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IPCG

INTERNATIONAL POLYMER COLLOIDS GROUP

IPCG Newsletter February 2003

Conference announcement

Gordon Conference on Polymer Colloids
Tilton, New Hampshire, June 29 - July 4, 2003

Application forms and further information will be sent to all IPCG members. You can also check the Gordon Conference website:
http://www.grc.uri.edu

or contact the Conference Chair, Bob Gilbert:
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INTERNATIONAL POLYMER COLLOIDS GROUP NEWSLETTER

Contribution from the Institute for Polymer Materials "POLYMAT" and Grupo de Ingeniería Química, Facultad de Ciencias Químicas, Universidad del País Vasco, Apdo. 1072, E-20080 Donostia-San Sebastián, Spain.

Reported by José M. Asua

January 2003

Recently published articles:

SEEDED SEMIBATCH EMULSION POLYMERIZATION OF N-BA: EFFECT OF THE SEED PROPERTIES

C. Plessis, G. Arzamendi, M. Agnely, J.R. Leiza, J.M. Asua

J. Polym. Sci. Part A: Polym. Chem. 40, 2878 (2002). (Abstract in the previous IPCGN).

MAXIMIZING PRODUCTION AND POLYMER QUALITY (MWD AND COMPOSITION) IN EMULSION POLYMERIZATION REACTORS WITH LIMITED CAPACITY HEAT REMOVAL

M. Vicente, J.R. Leiza, J.M. Asua.

Chem. Eng. Sci. 58 (1), 215 (2003). (Abstract in the previous IPCGN).

COPOLYMERS

J.R. Leiza, J.M. Asua

Kirk-Othmer Encyclopedia of Chemical Technology. On-line Edition. John Wiley & Sons, New York (2002).

The preparation, properties, use and characterization of synthetic copolymers is reviewed and the future trends discussed. The different copolymer structures are detailed and the nomenclature explained. The copolymerization reactions (free radical including controlled free radical, anionic, cationic, ring-opening, catalytic and step-growth) are discussed emphasizing the copolymer structures attainable through each polymerization mechanism. Industrially important random, alternating, block, graft, star and hyperbranched copolymers are discussed in terms of the processes used to produce them and the properties achieved. Their main uses and trade names are also detailed. Future trends are discussed.

KNOWLEDGE BASED CHOICE OF THE INITIATOR TYPE FOR MONOMER REMOVAL BY POST-POLYMERIZATION

P. Ilundain, D. Alvarez, L. da Cunha, R. Salazar, M.J. Barandiaran, J.M. Asua

J. Polym. Sci. Part A: Polym. Chem. 40, 4245 (2002).

The mechanisms involved in the monomer removal by post-polymerization were investigated with the aim of establishing a criterion to select the most effective initiator systems. Three redox systems yielding radicals of different hydrophobicity were studied. It was found that efficiency in monomer removal by post-polymerization increased with the hydrophobicity of the radical formed from the initiator system. This result was independent of the water-solubility of the residual monomer. The mechanistic reasons for this result are discussed.

CONTROL OF THE ADHESIVE PROPERTIES OF N-BUTYL ACRYLATE/STYRENE LATEXES

O. Elizalde, M. Vicente, J.R. Leiza, J.M. Asua.

Polym. React. Eng. 10 (4), 265 (2002).

A model relating the adhesive properties and the complete molecular weight distribution of n-butyl acrylate/styrene latexes of fixed copolymer molar composition (85/15) was constructed using partial least squares regression (PLS-R). This quantitative relationship allows the prediction of the adhesive properties of the latexes from MWD measurements. After validation of the model, it was combined with a control strategy, which allows the production of latexes of controlled copolymer composition and MWD. The resulting system can be regarded as a method for the control of the adhesive properties of the latex. This methodology was satisfactorily validated experimentally by the production of two latexes of different adhesive performance.

Coming articles

MODEL REDUCTION IN EMULSION POLYMERIZATION USING HYBRID FIRST PRINCIPLES/ARTIFICIAL NEURAL NETWORKS MODELS

A. d´Anjou, F J. Torrealdea, J.R. Leiza, J.M. Asua, G. Arzamendi

Macromolecular Theory & Simulations (accepted)

A first-principles mathematical model for emulsion polymerization was reduced by using a hybrid mathematical model composed by artificial neural networks (ANN) and material balances. The goal was to have an accurate model that may be integrated fast enough to be used for on-line optimization purposes. In the reduced model the polymerization rate and the instantaneous weight-average molecular weight were calculated by means of artificial neural networks. These ANNs were incorporated to first principles material balances. The accuracy of the reduced model under a wide range of conditions was assessed. Savings in computer time were achieved by using the reduced model, which makes it suitable for on-line optimization purposes.

POST-POLYMERIZATION VS DEVOLATILIZATION FOR MONOMER REMOVAL IN LATEXES

R. Salazar, D. Alvarez, P. Ilundain, L. da Cunha, M.J. Barandiaran, J.M. Asua

Progress Colloid & Polym. Sci. (accepted)

The efficiency of post-polymerization and devolatilization for residual monomer and VOC removal was investigated. It was found that mass transfer from aqueous phase to gas phase was the rate-determining step for devolatilization. The effect of the thermodynamic equilibrium coefficients on the latex devolatilization efficiency was studied. A strategy in which post-polymerization and devolatilization was applied simultaneously was found to be the most efficient one in both the removal of the residual monomer and VOC present in the latex, since it took advantage of both processes.

NOVEL INSIGHT INTO THE MINIEMULSIFICATION PROCESS: CFD APPLIED TO ULTRASONIFICATION

M. do Amaral, A. Arevalillo, J.L. Santos, J.M. Asua

Progress Colloid & Polym. Sci. (accepted)

Miniemulsion and miniemulsion polymerization are experiencing a kind of revival. Nevertheless, despite the multitude of publications on miniemulsion, some fundamental aspects still remain unclear, like the possible influence on the miniemulsion characteristics given by a selected emulsification device. In this work, Computational Fluid Dynamics, CFD, was used to further elucidate the miniemulsification process during sonication. The flow pattern given by CFD was used as input for the model of the evolution of droplet size distribution. The effect of the intensity of the ultrasound device, the effect of agitation, as well as the effect of the geometry of the system on the miniemulsion final droplet size distribution were analyzed.

EVIDENCE OF BRANCHING IN POLY(N-BUTYL ACRYLATE)

C. Plessis, G. Arzamendi, J.M. Alberdi, A.M. van Herk, J.R. Leiza, J.M. Asua.

Macromolecular Rapid Communication (accepted)

It was found that a branched poly n-butyl acrylate was obtained in bulk and solution pulsed-laser polymerizations carried out temperatures between -16 to 60ºC. The branches are predominantly short branches formed by backbiting reactions. Using this information an estimation of the Arrenhius temperature dependence of the rate constant for backbiting is calculated in this work. The activation energy of this process is ca. 30 kJ/mol, remarkably larger than that of the propagation step (~ 17 kJ/mol). This means that branching relative to propagation, increases with temperature leading to broader SEC traces at higher temperatures and therefore causes difficulties in the accurate determination of kp rate constants of n-BA.

DISTRIBUTION OF SURFACTANTS NEAR ACRYLIC LATEX FILM SURFACES: A COMPARISON OF CONVENTIONAL AND REACTIVE SURFACTANTS (SURFMERS)

E. Aramendia, J. Mallegol, C. Jeynes, M.J. Barandiaran, J.L. Keddie, J.M. Asua

Langmuir (accepted)

The use of reactive surfactants is a promising way of avoiding the deleterious effects on film properties caused by the segregation of conventional surfactants. In this work, the distribution of conventional and reactive anionic surfactants in acrylic latex films was investigated. Atomic force microscopy was used to examine the surface of the films cast from high solids acrylic latexes, and Rutherford backscattering spectrometry provide depth profiles of the surfactants. It was found that the use of surfmers is thus an effective way of eliminating unwanted surfactant exudation. The amount of conventional surfactant exuded to the surface increased with the temperature at which the films were annealed (60, 90 and 125 °C), but the migration of the surfmer was not affected. An unexpectedly large amount of conventional surfactant was exuded to the film surface when annealed at 125 °C. This result suggests that the transport of the conventional surfactant to the surface might be facilitated by the enhanced mobility of poly(acrylic acid) shells at temperatures above its glass transition temperature (*ca*. 106 ºC).

Submitted articles

MOLECULAR WEIGHTS IN EMULSION COPOLYMERIZATION OF BUTYL ACRYLATE/STYRENE (50/50)

N. Zoco, L. López de Arbina, J.R. Leiza, J.M. Asua, G. Arzamendi

J. Polym. Sci. Part A: Polym. Chem.

A model relating the adhesive properties and the complete molecular weight distribution of n-butyl acrylate/styrene latexes of fixed copolymer molar composition (85/15) was constructed using partial least squares regression (PLS-R). This quantitative relationship allows the prediction of the adhesive properties of the latexes from MWD measurements. After validation of the model, it was combined with a control strategy, which allows the production of latexes of controlled copolymer composition and MWD. The resulting system can be regarded as a method for the control of the adhesive properties of the latex. This methodology was satisfactorily validated experimentally by the production of two latexes of different adhesive performance.

