monomer Feed Rate During Second Stage Polymerization

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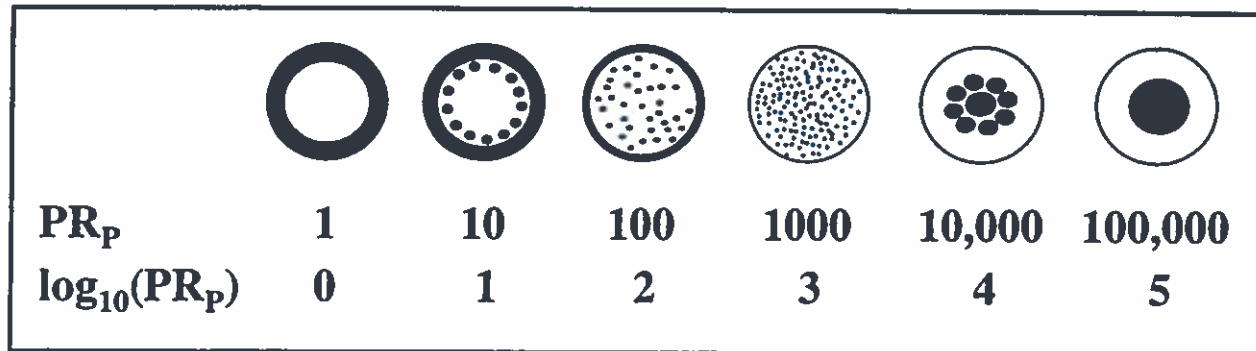
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The reaction temperature and method of monomer feeding during the second stage polymerization are potentially important parameters in controlling the particle morphology. Temperature has an effect on the initiator dissociation rate, the polymerization rate coefficients and the internal viscosity of the particles during reaction. Monomer feeding may also influence the latex morphology by creating high levels of viscosity in the particles (i.e. at very slow feed rates). Such effects can influence the tendency for the conditions in the particle to deviate from thermodynamic equilibrium and to result in "kinetically controlled" morphology.

For a polar, glassy seed [poly-methyl methacrylate (PMMA)] and a non-polar second stage [poly-styrene (PS)] or a polar, non-glassy seed [poly-methylacrylate (PMA)] and a non-polar second stage (PS), the expected equilibrium latex particle morphology may be inverted core shell (ICS) with the non-polar PS forming the core. A concept of penetration ratios for monomer, PR_M , and polymer radicals, PR_P , moving into the seed particles was developed for such a system. The PR_M was defined as the quotient between the relative frequency for the monomer to diffuse within the polymer particle divided by the relative frequency for the monomer to react, and the PR_P was defined as the quotient of the relative frequency for the polymer radicals to diffuse within the polymer particle and the relative frequency for the radicals to terminate. If the penetration ratios, PR , are large the probability for diffusion is larger than reaction, and conversely for a small PR the probability for reaction is larger than diffusion.

The study showed that monomer easily should penetrate the latex particles and most likely form a uniform concentration profile across the particles, even during slow feeding of the monomer and even for seed polymers that are glassy and have particle sizes on the order of $0.5 \mu\text{m}$. On the other hand, polymer radicals were found to be restricted to the periphery of the particles when the radical flux was high enough and the monomer feed was slow enough for glassy seed polymers, but free to penetrate for low T_g seed polymers. The morphology expectations for the studied system are presented in the Figure below. The light portion in the particles represents the seed phase and the dark phase represents the second stage polymer. At the left part of the figure a core shell morphology is drawn, and moving to the right the morphologies shown have a decreasing polymer shell and an increasing amount of second stage polymer in the particle cores. The inverted core shell morphology to the extreme right and may represent the equilibrium structure for the studied system. The core shell morphology represents the situation where the internal particle viscosity may be high enough such that the penetration of the second stage polymer into the seed particle is completely restricted. Moving to the right in the figure also suggests that the internal particle viscosity may be lower during polymerization (i.e., faster monomer feed rates) and the final particle morphologies get closer to equilibrium as the second stage polymer radical penetration is increased.



Penetration ratios values were calculated and correlated with various experimentally observed particle structures as shown in the Figure. Based on these approximate placements we assigned order of magnitude values to the penetration ratios and correlated each with a particular morphology, as shown in the top row. The log of the assigned PR_p values indicate a "type", or category of particle structure. Here Type 0 is a core shell and Type 5 is an inverted core shell, with Types 1-4 representing various non-fully phase separated particles. The penetration model shows that the relation between the monomer diffusion coefficient and the monomer concentration in the particles is one of the critical factors in understanding the development of non-equilibrium latex particle morphologies.

We have learned that one can not assume that the nucleation of occlusions forms throughout the particle during starve fed reactions. The problem must be approached by considering diffusion of polymer radicals and monomer from the surface of the particle towards it's center. Additionally, the challenge for all models will be the ability to predict reaction rates (i.e., \bar{n}) in these phase separated particles.

Competitive Adsorption of Anionic Surfactant on Blends of Polymer Latices

Interfacial tension of polymers against water has been shown to be crucial in determining equilibrium morphology of composite particles produced by seeded emulsion polymerization. Since the presence of surfactant on the particle surface greatly affects this interfacial tension, knowledge of how much surfactant adsorbs on a given polymer surface is equally important. Thermodynamics leads to the idea that the packing of surfactant on a surface at a fixed temperature is a function only of the concentration of the surfactant in the water phase since, at equilibrium, the chemical potentials of the surfactant in the water and on the surface must be equal. Surfactant packing as a function of the concentration in the water phase is referred to as the adsorption isotherm. It should be possible to predict the total amount of surfactant present in a composite latex (Fig. 1) of the two polymers, P1 and P2, as a function of the surfactant concentration in the water phase based on 1) the total surface area of P1 in the latex, 2) the total surface area of P2 in the latex and 3) the adsorption isotherms for the individual latices. A blend of two single polymer latices should mimic the behavior in a composite latex while allowing control over the total surface area of each polymer in the blend. Experiments have been performed to test this

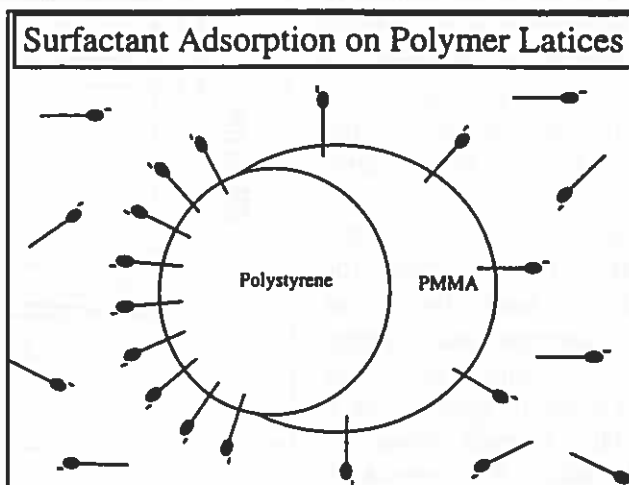


Figure 1: Competitive Adsorption of surfactant on a composite particle

hypothesis, i.e., that the packing on each polymer surface in a composite latex or latex blend is a function only of the surfactant concentration in the water at the temperature of the experiment.

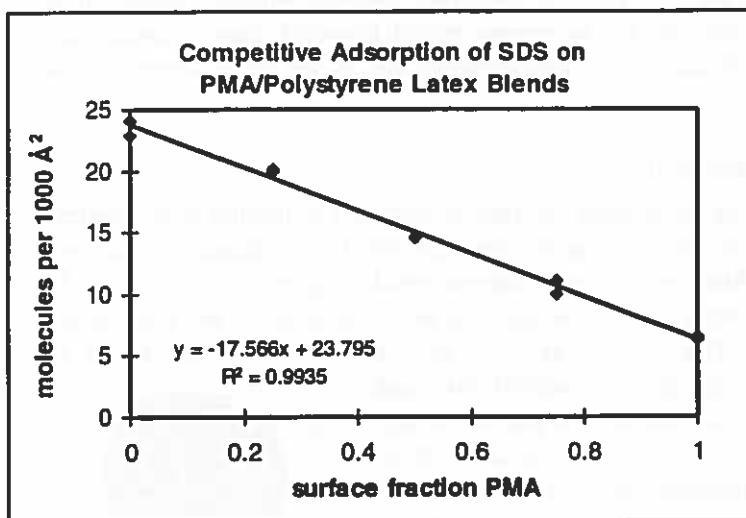


Figure 2: Saturation adsorption of SDS on latex blends as a function of polymer surface fraction