MATHEMATICAL MODELING OF MULTIMONOMER (VINYLIC, DIVINYLIC, ACIDIC) EMULSION COPOLYMERIZATION SYSTEMS

M. Zubitur, P.D. Armitage, S. Ben Amor, J.R. Leiza, J.M.Asua

Polymer Reaction Engineering

A mathematical model for free-radically initiated semi-continuous emulsion polymerizations of a multimonomer systems containing vinylic, divinylic and acidic monomers in the presence of chain transfer agent (CTA) was developed. In addition to the more traditional aspects of emulsion polymerization, the model takes into account both the presence of water soluble monomers and the formation of gel due to the polymerization of a divinylic monomer in the presence of CTA. The outputs of the model are the time evolution of monomer conversions, copolymer composition, molecular weight of the sol polymer and gel fraction.

TOWARDS THE PRODUCTION OF GREEN/ODORLESS LATEXES

R. Salazar, D. Alvarez, P. Ilundain, L. da Cunha, M.J. Barandiaran, J.M. Asua

RSC Books

The main aspects of postpolymerization and devolatilization for cleaning industrial latexes were analyzed. Monomer partitioning was studied finding that most of the monomer was in the polymer particles, independently of its water solubility. The knowledge of the mechanisms involved in monomer removal by postpolymerization allowed the development of a mathematical model, able to predict both, monomer removal and new VOCs formation when the very efficient organic hydroperoxides were used as initiators. Using this model, the optimal conditions for the removal of the residual monomer in a minimum process time and minimizing the production of new VOCs were determined.

Devolatilization involves the mass transfer of monomers and VOCs from polymer particles to the aqueous phase and from this phase to the gas phase. The latter is the rate determining step. In this work, the effect of one of the variables involved in this stage, that is, the gas flow rate on the devolatilization efficiency was studied, and the relationship between the minimum gas flow rate and total process time, needed to reach a known VOC content, was determined.

EFFECT OF THE INTRAMOLECULAR CHAIN TRANSFER TO POLYMER ON PLP-SEC EXPERIMENTS OF ALKYL ACRYLATES

G. Arzamendi, C. Plessis, J.R. Leiza, J.M. Asua

Macromolecular Theory & Simulations

The polymerization of alkyl acrylate monomers produces polymers with a significant amount of branches (1-4%). Although both short and long chain branches are formed by intra and inter- molecular chain transfer to polymer mechanisms, recent experimental evidence shows that short branches formed by the intramolecular, so called backbiting process are predominant. In this work the effect of this process on the molecular weight distribution trace of poly n-butyl acrylate obtained by pulsed-laser polymerization is shown by simulation. The experimental difficulties encountered to accurately determine the kp values at temperatures above 30ºC are predicted and the featureless broad SEC traces attributed to the backbiting mechanism, that is negligible as temperature decreases due to the large activation energy of this process.

REACTIVE SURFACTANTS IN EMULSION POLYMERS

E. Aramendia, J. Mallegol, C. Jeynes, J. Grade, T. Blease, M.J. Barandiaran, J.L. Keddie, J.M. Asua

RSC Books.

The aim of this work is to contribute to the understanding of the mechanism of polymerization of reactive surfactants (surfmers) in the high solids content emulsion polymerization of acrylic monomers as well as the effect of surfmers on film properties. The non-ionic Maxemul 5011^{TM} surfmer is used here in emulsion polimerization. Our experimental study of the effect of the initiator type and the particle size of the seed on the surfmer incorporation into the acrylic polymer particles showed that the surfmer reacted mainly by copolymerization with the monomers in the enter shell of the polymer particles. The performance of acrylic and vinylic latexes synthesized with surfmers was investigated and compared to similar latexes stabilized by conventional surfactants. The use of surfmer showed better performance in tests of freeze-thaw, water up-take, water permeability. This is likely due to the non-migratory character of the surfmer.

RESIDUAL MONOMER PARTITIONING IN EMULSION POLYMERIZATION

R. Salazar, P. Ilundain, D. Alvarez, L. da Cunha, M.J. Barandiaran, J.M. Asua

J. Chem. & Eng. Data

Monomer partitioning measurements of vinyl acetate and butyl acrylate present at very low monomer concentration (100-5000 ppm) in vinylic and acrylic latexes were performed. The results were validated by using two different techniques: static vapor pressure and dialysis. Results showed that monomer partitioning is insensitive to polymer composition at this level of monomer content. An slightly increase in the partition coefficient when temperature decreases was found. Different mathematical equations reported in literature were compared to experimental data. The Vanzo equation was able to predict all the experimental results.

KNOWLEDGE-BASED CONTROL OF EMULSION POLYMERIZATION: TAYLORING ADHESIVE PROPERTIES

O. Elizalde, M. Vicente,C. Plessis, J.R. Leiza, J.M. Asua

J. Coating Technology, “El-Aasser Tess Award Issue”.

An on-line control strategy to produce copolymer latexes with desired adhesive properties (resistance to shear and resistance to peel) has been developed. The strategy required a quantitative model relating adhesive properties and molecular weight distribution that was build using partial least squares regression. The model was used to determine the set-point trajectories of the monomers and chain transfer agent that are used as manipulated variables in the control strategy. The control strategy was experimentally verified to produce a n-butyl acrylate/styrene copolymer latex with a resistance to shear of 1310 s and resistance to peel of 3.1 N/100 mm.

Contribution from the Department of Polymerization Reactions,
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Reported by **Jaroslav Bartoň**
(December 20, 2002)

Chain association of water-soluble monomers in o/w microemulsion monitored by pyrene fluorescence.

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2) Department of Chemical Engineering, National Taiwan University of Science and Technology, Taipei 106, Taiwan

Abstract: The extent of intra- and inter-chain associations of charged water-soluble monomers and its transfer into the oil-in-water micelle were studied by using a steady-state fluorescence spectroscopy. These experiments were carried out with both uncharged (acrylamide; AAm) and charged hydrophilic monomers [zwitterionic N,N-dimethylacryl ammonium propane sulfone (DMAPS), etc.] and pyrene (Py) as a probe. The value of the Stern-Volmer constant (K_{SV}) was taken as the measure of monomer incorporation into the micelle. The phase transfer of monomer from the aqueous phase to the micellar phase proceeds via a complex of monomer with emulsifier. Under the circumstances, the complexed hydrophilic monomer (quencher) is transformed to the organic phase saturated with probe. The quenching of Py emission by (un)charged hydrophilic monomer depends on the partitioning of monomer between the aqueous phase and the micelles. The main microenvironment for the quenching was suggested to be the oil-water interface. The synergistic effect was observed in the presence of a small amount of salt, polymer and poor coemulsifier. Strong coemulsifier, however, creates barrier for entering of monomer (quencher) into the interface layer and, thereby, the quenching is decreased.

Introduction: Pyrene (Py) has been widely used to probe the microenvironment of organized host media such as micelles and microemulsions [1]. Pyrene as a probe is particularly attractive because of its relatively long fluorescence lifetime, its ability to measure the polarity of its microenvironment, and its tendency to form excimers with a distinct fluorescence [2]. Thus, Py is useful indicator of the polarity via the ratio of intensities of the first to the third peaks in the fluorescence emission spectrum of Py, I_1/I_3. Furthermore, the excimer-to-monomer ratio I_E/I_M is a characteristic of the system that can serve as an indicator of a local concentration of probe in the micelles. When plotted against [Py]/[E], the excimer-to-monomer ratio is a characteristic feature of a micellar system, provided that the size and aggregation number do not change. [E] represents the concentration of emulsifier. The aim of this study is a systematic investigation of interaction between charged emulsifiers and/or micelles with unsaturated (un)charged hydrophilic monomers.

Results and discussion.

Tables 1-3 indicate that the quenching of Py* by DMAPS is much stronger in the homogeneous solution than in the micellar one. The lower K_{SV} in the micelle results from the increased isolation of Py and the quencher, that is, the partitioning of ingredients between the continuous water phase and micelles decreases the average concentration of Py and quencher in the common domain (Py accumulates in the micelle core while DMAPS in the continuous phase). This is a reason why the interaction between Py and DMAPS is depressed in the micellar system. However, the interaction net in the micellar solution is more complex. The competitive interaction between DMAPS molecules themselves and with SDS also varies K_{SV}. The similar behavior was observed in quenching of excited methylpyrene by AAm in homogeneous and micellar solutions [3] in the micelle solution was attributed to low polarity of microenvironment provided by micelles.