Adsorption isotherms were obtained by performing conductometric titrations with SDS for pure water and individual latices of Polystyrene, PBMA, PMMA and PMA. Latices were passed over ionic resins prior to titrating to remove surfactant and residual initiator. Conductivity was normalized respective to the value at a surfactant concentration of zero and at saturation. For a latex titration, the concentration of surfactant in the water is determined by relating the normalized conductivity to that for a pure water titration. Combining this with the material balance for the titration determines the adsorption isotherm. Adsorption areas at saturation, A_s , for SDS on the four polymers studied were 42.6, 57.9, 93.1, and 158.6 Å²/molecule for PS, PBMA, PMMA, and PMA respectively, and are seen to be increasing as the polarity of the polymer increases. Numerous blends of these latices were

then made for different polymer pairs at various surface fractions, $P1/(P1+P2)$. The average A_s of SDS on each blend was found to be a linear function of the surface fraction which is expected if adsorption on one polymer is not affected by the presence of the other. An example of this linearity is shown in figure 2 for Polystyrene/PMA blends. Predictions were also made for adsorption on latex blends at surfactant concentrations ranging from zero to saturation. An example is given in figure 3 for a 50/50 surface fraction blend of PMA and PBMA. The individual lines for PMA and PBMA are predictions of the amount of SDS

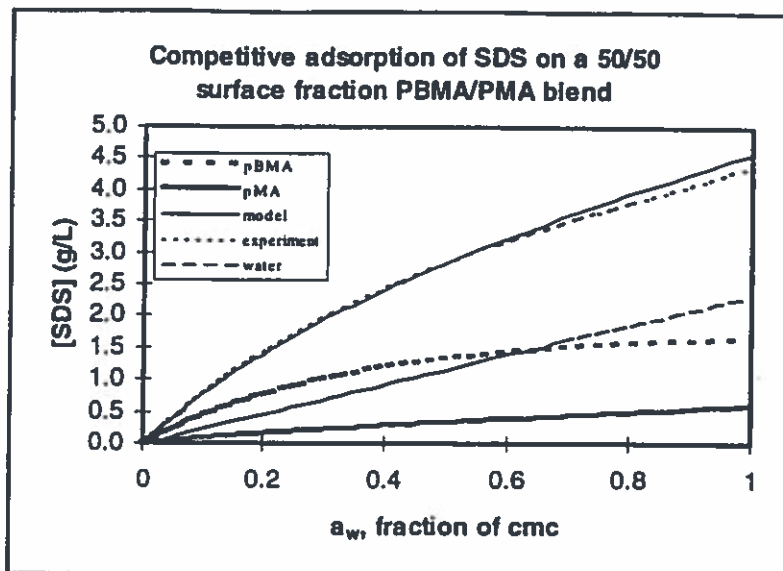


Figure 3: Adsorption of SDS on a latex blend as a function of SDS concentration in water

that should be on each surface based on their adsorption isotherms and the line labeled 'predicted' represents the sum of the predictions for the SDS on the two surfaces and in the water. The line labeled 'experiment' represents the actual titration of this blend. Clearly this graph shows good agreement between the prediction and the experiment, confirming the hypothesis that the adsorption on each surface only depends on the concentration of SDS in the water phase. Similar results have been obtained for blends of PMA/PS, PBMA/PS, PMMA/PS, and PBMA/PMA.

Studies are currently being conducted on the effect of monomer swelling on the adsorption of surfactant on latex particles. These experiments are by no means trivial however, due to significant lowering of the cmc due to the presence of monomer in the water (especially for the more water soluble monomers) and other experimental difficulties.

UNHLATEX Morphology Software Development

Over the past several years we have been developing interactive software to predict latex particle morphology. In order to simulate experimental evidence in the form in which it is obtained, we have created an electron microscopy simulation within the software. The morphology predictions (core-shell, hemisphere, partial engulfment, etc.) are converted to electron micrographs which allow the user to see how such particles would appear in both the TEM and SEM. For the TEM the user can choose to observe whole particles or microtomed sections, and can selectively stain either or both phases of the particles. The software allows the user to change the microscope magnification level and contrast, to view different areas of the simulated grid on which randomly oriented particles are distributed, and to select the thickness of microtomed sections. The results are projected in gray tones to allow direct comparison to actual micrographs.



Fig. 1.