Table 1. Variation of Stern-Volmer constants a) for aqueous pyrene solution at 25 °C

Run	Quencher b)	Ksv (M^{-1})		Surfactant(g/dL)
A	DMAPS	566.61c)	562.02d)	0
B	DMAPS	16.18c)	15.41d)	0.036
B	AAm	10.09c)	9.93d)	0.036
C	DMAPS	278.92c)	257.60d)	0.2
D	DMAPS	26.11c)	25.63d)	0.036
D	AAm	8.21c)	7.06d)	0.036

a) 9.5 ml H_2O, 0.5 ml Py solution, [Py] = $5*10^{-7}$M; Py solution: 0.00202 g Py +500 ml methanol+500 ml $H_2O(10^{-5}M)$.

b) I_1/I_3 : Florescence emission at 374 nm (I_1) and Florescence emission at 384 nm (I_3).

c) Florescence emission at 374 nm, d) Florescence emission at 392 nm.

Table 2. Variation of Stern-Volmer constants a) for pyrene in the o/w microemulsion with anionic emulsifier at 25 ºC

Run b)	I_1/I_3	I_E/I_M	Quencher	Ksv (M^{-1})	
A	0.89	0.025	DMAPS	74.97 c)	75.99d)
B	0.93	0.025	DMAPS	200.94 c)	213.18d)
C	0.95	0.025	DMAPS	215.99 c)	225.93 d)
A	0.89	0.025	AAm	17.68 c)	17.97d)
B	0.93	0.025	AAm	33.31c)	33.38d)
C	0.95	0.025	AAm	37.21 c)	37.50 d)

a) 2 g SDS+0.5 ml Py solution;

b) Run A: 20 ml H_2O, [Py] = $2.44*10^{-7}$M; Run B: 40 ml H_2O, [Py] =$1.23*10^{-7}$M; Run C: 60 ml H_2O, [Py] =$8.26*10^{-8}$M; Py solution:0.0101 g Py, 10 ml Toluene, 490 ml Hexane.

c) Florescence emission at 374 nm, d) Florescence emission at 392 nm.

Table 3. Variation of Stern-Volmer constants a) for pyrene in the o/w microemulsion with anionic emulsifier at 25 ºC

Run b)	I_1/I_3 c)	Ksv (M^{-1})		Quencher
A1	0.89	94.50d)	95.14e)	DMAPS
A2	0.89	369.03 d)	370.02e)	TMMEAMS
A3	0.89	53.01 d)	52.98e)	DMAEMA
A4	0.89	16.91d)	16.85e)	AAm
A5	0.89	5.88d)	5.99e)	SPM

a)[Py] = $2.44*10^{-7}$M; b) Run A1 – A5: 20 ml H_2O+2 g SDS+0.5 ml Py solution; Py solution: 0.0101 g Py +10 ml Toluene+490 ml Hexane(10^{-5}M); c) I_1/I_3 : Florescence emission at 374 nm (I_1) and Florescence emission at 384 nm (I_3),d) Florescence emission at 374 nm, e) Florescence emission at 392 nm.

K_{SV} increases with increasing the weight ratio of water to SDS or the weight ratio of water to the oil phase (toluene + hexane). This is connected with the increased number of hexane/toluene swollen micelles. I_1/I_3 ca. = 0.9 indicates that the microenvironment is more hydrophobic than that in SDS micelles, 1.12 [4]. This is due to the presence of hexane within the micelle interfacial layer isolating more Py from water. Furthermore, the value of I_1/I_3 increases with increasing water fraction. The very high concentration of SDS (electrolyte) suppresses dissociation of emulsifier and penetration of water into the micelle. The dilution of micellar solution with water increases the fraction of free ions as well as the number of micelles [5]. Under the circumstances (increased number micelles or interfacial area), Py is allocated close to the interfacial layer and senses the higher polar medium. The relatively large K_{SV} suggests that DMAPS efficiently penetrates into the interface (or the micelle core). This is promoted by the strong electrostatic attraction between DMAPS and SDS. The reorganization of the interfacial layer and the formation of aggregates with a critical aggregation concentration lower than a CMC influence the interaction between Py and DMAPS. However, the role of DMAPS in the quenching mechanism is very complex because monomer can act as quencher, electrolyte and coemulsifier as well. Besides, we should consider the distribution in the probe concentration, from center to the outer surface of the micelle core. Some probes may be accommodated in the inner layers of the corona as well. Thus, there may be two types of Py, inside and outside (interface) of the droplet core, and that the exchange rate between them will be slow compared to the fluorescence lifetime.

The similar trend was observed with polar AAm but K_{SV} values are much smaller. The polar uncharged AAm is much less sensible to the variation of the free ion concentration than DMAPS. The I_1/I_3 value ca. 0.9 indicates that the quenching proceeds in a relatively hydrophobic domain. The contribution of emission quenching in the continuous aqueous phase in the micellar solutions is negligible. The water-phase quenching is limited due to the very low water-solubility of Py. The penetration of polar AAm into the droplet surface results from the coemulsifier activity of the quencher [3]. It was estimated that less than 3% of the AAm is associated with the SDS micelles [3]. The bimolecular quenching rate constant decreases when SDS concentration increases. This decrease implies that the average environment of the probe becomes less polar when SDS concentration increases, producing a decrease in the local AAm concentration and/or bimolecular quenching rate constant. This is attributed to a partial dehydration of the micelles due to an increased free-ion concentration [6]. Below the CMC (or without SDS) the pyrene fluorescence spectrum corresponds to a polar environment. Mixing of SDS (or DS^- ion) with zwittrionic DMAPS may lead first to the complex formation (DS^----$^+DMAPS^-$) or the precipitation of ion-pairs aggregates which are colloidally dispersed by an excess of DS^-. At the onset of DS^- micellization, these aggregates are solubilized in the form of mixed SDS/DMAPS micelles. Adsorption of DMAPS occurs also through van der Walls interaction with micellar DS^- moieties.

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Water Phase Titration Studies of Winsor IV (w/o) Inverse Microemulsions.

Jaroslav Bartoň *) and Ignác Capek

Abstract : Classical toluene-based (w/o, water in oil) single-phase Winsor IV inverse microemulsions composed from toluene/ sodium bis(2- ethylhexyl) sulfosuccinate (AOT)/ Water/acrylamide (AAm) /sodium dodecyl sulphate (SDS) and containing besides acrylamide also an oil-soluble vinyl monomer (butyl acrylate, BA, styrene, S, or ethyl acrylate, EA) of various solubility in the water phase of inverse microemulsions, were titrated by aqueous titrating systems (TS) composed from water (TA), water solutions of acrylamide (TB),. water solutions of sodium dodecyl sulfate (TC), and/or water solution of acrylamide and sodium dodecyl sulphate (TD). The amount of TS absorbed by the inverse microemulsion during titration (i.e. before transformation of single-phase Winsor IV (w/o) inverse microemulsion to the two-phase Winsor II (w/o) microemulsion and/or before phase inversion to the Winsor I (o/w) microemulsion) depended only slightly on the nature of the oil soluble vinyl monomer. It was found, however, that the ratios of intra-phase and inter-phases compositional parameters such as Toluene/AOT and AOT/SDS of the single-phase Winsor IV (w/o) inverse microemulsions considerably affect the value of the volume fractions of the aqueous phase, Φ_{aw2} , necessary for the formation of a two-phase Winsor II (w/o) and/or Winsor I (o/w) microemulsion systems. The composition of the titrating systems TS influenced also the Φ_{aw2} values at which the phase separation, and/or phase inversion of the single-phase Winsor IV (w/o) inverse microemulsion, were observed. Thus, for example, titration systems of the series TD yielded Winsor I (o/w) microemulsions, if condition $0.32 < \Phi_{aw2} < 0.42$ (for molar ratio [Toluene] / [AOT] = 19.4 in parent Winsor IV (w/o) inverse microemulsion) was met during titration. For Winsor IV (w/o) inverse microemulsion with [Toluene] / [AOT] = 11.7 , the phase inversion to Winsor I (o/w) microemulsion occurred if $\Phi_{aw2} \approx 0.49$.

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reported by **Françoise CANDAU**

Synthesis and characterization of amphiphilic statistical copolymers obtained by surfactant-free emulsion polymerization.

(V. Arbez-Gindre, J.M. Corpart, M. Pabon, J. Selb, F. Candau)

A series of amphiphilic copolymers of low molecular weights ($M_w \approx 6\,000$-$40\,000$) based on methacrylic acid (MAA) and styrene (S) in variable proportions (20 mol % < MAA < 70 mol %) have been synthesized by means of a free-surfactant emulsion polymerization technique. The stability of the latexes was ensured thanks to specific conditions: $T_{polym.}$ > LCST of poly(methacrylic acid), high stirring rate, a judicious choice of the initiator and of the chain transfer agent, and the use of a semi-continuous process.

The molar composition of the MAA/S copolymers has been determined by ^1H NMR measurements and was found to be in excellent agreement with the molar composition of the monomers in the feed. A size exclusion chromatography study (using a triple detection: RI, UV and MALLS) performed on the aqueous copolymer solutions shows that the compositional drift is quite negligible. This result, combined with the observation that the turbid latexes become optically clear upon neutralization are strongly in favor of a quasi-random copolymer microstructure.

Characterization of PMAA/PS latex particles in the dry state and in aqueous suspension.

(V. Arbez-Gindre, J.M. Corpart, M. Pabon, M. Duval, J. Selb, F.Candau)

A detailed study on the PMAA/PS latex particles obtained according to the technique described above, has been performed by transmission electron microscopy (TEM) and atomic force microscopy (AFM). Both techniques lead to concordant results. In particular, it is found that an increase in the MAA content in the latex goes with a significant decrease of the particle size (diameter D). As an example, D = 134 nm for the PMAA/PS (20/80 molar) latex and becomes D = 76 nm when the MAA/S molar ratio is equal to 70/30. The latexes have a narrow particle size distribution that broadens up with an increase in the MAA content. These behaviors have been correlated to: *i)* a variation of the number of polymer chains in the latex particle with the copolymer composition and *ii)* an inevitable plastification by water of the PMAA/PS latex films which takes place upon increasing the MAA content.

The characterization of the latex particles in aqueous suspension has been carried out by static light scattering and quasi-elastic light scattering. These techniques corroborate the observations made on the particles in the dry state. The values of the variance are low (< 0.03), whatever the PMAA/PS latex composition, but nevertheless tend to increase with the MAA level in the feed. Similarly, the decrease in the hydrodynamic and gyration radii of the particles, which is observed when the copolymers become richer in MAA, reflects their marked hydrophilic character.

Fluorescence and surface tension experiments have been performed on a series of PMAA/PS copolymers in aqueous solution, as a function of their neutralization degree. The progressive aggregation of the neutralized copolymers with concentration demonstrates the amphiphilic character of the macromolecules. This allows the use of these low molecular weight copolymers as efficient emulsifying agents in the emulsion polymerization of styrene. Studies on these systems are in progress and will be described in the next report.

Compositional heterogeneity effects in "multisticker" associative polyelectrolytes prepared by micellar polymerization

(P. Kujawa, A. Audibert-Hayet, J. Selb, F. Candau)

An aqueous micellar radical polymerization technique has been used to prepare water-soluble polyelectrolytes of acrylamide (AM) and sodium 2-acrylamido-2-methylpropanesulfonate (NaAMPS), hydrophobically modified with low amounts (2-4 mol%) of *N,N*-dihexylacrylamide (DiHexAM). This synthesis method leads to "multisticker" polymers, in which the number and the length of the hydrophobic blocks vary with the degree of conversion. Kinetic studies show an appreciable compositional heterogeneity for these polyelectrolytes, in contrast with their neutral analogues (i.e. AM/DiHexAM copolymers). The drift in composition observed for the AM/NaAMPS/DiHexAM terpolymers is attributed to the electrostatic repulsion between the negatively charged growing polymeric chains, located in the aqueous continuous medium, and the anionic sodium dodecyl sulfate (SDS) micelles, inside of which the hydrophobic monomer is located. It is shown that an optimization of the polymerization process can be achieved, which gives terpolymers of homogeneous and well-defined compositions. The thickening ability of the hydrophobically-modified polyelectrolytes is directly affected by the extent of their compositional heterogeneity: an increase in the sample homogeneity leads to a significant viscosity enhancement and marked elastic properties of the polymer solutions.

RECENT PUBLICATIONS

1. *Synthesis in Inverse Emulsion and Associating Behavior of Hydrophobically Modified Polyacrylamides.*
M. Pabon, J-M. Corpart, J. Selb, F. Candau. (submitted)

2. *Compositional Heterogeneity Effects in "Multisticker" Associative Polyelectrolytes Prepared by Micellar Polymerization*
   P. Kujawa, A. Audibert-Hayet, J. Selb, F. Candau. (submitted)

3. *Synthèse, caractérisation et propriétés émulsifiantes de copolymères amphiphiles statistiques (Synthesis, characterization and emulsifying properties of statistical amphiphilic copolymers).* **V. Arbez-Gindre**, Thesis, Université Louis Pasteur, Strasbourg, 2002**.**

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1- Work in progress

B. Charleux

Papers in preparation

Structural Characterization of High Molar Mass Poly(n-Butyl Acrylate) from SG1-Mediated Controlled Free-Radical Polymerization.

Julien Nicolas, Céline Farcet, Bernadette Charleux

Submitted papers

Nitroxide-Mediated Polymerization in Miniemulsion: A Direct Way From Bulk to Aqueous Dispersed Systems.
B. Charleux
Submitted to ACS Symp Series (K. Matyjaszewski editor)

Owing to fundamental differences with bulk polymerization, the special features of nitroxide-mediated CRP in miniemulsion and the key for success are discussed in this article. The miniemulsion process, where polymerization is initiated by a SG1-based alkoxyamine, is examined in terms of initiation / nucleation, kinetics, monomer transport, and their consequences on control of molar mass and distribution.

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[1] On leave in September 2003 to the Laboratory of Macromolecular Chemistry, UMR (CNRS) 5076, Ecole Nationale Supérieure de Chimie de Montpellier, 8 rue Ecole Normale, 34296 Montpellier Cedex 05, France

Simulation of Molecular Weight Distributions Obtained by Pulsed Laser Polymerization (PLP). New Analytical Expressions Including Intramolecular Chain Transfer to Polymer.
Anatoly N. Nikitin, Patrice Castignolles, Bernadette Charleux, Jean-Pierre Vairon

Submitted to Macromol. Theory and Simul.

A new approach for simulation of PLP (Pulsed Laser Polymerization) is presented. This approach allows to obtain new analytical solutions for different polymerization schemes, including either chain transfer to monomer or intramolecular chain transfer to polymer. The first results of simulation of PLP experiment on n-butyl acrylate at 20 °C and ambient pressure are presented.

Propagation Kinetic Parameters of some Alkyl Acrylates from Pulsed Laser radical Polymerization and Triple Detection SEC Molecular Weight Determination
Patrice Castignolles, Laurence Couvreur, Bernadette Charleux, Jean-Pierre Vairon, Stéphane Lepizzera.
Submitted to Macromol. Symp. (Macro IUPAC Beijing, July 2002)

Pulsed-laser photoinitiated polymerization was used to determine, in toluene solution, the propagation kinetic parameters of a series of acrylates with increasing size of the alkyl side group. Depending on the nature of the acrylate and on the PLP conditions, more or less abundant intramolecular and intermolecular transfer to polymer takes place. Long chain branching (LCB) can thus critically interfere on the SEC analysis. Indeed, the Mark-Houwink-Sakurada parameters, which could be used to calculate the molecular weight at the inflection point, strongly depend on the polymer structure and their use could lead to errors. This has been shown by the use of Triple Detection SEC. In order to use adequatly this triple detection technique, a new method of treatment of the chromatograms has been developed ; this method allows to determine a correctly-fitted low-noise Molecular Weight Distribution.

Controlled Free-Radical Copolymerization of Styrene and Maleic Anhydride by Reversible Addition-Fragmentation Chain Transfer (RAFT)
Elena Chernikova, Polina Terpugova, Chuong Bui and Bernadette Charleux

Submitted to Polymer

Controlled free-radical copolymerization of styrene and maleic anhydride was performed in 1,4-dioxane and THF solution at 60 °C using the RAFT technique. The effect of monomer feed ratio on copolymerization kinetics and on control over molar mass and molar mass distribution was examined. In particular, the quality of control was poorer when the proportion of maleic anhydride in the monomer feed was larger. This feature was assigned to a change in the chain transfer constant, mainly due to an increase in the apparent rate constant of propagation with the proportion of maleic anhydride.

F. Ganachaud

Paper in preparation

Anionic and Cationic Polymerization in Aqueous Media of Non-Silicone Monomers: A Mechanistic Survey
F. Ganachaud
To be submitted on a special issue of Comptes Rendus de l'Academie des Sciences

> This review article reports current and "rediscovered" studies dealing with anionic or cationic polymerization in aqueous media. First is presented the requirements for a monomer to be successfully polymerized ionically in water. Then, a general mechanism of polymerization is provided, insisting particularly on the interfacial location of the various reaction steps (initiation, propagation, termination). Follows a brief overview of the various studies published in the literature, divided in two series depending on the faith of the polymer extremities (reactivated or not not) rather than on the structure of the monomers (cyclic or vinyl like). A description of the influence of the physico-chemistry of the system (miniemulsion, microemulsion, inverse emulsion) on the final structure and dispersity of the objects (nanoparticles or nanocapsules) completes the picture. Finally, some examples of efficient metal catalysis open the discussion on the future of the process.