Figures 1-4 demonstrate the types of results that are achievable. Here we have simulated the TEM's for a system for which we would predict a partially engulfed structure at a stage ratio (relative mass of second stage to seed polymer) of 100%, with the second stage being stained darker than the seed. Figure 1 shows the morphology as seen by a "perfect" section through the particle. Figure 2 demonstrates how such particles would appear in the TEM as whole particles, stained to a chosen level to obtain contrast. Figure 3 shows the same display for the condition in which the staining does not allow as good contrast as seen in Figure 2. In our

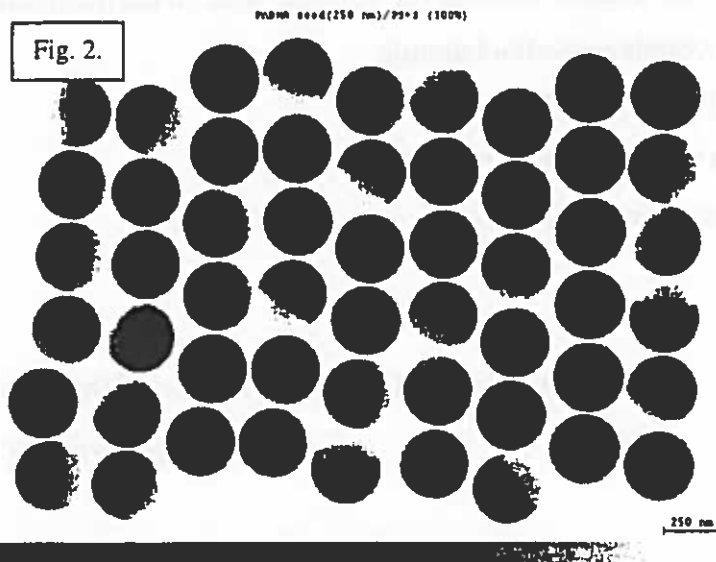
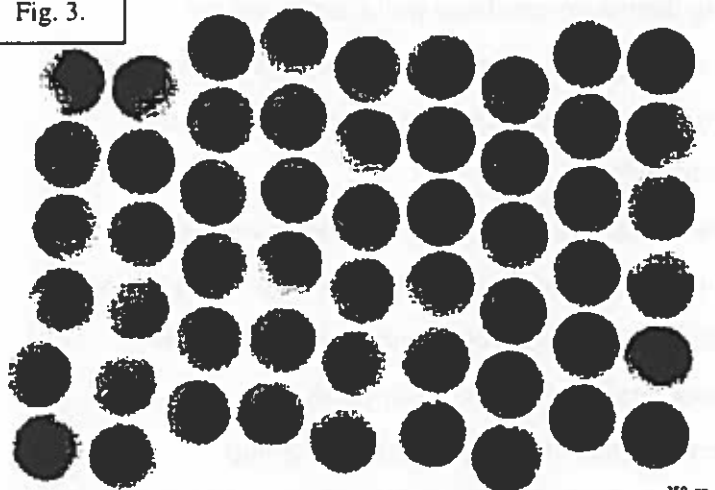


Fig. 2.

250 nm

Fig. 3.



250 nm

experience this is not an uncommon difficulty in actual electron microscopy work. To compare with the whole particle TEM, Figure 4 displays the predicted results for microtomed sections of these particles. Here we have chosen the section thickness to be 90 nm for the 250 nm diameter seed latex particle, and have selectively stained the polymer phases to provide good contrast. This micrograph displays various sized sections of particles created by the microtoming and demonstrates how many different apparent shapes and sizes are to be expected when observing the TEM results for even the simple particle shown in Figure 1.

The microscopy tool within the morphology software gives us a very helpful way to compare our predicted results to actual experimental results. Side by side comparisons of the experimental and predicted TEM micrographs is far superior to viewing just the experimental TEM picture and trying to convince oneself that Figure 1 represents the true structure of particles.

Although not shown, similar comparisons can be made for SEM micrographs.