Submitted papers

Synthesis of Polydimethylsiloxane Microemulsions by Self-Catalyzed Hydrolysis/ Condensation of Dichlorodimethylsilane
G. Palaprat, F. Ganachaud
Submitted to J. Polym Sci. Part A

> The preparation of PDMS microemulsions was carried out by adding at controlled rate dichlorodimethylsilane (DCMS) in a solution of sodium dodecylpolyoxyethylene(4) sulfate. The instantaneous hydrolysis of DCMS produces the di-hydroxy silane that quickly condenses and cyclizes to generate dispersions of cyclosiloxanes of small sizes (4 to 6 units). The high load of ions released during the hydrolysis step (H^+ and Cl^-) requires the presence of the above mentioned electrosteric surfactant to avoid rapid coagulation of the dispersion. In addition, its sulfate end-group captures a proton to generate *in situ* a surfactant/initiator (INISURF) that catalyzes the ring opening polymerization of cyclosiloxane as well as the polycondensation of disilanol PDMS chains. Final particles exhibit a diameter of about 50 nm for a polydispersity index of less than 1.1. They are constituted of PDMS chains exclusively linear ($\overline{M_{n,\max}} \approx 60,000$ g/mol; $\overline{M_w}/\overline{M_n} \approx 2$) and of small cycles in low contents (less than 5 wt.% in best conditions).

Multiblock Silicones I. Vinyl Functionalized Polydimethylsiloxane
C. Ivanenko, C. Maitre, F. Ganachaud, P. Hémery
Submitted to e-polymers

The first part of this series is devoted to the preparation of vinyl functionalized multiblock by the process of anionic ring opening polymerization in miniemulsion. The advantage of working in dispersed media is that different scales of reactivities are found between one-chain reactions, taking place at the interface (propagation, backbiting) and two-chain reactions, located in the bulk of the particles (polycondensation and intermolecular redistribution). First, homopolymerizations of octamethylcyclo tetrasiloxane (D_4) and tetramethyl-tetravinylcyclotetrasiloxane (D_4^V) were carried out and compared, focusing specifically on the rates of polymerization, backbiting and polycondensation processes. Copolymerization of D_4 with D_4^V then gave insight into the extent of mixed cycles formations and particularly how to avoid these. On this basis, recipes were carefully selected so that homopolymerization and scarce co-polycondensation and redistribution progress at the expanse of backbiting reactions and thus form multiblock copolymers, which microstructure was confirmed by ^{29}Si NMR.

2- Thesis

B. Charleux

Florence Mazuel	Design of new functional monomers to be used as crosslinking agents in latex films. Defense on february the 21st, 2003.
Patrice Castignolles	Pulsed laser polymerization (PLP) of acrylic esters.
Laurence Couvreur	Controlled radical polymerization of acrylic acid.
Julien Nicolas	Nitroxide-mediated controlled radical polymerization in miniemulsion and emulsion.
Maggy Manguian	Application of controlled-radical polymerization to the synthesis of amphiphilic block and gradient copolymers.
Catherine Lefay	Stabilization of latex particles by amphiphilic copolymers.
Sébastien Fréal-Saison	Controlled radical polymerization in miniemulsion and emulsion.

F. Ganachaud

Séverine Cauvin	Cationic polymerization in miniemulsion using rare earth triflate catalysts.

Guillaume Palaprat	Mesogen cristal liquids prepared by ionic polymerization in emulsion in molecular imprinting technique.

3- List of recently published papers

B. Charleux

Kinetic Study of Nitroxide-Mediated Controlled Free-Radical Polymerization of n-Butyl Acrylate in Aqueous Miniemulsion.
Céline Farcet, Julien Nicolas, Bernadette Charleux
J. Polym. Sci. Part A: Polym. Chem. 40(24), 4410-4420 (2002)

Formation and reorientation dynamics of nitroxides in the controlled radical polymerisation of styrene initiated by a bisalkoxyamine.
Claude Chachaty, Wenli Huang, Lucien Marx, Bernadette Charleux, André Rassat
Polymer 44(2), 397-406 (2003)

Characterization of aqueous micellar solutions of amphiphilic block copolymers of poly(acrylic acid) and polystyrene prepared via ATRP. Toward the control of the number of particles in emulsion polymerization.
C. Burguière, C. Chassenieux and B. Charleux
Polymer 44(3), 509-518 (2003)

Nanocrystalline Transition Metal Oxide Spheres with controlled multi-scale porosity.
David Grosso, Galo J. de A.A. Soler Illia, Eduardo Crepaldi, Bernadette Charleux, Clément Sanchez
(*Advanced Functional Materials*, in press, January 2003)

Controlled free-radical polymerization: a way to design polymer architecture and surface properties of latex particles
C. Farcet, C. Burguière and B. Charleux
Colloidal Polymers: Preparation and Biomedical Applications.
Abdelhamid Elaissari Editor, *Marcel Dekker, Inc.*

F. Ganachaud

Cationic Polymerization of p-Methoxystyrene in Miniemulsion
S. Cauvin, A. Sadoun, R. Dos Santos Costa, J. Belleney, F. Ganachaud, P. Hémery
Macromolecules, 35, 7919-7927 (2002)

Anionic Polymerization of n-Butyl Cyanoacrylate in Emulsion and Miniemulsion
C. Limouzin, A. Caviggia, F. Ganachaud, P. Hémery
Macromolecules, 36, ASAP (2003)

Diffusion Limited Chain Transfer in Styrene Emulsion Polymerization: Use of n-Dodecanethiol to Regulate Molecular Weight

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Abstract

Low volatility chain transfer agents such as n-dodecanethiol (n-DDT) are important for controlling molecular weight in the production of polymers containing styrene. The high reactivity of n-DDT towards the styrl radical, coupled with its low solubility in the aqueous phase, often leads to conditions of diffusion limited chain transfer in which the transport rate of n-DDT from the monomer droplets to the polymerizing particles is inadequate to maintain equilibrium concentration in the particles. The extent to which the particles are "starved" of n-DDT has been studied by measuring n-DDT consumption and molecular weight during styrene emulsion polymerizations. Varying surfactant and/or initiator concentrations is shown to alter the n-DDT consumption and the molecular weight profiles. The two-film diffusion theory was applied to our data using monomer droplet and polymer particle measurements. Experimental data and theoretical considerations support the existence of monomer droplets beyond the expected end of Interval II for styrene emulsion polymerization.

Submitted to *Polymer Reaction Engineering.*

Nitroxide-Mediated Living Radical Polymerization in Dispersed Systems

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Presented at Polymer Colloids: Preparation & Properties of Aqueous Polymer Dispersions, July 2002, Irsee, Germany

Abstract

Living/controlled radical styrene miniemulsion polymerizations mediated by the nitroxide TEMPO were run at 135 °C. A coordinated experimental and modelling program has shown that preserving livingness in these systems involves finding an optimum solution between loss of livingness due to biradical termination and loss due to disproportionation. Long reaction times lead to greater dead chain formation through disproportionation, while high reaction rates can result in high biradical termination rates. Hexadecane-free runs were found to give >95% conversion in <3 hours while maintaining polydispersities ~1.3, but only at high concentrations of the surfactant SDBS.

To appear in *Colloid and Polymer Science*.

Mathematical Modeling of Particle Morphology Development Induced by Radical Concentration Gradients in Seeded Styrene Homopolymerization

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Abstract

The development of concentration gradients in the seeded emulsion homopolymerization of styrene has been studied using a mathematical model. Under ideal conditions, emulsion polymer particles are expected to be relatively uniform across their radius. When this is true, kinetic models can be reliably used to predict the reaction rates, molecular weight, and composition (for copolymerizations). However for large particles, large radial gradients in the polymer radical concentration can develop during polymerization. While gradients in the monomer concentration are not observed, the radical concentration gradients result in non-uniform reaction rates across the particle radius, rendering conventional models unreliable. This study examines the effect of seed particle diameter and various kinetic parameters on the development of particle morphology.

Polymer Reaction Engineering, **10**, 135-162, 2002.

Contribution

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D.I. Lee, Progress in Organic Coatings 45 (2002), 341-358

The structure of model coatings: Latex-bound plastic pigment coatings

Abstract

The immobilization and consolidation of model coatings based on monodisperse polystyrene (plastic pigment) and S/B latexes of known particle sizes were studied in terms of their packing volumes and the extent of latex shrinkage, which was found to increase with increasing pigment volume up to the critical pigment volume concentration (CPVC). The maximum latex shrinkage was estimated from the CPVC. Then, the porosity of model coatings was calculated based on three proposed latex shrinkage models: Maximum, Minimum, and Linearly Decreasing Latex Shrinkage. The number of pores and the average equivalent spherical pore diameters were subsequently calculated. The opacity and gloss of model coatings on polyester films were measured and their porosity was also determined by a simple coat weight-thickness method. The CPVC values determined by the opacity, gloss, and porosity vs. PVC relationships, respectively, agreed very well with each other. 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 linearly decreasing 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. Additionally, a minimum crack-free temperature (MCFT) of latex-bound coatings was proposed to better predict the behaviors of latexes as pigment 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.

Keywords: Model coatings; Coating immobilization and consolidation; Coating structure; CPVC; Optical properties

Gast Group MIT/Stanford

Published Papers

1. Two-dimensional streptavidin crystals on giant lipid bilayer vesicles Ratanabanangkoon, P.; Gropper, M.; Merkel, R.; Sackmann, E.; Gast, A. P. *Langmuir* **2002**, *18*, 4270-4276

Streptavidin was crystallized on giant bilayer vesicles (20-60 mum) in sucrose solution at various pH values. The streptavidin-coated vesicles exhibited unique roughened spherical and prolate ellipsoidal shapes, illustrating resistance to curvature of the two-dimensional crystals. Studies indicated that the spheroids and prolate ellipsoids correspond to different crystal morphologies. Through confocal microscopy, the various crystal morphologies on vesicle surfaces were observed under different solution conditions. Unlike two-dimensional (2D) streptavidin crystals grown in ionic buffer that assume the P1, P2, and C222 lattices at pH 4, 5.5, and 7, respectively (Wang et al. Langmuir 1999, 15, 154 1), crystals grown in sucrose with no added salt show only the lowest density C222 lattice due to strong electrostatic interactions

2. Mechanics of Streptavidin-Coated Giant Lipid Bilayer Vesicles: A Micropipette Study P. Ratanabanangkoon, M. Gropper, R. Merkel, E. Sackmann, A. P. Gast, *Langmuir*, in press 2003

To understand the effects of a crystalline protein layer on bilayer properties, we studied the mechanical properties of avidin and streptavidin coated giant lipid bilayer vesicles. The giant vesicles (20-60 mm) are made from a mixture of SOPC and biotinylated phospholipids via electroformation. Using micropipette manipulation, we showed that the presence of a monomolecular layer of noncrystalline avidin on the vesicle surface increases the membrane bending rigidity but does not significantly alter the elastic area expansion modulus of the vesicle. When the vesicles were coated with streptavidin, the protein crystallizes on the bilayer surface, resulting in a rigid polycrystalline membrane. These vesicles display unique roughened spherical or prolate ellipsoidal shapes depending on the differences in crystal morphologies. Upon aspiration with micropipettes, the vesicles first showed rapid permanent deformation at low strain, followed by a slower viscoelastic response above a certain threshold. Despite their extremely rigid appearance, the existence of a polycrystalline shell does not increase the toughness of streptavidin-coated vesicles above that of uncoated vesicles. The origin of these properties can be traced to the unique ligand-receptor interactions between streptavidin and biotinylated phospholipids in the bilayer membrane. The findings offer greater understandings of complex phenomena involving crystalline protein layers on the surface of cell membranes.

Unpublished Papers

Mechanics of Semiflexible Chains Formed by Poly-Ethylene-Glycol Linked Paramagnetic Particles Sibani Lisa Biswal, Alice P. Gast to be submitted to PRE, 2003

Magnetorheological particles, permanently linked into chains provide a magnetically actuated means to manipulate microscopic fluid flow. Paramagnetic colloidal particles form reversible chains by acquiring dipole moments in the presence of an external magnetic field. By chemically connecting paramagnetic colloidal particles, flexible, magneto-responsive chains can be created. The chain flexibility is determined by the length of the spacer molecule between particles and is quantified by the flexural rigidity or bending stiffness. To understand the mechanical properties of the chains, we use a variety of optical trapping experiments to provide measures of the flexural rigidity of these chains of magnetic particles.

Conference Presentations

Towards the design of diblock copolymers for use in novel catalytic applications

Cheryl M. Stancik[1], Jan Schütz [2], Adrien R. Lavoie[2], John A. Pople[3], Alice P. Gast[4], Robert M. Waymouth[2] Poster Presentation at SSRL Users Meeting, October 7-9, 2002

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We characterize a series of diblock copolymers using scattering techniques and work to build architecture-property relationships that will enable us to optimize their use for catalytic applications. The diblock copolymers comprising a polystyrene block and an imidozolium organic liquid functionalized polystyrene block self-assemble into spherical micelles. Using both small angle x-ray scattering (SAXS) and small angle neutron scattering (SANS), we demonstrate that the aggregation number and the size of the micelles given by their radius of gyration, R_g, are correlated to the diblock copolymer architecture. Through dynamic light scattering (DLS) studies, we measure the hydrodynamic radius, R_h, of the micelles and investigate relationships between R_h and the diblock architecture. We demonstrate that the nature of the density distribution within these micelles, as given by R_g/R_h, indicates a star-like micelle geometry with a compact core. To assess the capacity of the micellar core to act as a nano-reactor, we investigate the ability of micelles with an organic liquid functionality in the core to solvate free ionic liquid molecules where the bulk environment is a non-solvent for these molecules. Following addition of the ionic liquid molecules to micellar solutions, we see an increase in the micelle radii, indicating that ionic liquid molecules partition themselves to the cores of these micelles to escape the poor solvent environment of the bulk. We desire to use these organic liquid moieties in the novel environment of the micelle core for catalysis and present our preliminary findings in this direction.

4. Magnetically Actuated Colloidal Chains in Microchannels

Sibani Lisa Biswal, Alice P. Gast, Poster Presentation at Micro Total Analysis Systems 2002, November 3-7, 2002

Paramagnetic particles have grown increasingly useful by forming magneto-responsive structures to control microscopic fluid flow. Under the influence of an external magnetic field, paramagnetic particles acquire dipole moments and aggregate to form chains. These chains can be chemically cross-linked to form a unique, magnetically activated structure. We have created linked chains by inserting a flexible poly-ethylene-gylcol (PEG) spacer between paramagnetic polystyrene beads using the binding reaction between streptavidin and biotin. These cross-linked paramagnetic particles form dynamic, flexible chains which can move and bend freely. In the presence of a magnetic field, the chains stiffen and orient in the direction of the magnetic field. When the field is removed, the chains relax and its orientation becomes controlled by the surrounding fluid.

In order to design an effective magneto-responsive structure, we have studied chain flexibility. Bending experiments have been done with the use of optical tweezers to measure the rigidity of the chains. The need for efficient and rapid mixing at the micron scale remains a challenge in the optimization of microanalytical systems. These magnetically actuated chains can be used as a simple rotational device to mix fluids. A linked magnetic chain under the influence of a rotating magnetic field in a microdevice will follow the magnetic field with the same frequency as the magnetic field, but with a phase lag. Our rotating magnetic field is designed using two pairs of coils to create magnetic fields in two perpendicular directions. By placing AC currents through the coils shifted by 90 degrees, a rotating magnetic field is created. The small size of these chains make them ideal as micro-stirrers in microfluidic channels.

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

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The Key Centre for Polymer Colloids currently comprises about 25 researchers. The Director is Professor Robert G Gilbert, Dr Brian S Hawkett is Development Manager, Dr Christopher M Fellows is Scientific Projects Officer, Dr Reza Mahidasht is Laboratory Manager, plus a team of graduate students, researchers and visiting scholars from around the world. More information about the Centre can be found on the website given above.

Papers submitted or in press

Diffusion coefficients of monomer and oligomers in hydroxyethyl methacrylate (HEMA). J Strauch, J McDonald, BE Chapman, PW Kuchel, BS Hawkett, GE Roberts, MP Tonge, RG Gilbert. *submitted.*

The diffusion coefficients are reported of rubbery ternary systems comprising polymer, monomer analog (i.e. the saturated equivalent of monomer), and trace quantities of oligomers (dimer, trimer, tetramer and hexamer) for 2-hydroxyethyl methacrylate (HEMA). These were obtained using pulsed-field-gradient NMR spectroscopy, with polymer weight-fraction f_p over the range $0 \leq f_p \leq 0.4$. The oligomers were macromonomers synthesized using a cobalt catalytic chain transfer agent. The diffusion coefficients were about an order of magnitude smaller than for monomers such as methyl methacrylate, an effect ascribed to hydrogen bonding in HEMA. The diffusion coefficient D_i of an i-meric oligomer was found to fitted with moderate accuracy by an empirical "universal" scaling relation $D_i(f_p)/D_1(f_p) \approx i^{-(0.66+2f_p)}$, previously found to provide an adequate fit to corresponding data for styrene and for methyl and butyl methacrylates [Griffiths, M.C., Strauch, J., Monteiro, M.J., and Gilbert, R.G., Macromolecules 1998, 31, 7835]. The data were also fitted to obtain free-volume parameters for the monomer diffusion coefficient. The approximate empirical scaling relation seems to hold for a remarkably wide range of types of monomer/polymer systems. These results are of use in modeling rates and molecular weight distributions in free-radical polymerization, in particular for taking into account termination (which is chain-length dependent and controlled by the diffusion coefficient of chains of the low degrees of polymerization studied here).

Expansion study of rice starch polymers in aqueous solution. H Chiou, RG Gilbert, MA Fitzgerald, CM Fellows. *submitted.*

DLS data are reported for rice starch solutions as a function of ionic strength. The hydrodynamic diameter of starch from all the rices examined was ~200 nm, and increase with increasing ionic strength. The expansions are attributed to the uncoiling of amylose and amylopectin, and the data provide information on the hydrocolloid microstructure.

Water sensitivity of latex-based films. L Butler, CM Fellows, RG Gilbert. *Ind. & Eng. Chem. Research*, in press (ASAP – DOI 10.1021/ie020611v).