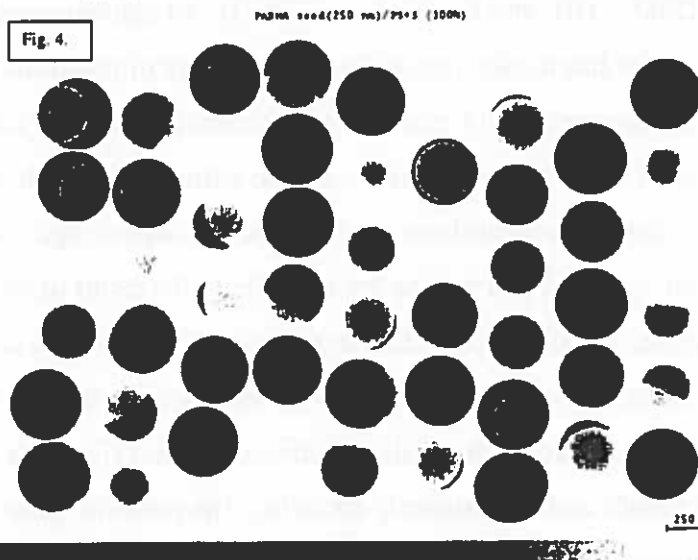


Fig. 4.

250 nm

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“Polymer End Groups in Persulfate Initiated Styrene Emulsion Polymerization”

The waterborne oligomers which are nucleating during an emulsion polymerization are located inside the polymer particles at the end of the polymerization. An investigation of their chemical structure in the presence of the high molecular weight polymers grown inside the polymer particles requires advanced analytical techniques.

MALDI-TOF-MS investigations of the polymer inside the particles at the end of a persulfate initiated emulsifier-free emulsion polymerization of styrene reveal - beside sulfate end groups as the result of primary radical initiation - a variety of different end groups of the polymer molecules almost independent of the buffer concentration employed during the polymerization. The results support at least the existence of the following end group combinations: H - H, H - OH, $K^+OO - OH$, $K^+OO - K^+OO$, HO - OH, $K^+OSO_3 - H$, $K^+OSO_3 - OH$, and $K^+OSO_3 - K^+OSO_3$. An explanation of those on the first view astonishing results has to take into account the variety of reactions which free radicals may undergo in aqueous media [1]. So, the hydrogen end groups are either a result of chain transfer reactions or of water phase chemistry of free radicals and the hydroxyl end groups are the result of either acidic hydrolysis of sulfate end groups or again of water phase chemistry [1]. Whereas, the carboxyl end groups are very likely the result of an oxidation of hydroxyl end groups by either persulfate or hydrogen peroxide formed in the aqueous phase [1].

These results are significant with respect to particle nucleation as well as radical entry as all products except the chains containing carboxyl groups are initiated by the corresponding radicals and subsequently came into the particles either by radical entry or during the nucleation step. The entering radicals can be either corresponding primary radicals (H-, HO-, or O_3SO -radicals) or oligomer radicals. In any case, these results do not suggest that surface activity of radicals is a prerequisite for entry into particles.

With respect to nucleation the results underline the importance of aqueous phase reactions as the initiating radicals govern the solubility of waterborne species and hence also nucleation. Within the frame of non-micellar nucleation models [2 - 4] the species with the lowest solubility in the aqueous phase will nucleate. In a first approximation it is reasonable to assume that in the order H - H, H - OH, HO - OH, $K^+OO - K^+OO$, $K^+OSO_3 - H$, $K^+OSO_3 - OH$, and $K^+OSO_3 - K^+OSO_3$ the water solubility increases and hence the probability of nucleation decreases provided the concentrations of all species are comparable. For basic investigation as well as for modelling of particle nucleation the observed variety of end groups means that KPS is a very unsuitable initiator. Other initiating system leading to none or much less side reaction as for instance water-soluble azo initiators seems to be much more suited.

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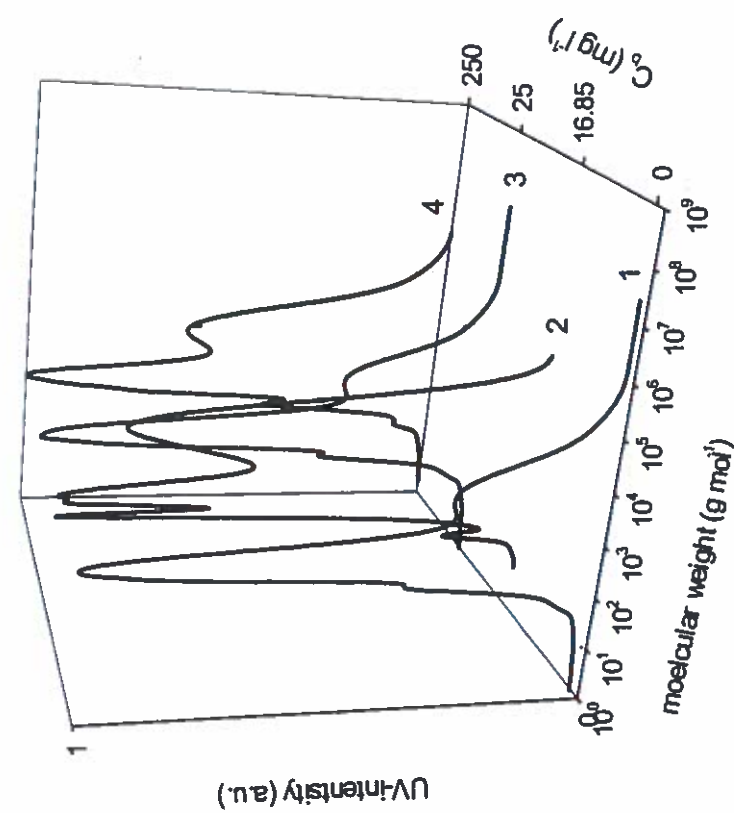