A series of polymer latices based on Me methacrylate (MMA) and Bu acrylate (BA) incorporating electrosteric stabilizers contg. acrylic acid (AA) and methacrylic acid (MAA) was prepd., and the water sensitivity of films formed from these latices was investigated by immersion tests. A no. of variables were considered, including the concn. of the hydrophilic monomer, the presence/absence of a free-radical inhibitor, and the use of various chaser systems to remove residual monomer. Water sensitivity did not increase proportionally to the amt. of hydrophilic monomer in the feed and was not directly related to the amt. or mol. wt. of ungrafted polyelectrolyte or to the length of the grafted polyelectrolyte chains. A model is advanced suggesting that the primary role of the electrosteric stabilizer in reducing water resistance is connected with its ability to prevent coherence of the polymer particles to form a continuous film. This ability should be related to a poor capacity to stabilize water-in-oil emulsions.

Synthesis of latices with hydrophobic cores and poly(vinyl acetate) shells. 2. use of poly(vinyl acetate) seeds. CJ Ferguson, GT Russell, RG Gilbert. *Polymer*, in press.

A strategy is explored for synthesizing latex particles with polystyrene cores and poly(vinyl acetate) shells. The seed particles are poly(vinyl acetate), which theory indicates should be immune to secondary particle formation when a second-stage seeded emulsion polymerization with styrene is carried out. The objective is to form a single hydrophobic core by inversion of the second and first stages. While this morphology is favoured thermodynamically, conditions need to be optimized so that it is kinetically achievable: many attempts to implement this using straightforward synthetic procedures result in either no core (acorn morphology) or multiple polystyrene cores. A series of experiments enables this goal to be implemented by ensuring sufficiently fast diffusion of the first-stage hydrophylic polymer (using chain-transfer agent to reduce the molecular weight and, more importantly, the degree of branching of the parent poly(vinyl acetate) seed polymer), an initiator which minimized grafting between the first- and second-stage polymers, and modifying the seed poly(vinyl acetate) to increase its hydrophilicity.

Using the aggregation of latex polymers in the fabrication of reproducible enzyme electrodes. W Rahmat, J Fischer, DB Hibbert, RG Gilbert, JJ Gooding. submitted.

An enzyme electrode for glucose is described as a model system to demonstrate a fabrication method using latex aggregation and entrapment of enzyme. Electrostericallystabilized latex particles synthesized by emulsion polymerization in batch from acrylic acid, methyl methacrylate and butyl acrylate, and glucose oxidase were coagulated together at pH 5.5 with ethanol. A platinum disk electrode dipped in the solution becomes coated with latex/enzyme. The thickness of the film and amount of enzyme may be controlled by the time the electrode is in contact with the solution. The enzyme was then immobilised by covalent attachment of amine groups to carboxylic moieties in the polymer using 1-ethyl-3(3-dimethylaminopropyl)-carbodiimide hydrochloride and N-hydroxysuccinimide. Five minutes contact with the latex/enzyme solution and subsequent amide coupling, gave electrodes with a reproducibility of 5.7 % RSD, a wide dynamic range (0 – 100 mM) and good storage properties.

SANS study of electrosterically stabilized polystyrene latex. H De Bruyn, RG Gilbert, JW White and JC Schulz, *Macromolecules*, in press.

Electrosterically stabilized polystyrene latexes with a poly(acrylic acid) hydrophilic layer with either perdeuterated core or perdeuterated hydrophilic layer were prepared in-situ in a styrene/acrylic acid copolymerization, in a manner similar to that commonly employed industrially. Small angle neutron scattering (SANS) measurements were made over a range of contrasts for three latexes at high and low pH. Parameters obtained by fitting to standard core/shell models were consistent with the shell being highly hydrated (about 90% at low pH and about 95% at high pH). The core was found to contain about 3% acrylic acid. Doubling the proportion of acrylic acid in the recipe increased shell thickness by about 20%, slightly reduced particle size and slightly increased the proportion of acrylic acid incorporated into the core. The maximum degree of polymerization of the entering (and therefore grafted) species was estimated from the shell thickness to be about 44 monomer units for 0.02M acrylic acid and 66 for 0.04M. The observed dependence of hairy-layer (shell) thickness on the initial amount of acrylic acid suggests that the critical degree of polymerization for entry (and therefore true grafting) of the electrosteric stabilizer is thermodynamically (not kinetically) controlled.

Latex particles bearing hydrophilic grafted hairs with controlled chain length and functionality synthesized by RAFT. F d'Agosto, M.-T. Charreyre, C. Pichot, RG Gilbert. *J. Polym. Sci. Part A Polymer Chem.* in press.

Amino-functionalized particles were obtained by emulsion free radical polymerization of styrene with an hydrophilic functional comonomer (aminoethyl methacrylate hydrochloride) and grafting reactions between -NH_2 bearing polystyrene particles and polyNAM chains were performed. Well-controlled hairy particles were obtained and characterized by SEC chromatography of the resulting dry extract or by ^{1}H NMR analyses performed either on the resulting dry extract or directly on the latex itself.

Entry in Emulsion Polymerization: Effects of Initiator and Particle Surface Charge. KY van Berkel, GT Russell and RG Gilbert, in press.

The rate coefficient for radical entry into latex particles in emulsion polymerizations is measured for styrene systems in which the entering species are anionic (from persulfate) and cationic (from 2,2′-azobis-(2-methylpropionamidine) dihydrochloride, or V-50). These entry rate coefficients ρ are obtained by measuring rates in seeded emulsion polymerizations where the seeds have either cationic or anionic groups on the surface; 'zero-one' conditions are employed, because these offer the advantage that particle size is sufficiently small (≈ 70 nm diameter) that termination is not rate-determining. Data comprise steady-state rates with chemical initiator, combined with loss rates obtained using γ-radiolysis initiation and following the relaxation behavior following removal from the radiation source. Values for ρ as a function of initiator concentration can be meaningfully compared for different initiators through the dependence of initiator efficiency f_{entry} on primary radical generation rate (radical flux). For the anionic latex, this dependence is seen to differ depending on the nature of the initiator used. This may be explained by the entry model (Maxwell, I. A.; Morrison, B. R.; Napper, D. H.; Gilbert, R. G. *Macromolecules* **1991**, *24*, 1629) wherein the rate-determining steps in entry are assumed to be only aqueous-phase propagation and termination to form surface-active *z*-meric oligomeric radicals; entry is solely by *z*-mers, for which actual entry into the particle is so fast as not to be rate-determining. The cationic latex shows a high rate of spontaneous initiation, which can be explained in terms of amidino radical chemistry; this can be reduced by heat treatment. Accurate f_{entry} values are obtained using the heat-treated cationically-stabilized latex for seeded studies. The f_{entry} data are also consistent with the model for both cationic and anionic species entering the cationic latex. Values of z so inferred (≈ 2 for persulfate, ≈ 1 for amidinium) can be understood in terms of the hydrophobic free energy of these species. The results refute alternative models in the literature that entry may be controlled by double-layer (colloidal) interactions, surfactant displacement or diffusion control.

Molecular weight and functional end group control by RAFT polymerization of a bi-substituted acrylamide derivative. F. D'Agosto, R. Hughes, M.-T. Charreyre, C. Pichot and RG Gilbert, *Macromolecules,* in press: ASAP DOI: 10.1021/ma025646l.

Controlled radical polymerization of the bi-substituted acrylamide derivative N-acryloylmorpholine (NAM) has the potential to yield polymers grafted to latex particles to which can be attached a wide range of functionalities with applications in molecular biology and biomedicine. The controlled polymerization of NAM using reversible addition-fragmentation chain transfer (RAFT) is performed using two new chain transfer agents S=C(Z)–SR bearing the same functional propionic acid group (R) and two different Z groups, benzyl (CTA 1) and phenyl (CTA 2). RAFT polymerization of NAM mediated by CTA 1 is very fast (>80% conversion in less than half an hour at 65°C). The linear evolution of $\overline{M}_{\mathrm{n}}$ and the low polydispersity indices ($\overline{M}_{\mathrm{w}}/\overline{M}_{\mathrm{n}} < 1.2$) are in accord with the expected characteristics of a living polymerization. CTA 2 leads to broader $\overline{M}_{\mathrm{w}}/\overline{M}_{\mathrm{n}}$s (< 1.4). The resulting CTA-capped polymers were further polymerized to yield an amphiphilic polyNAM-*block*-polystyrene. These α,ω-functionalized polyNAM chains were characterized by ^{1}H NMR and MALDI-ToF mass spectrometry.

The following publications have appeared since the previous Newsletter

Effective ab initio emulsion polymerization under RAFT control. CJ. Ferguson, RJ Hughes, BTT Pham, BS Hawkett, RG Gilbert, AK Serelis and CH Such. *Macromolecules*, **35**, 9243-5 (2002).

Synthesis of Latices with Polystyrene Cores and Poly(Vinyl Acetate) Shells. 1. Use of Polystyrene Seeds. CJ Ferguson, GT Russell, RG Gilbert. *Polymer*, **43**, 6371-6382 (2002).