Figure 1: Molecular weight distribution of the polymer inside the final latex particles in dependence on the buffer concentration

1 - without buffer; end-pH: 2.63

2 - with 16,85 mg l⁻¹ buffer; end-pH: 2.65

3 - with 25 mg l⁻¹ buffer; end-pH: 3.30

4 - with 250 mg l⁻¹ buffer; end-pH: 7.20

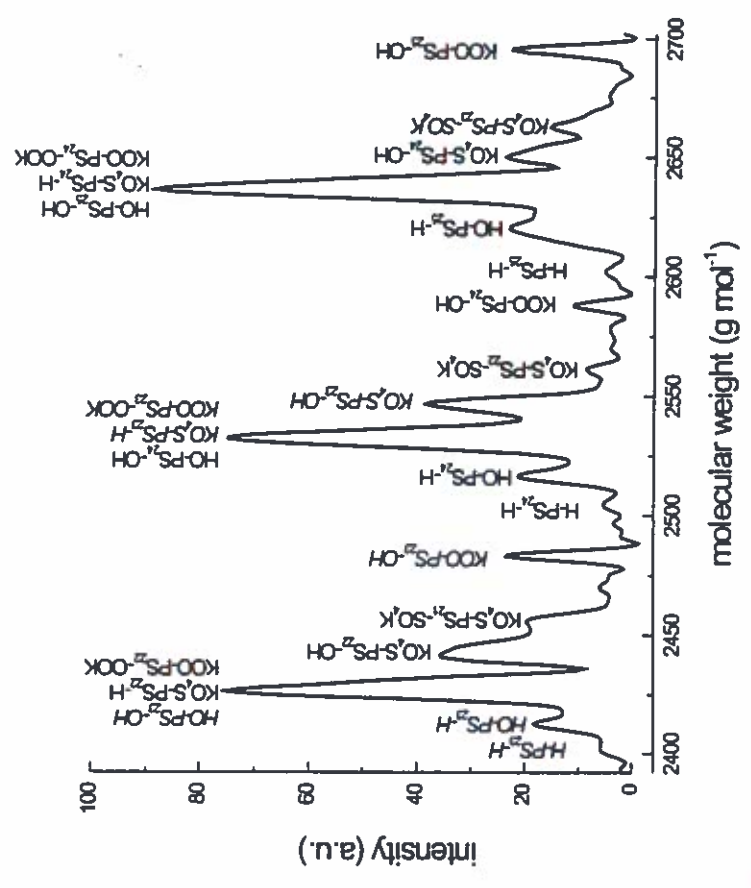


Figure 2: Peak assignment for the medium smoothed MALDI-TOF-

MS spectrum

**Film formation of polymeric emulsions:
Structure set-up and the pinhole effect characterized by microscopic
techniques**

Carsten Schellenberg, Klaus Tauer , Markus Antonietti*

- a contribution to the Festschrift honouring the achievements of Prof. Dr. Johan
Sjöblom in colloid science

ABSTRACT

Drying of emulsions of special polymeric core-shell latexes results in structured films and coatings with advantageous material properties. Here, we focus on so-called "container particles", consisting of a low viscosity core with a low glass transition (poly(2-ethylhexyl methacrylate), PEtHMA), covered by a thin shell of a cross-linked rubber (poly(*n*-butyl acrylate), PBA). These particles can be regarded as model emulsions of reactive polymeric oils with a very high colloidal stability.

The film formation of these latexes was studied by atomic force microscopy (AFM) in the tapping mode as well as by transmission electron microscopy (TEM). It is shown that the films stay nanostructured after the drying process, i. e. they exhibit both a controlled topography as well as a network superstructure originating from the characteristics of the original dispersions.

TEM allows to detect the whereabouts of the polar stabilizer. Both continuous surfactant films as well as inverted micelles are found. A geometrically induced demixing phenomenon is found which enriches the polar components and might be the molecular reason for the so-called pinhole-effect, the failure of water-born coatings in contact with water.

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Effect of Molecular Mass and Polymer Linearity of Styrene Butadiene Copolymers on Compatibility with Asphalt

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Asphalt, the complex residual mixture remaining after crude oil fractionation, is frequently "modified" by the addition of small amounts of polymers to improve a number of its application properties. Among these properties are resistance to flow under heat and pressure (road deformation at intersections) and resistance to cold brittleness and cracking (pothole formation). Polymers frequently, upon mixing into the hot asphalt, separate from the bulk mixture as a polymer-rich layer on the top of the asphalt. This inhomogeneity is typically known as "incompatibility" in the asphalt trade.

In this paper, the compatibility of cold-polymerized random styrene butadiene copolymers is studied in Cenex AC-20 asphalt. Relationships among varying molecular mass and linearity of the copolymers, compatibility, morphology and application properties are shown. Thermodynamically, the "compatibility" is improved with lower molecular mass polymers possibly by more effective solubilization of the polymer molecules. This is reflected somewhat by the morphology of the systems which move from high molecular mass polymers giving rise to networks of swollen of polymer in the continuous asphalt matrix to the lower molecular mass polymers giving rise to discrete domains of swollen polymer. Correlations between the system morphology and rheological properties of the modified asphalt will also be addressed.

FORMATION OF COLLOIDAL COMPOSITE PARTICLES USING PREFORMED POLYMER

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Composite colloidal particles are usually prepared by 'in-situ' polymerisation to produce one component in the presence of existing particles. The morphology of the derived particles depends on a number of factors and conditions operative during the process. Often the structures are not at equilibrium; in some cases rearrangement of the morphology may be induced by simple alteration of conditions such as by raising the temperature. A number of inorganic materials have been encapsulated by similar techniques¹.

Alternative processes which employ preformed polymer particles, obviating 'in-situ' polymerisation, offer some advantages including improved process control, relative ease of maintaining colloidal stability and the ability to incorporate components which would otherwise be adversely affected by free-radicals or other species required for polymerisation. These techniques may be used to prepare inorganic-polymer composites as well as polymer-polymer^{2,3}. Contact between the dissimilar particles is allowed or induced whilst avoiding flocculation of like particles; the interfaces are pre-selected or modified 'in-situ' so that at temperatures above the glassy transition, the polymer spreads over or engulfs the surface of the other particle. The processes appear to be thermodynamically driven by a reduction in interfacial energy. It has been suggested that this principle is important in phagocytosis⁴, a mechanism in physiology.

The Young expression for the three interfacial energies as used in the classic equation for contact angle, can be used to indicate the generalised type of structure which will be preferred⁵. Other workers have considered the three spreading coefficients⁶ to make these predictions; the two approaches have been compared⁷. If the individual interfacial energies and the volume ratio of the two components are known, the particle morphology representing the lowest interfacial energy may be described in detail⁸.

The engulfment process has been studied using well characterised particles to produce colloidal particles with a poly(butyl methacrylate) matrix and with multiple internal domains or 'cores' of polystyrene⁹. The core particles were made by surfactant-free emulsion polymerisation¹⁰ using an anionic initiator; the engulfing particles were made by a similar process except that the initiator was cationic and methoxy-poly(ethylene oxide) oligomeric chains were attached to the surfaces by an established technique¹¹ to provide them with steric stabilisation. In this work the acrylic engulfing particles were relatively large compared to the core particles. When the core particles were the larger species a modified procedure was required in which the smaller particles were first assembled at the surface of the cores and subsequently the temperature was raised above the glassy transition so that with the correct interfacial energies, the smaller particles spread over the surface of the cores¹². For this process an optimum number ratio for the two particle types was apparent. Using this optimum ratio and assuming that the interfacial polymer participated in the internal rearrangement to remain at the polymer-water boundary, the nominal spacing of the steric stabilising chains on the engulfing particles was repeated on the final composite particles. It was observed that the composite particles possessed the superior stability properties commonly associated with steric colloidal stabilisation.

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