Critically evaluated termination rate coefficients for free-radical polymerization, 1. The current situation**.** M Buback, M Egorov, RG Gilbert,V Kaminsky, OF Olaj, GT Russell, P Vana, G Zifferer. *Macromol. Chem. Phys.,* **203**, 2570-82.

Emulsion polymerization of vinyl *neo*-decanoate, a “water-insoluble” monomer. H de Bruyn, CM Miller, DR Bassett and RG Gilbert. *Macromolecules* **35**, 8371-7 (2002).

Strategies for optimisation and control of molecular weight and particle size distributions in emulsion polymerisation. J. Zeaiter, V.G. Gomes, G.W. Barton, J.A. Romagnoli, R.G. Gilbert, *Computer-Aided Chemical Engineering*, **9**, 823-8 (2001).

Water-binding and oxygen permeability in poly(vinyl alcohol) films. L Lien, CM Fellows, L Copeland, BS Hawkett, RG Gilbert. *Aust. J. Chem.,* **55**

TU/e technische universiteit eindhoven

Contribution of the researchgroup Van Herk/Meuldijk, Eindhoven University of Technology, The Netherlands

Composition of the group:
J. Meuldijk (associate professor)
B. Pierik (assistant professor)
R. Willemse (PhD on chain length dependent termination)
B. Staal (PhD on composition of oligomers in relation to entry in emulsion copolymerization)
M. Pepers (PhD on Raman spectroscopy applied to emulsion copolymerization)
X. Reynhout (PhD on modeling in emulsion polymerization)
D. Tillier (PhD on artificial latices of EPDM)
J. Pusch (PhD on transparent latices)
C. Boukaftane (Post-Doc on acrylate kinetics and chemistry)
C. Göttgens (techn.)
W. Gerritsen (techn.)

A small account of results obtained in the second halve of 2002 is given below, followed by a list of publications.

Process strategies have been developed to obtain homogeneous copolymers or copolymers of well-defined heterogeneity. It was shown that copolymers with the same average chemical composition but different CCDs show dramatic differences in mechanical properties.

The implementation of *on-line Raman spectroscopy* in emulsion copolymerization has been successful for several systems.

Living radical polymerizations were studied, since these may open very interesting perspectives for the preparation of (multi)block copolymers and in preparing narrow molar mass distributions. There is a strong incentive to apply 'living' radical polymerization (LRP) in water based emulsion polymerizations to produce *block copolymer latexes* in a cost-efficient way. LRP methods based on *dithiocompound reversible chain transfer agents*, such as MADIX and RAFT appear to be the most significant breakthrough in the field next to *Atom Transfer Radical Polymerization* (ATRP). Both mechanisms have been implemented in emulsion polymerizations and have led to successful reactions and interesting morphologies.

The replacement of conventional chain transfer agents by catalytic chain transfer agents in emulsion polymerization has been investigated.

Transparent latices are produced by means of microgel formation in emulsion polymerization. The bio-optical applications of these latices are currently under investigation together with the biomedical industry.

Latex production is in general carried out in large scale (semi-) batch processes. Research in the field of (semi-) batch processes was focused on the influence of operation and scale on the particle nucleation process. We have demonstrated that scale sensitivity of emulsion polymerisation reactors is mainly governed by the quality of emulsification which has a large influence on the course of the nucleation process and so on the particle size distribution of the product. We have also demonstrated that the rate of heating of the reaction mixture at the beginning of the emulsion polymerisation process is an essential parameter for the particle size distribution of the final product.

We have shown that the pulsed packed column (PPC) is a very useful reactor for the production of seed particles. The pulsed packed column combines low net flow rates with intensive radial mixing. Oscillation free production of seed latex without fouling is possible in the PPC. Homogeneous copolymers and copolymers with a bimodal chemical composition distribution can be produced in the PPC and a series of CSTRs The modeling of emulsion polymerization is implemented through the package Predici.

Publications in the area of emulsion polymerization and related areas 2002

Gregory Chambard, Bert Klumperman and Anton L. German
Experimental determination of the rate constant of deactivation of poly(styrene) and poly(butyl acrylate) radicals in atom transfer radical polymerisation
Macromolecules, 35 (2002) 3420-3425

Mark van den Brink, Michel Pepers and Alex M. van Herk
Raman spectroscopy of polymer latexes
J. Raman Spectrosc., 33 (2002) 264-272

Davy R. Suwier, Michael J. Monteiro, Alexander Vandervelden, Cor E. Koning
The iniferter technique in radical polymerization under UV and thermal conditions: a comparative study
e-Polymers, 025 (2002) 1-10

Martin Jung, Brian H. Robinson, David C. Steytler, Anton L. German and Richard K. Heenan
Polymerization of styrene in DODAB vesicles: A small-angle neutron scattering study
Langmuir, 18 (2002) 2873-2879

Auke Snijder, Bert Klumprman and Rob van der Linde
Kinetics of heterogeneous atom transfer radical polymerisation of methyl methacrylate
Macromolecules, 35 (2002) 4785-4790

H.J.A. Philipsen, B. Klumperman, F.A.M. Leermakers, F.P.C. Wubbe, A.L. German
Molar Mass Effects in Reversed-Phase Gradient Polymer-Elution Chromatography of Oligomers
Chromatographia, 55 (2002) 533-540

Sebastiaan C.J. Pierik, Rainer Vollmerhaus, Alex M. van Herk, Anton L. German
Shining a light on catalytic chain transfer
Macromol. Symp., 182 (2002) 43-52

Huiqi Zhang, Bert Klumperman and Rob van der Linde
Synthesis of Anthracene End-Capped Poly(methyl methacrylate)s via Atom Transfer Radical Polymerization and Its Kinetic Analyses
Macromolecules, 35 (2002) 2261-2267

Michael J. Monteiro and Jean de Barbeyrac
Preparation of Reactive Composite Latexes by “Living”Radical Polymerization Using

the RAFT Process. A New Class of Polymer Materials
Macromol. Rapid. Commun. 23 nr. 5/6 (2002) 370-374

F.A.M. Leermakers, H.J.A. Philipsen, B. Klumperman
Molecular modelling of chain end effects in separating oligomers by reversed-phase gradient polymer elution chromatography; adsorption transition as revealed by a self-consistent-field theory for polymer adsorption
J. Chromatography A, 959 (2002) 37-47

Auke Snijder, Bert Klumperman, Rob van der Linde
End-group modification of poly(butyl acrylate) prepared by atom transfer radical polymerization: Mechanistic study using gradient polymer elution chromatography
J. Pol. Sci., Part A. Polym. Chem.., 40 (2002) 2350-2359

Maartje Kemmere, Marcus van Schilt, Mascha Cleven, Alex van Herk and Jos Keurentjes
Reduction of residual monomer in latex products by enhanced polymerization and extraction in supercritical carbon dioxide
Ind. Eng. Chem. Res., 41 (2002) 2617-2622

Jan Jiskra, Henk A. Claessens, Carel A. Cramers, Roman Kaliszan
Quantitative structure-retention relationships in comparative studies of behaviour of stationary phases under high-performance liquid chromatography and capillary electrochromatography conditions
Journal of Chromatography A., 977 (2002) 193-206

Kenta Tanaka, Bunichiro Yamada, Robin Willemse and Alex M. van Herk
Pulsed Laser Polymerization of cyclohexyl acrylate involving fragmentation of mid-chain radical
Polymer J., 34, nr. 9 (2002) 692-699

Michael J. Monteiro, Raf Bussels, Sabine Beuermann and Michael Buback
High-Pressure “Living” Free-Radical Polymerization of Styrene in the Presence of RAFT
Aust. J. Chem., 55 (2002) 433-437

Handbook of radical polymerization, chapter 6 heterogeneous systems
A.M. van Herk, M. Monteiro p301-331 2002, ed. K. Matyjaszewski and T.P. Davis

Contribution to IPCG Newsletter from the Group of Polymer Particles

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Submitted papers

Effect of Reaction Parameters on Properties of Dispersion-Polymerized Hydrophilic Microspheres as Supports for Immobilization of Different Proteins. Horák D., Rittich B., Španová A. *Prog. Colloid Polym. Sci.*, in press.

Abstract. Particle size and polydispersity of hydrophilic microspheres prepared by dispersion polymerization of 2-hydroxyethyl and glycidyl methacrylate (HEMA, GMA) and 1-vinyl-2-pyrrolidone was compared with literature data on various polymer particles. Their properties depend on many reaction parameters of the polymerization, primarily on the solvency of the reaction medium for the polymeric particles represented in terms of liquid polarity and defined by the solubility parameters; however, the nature and concentration of the monomer, steric stabilizer (co-stabilizer) and initiator and polymerization temperature are of great importance as well. Monodisperse particles can be obtained only if the number of mature particles formed at the beginning of polymerization remains constant. Poly(HEMA) and hydrolyzed poly(GMA) microspheres were used as carriers of immobilized proteins, such as horseradish peroxidase, DNase I, RNase A, proteinase K and anti-*Salmonella*. Activation of hydroxy groups of the carrier via cyanuric chloride was the preferred immobilization method. Immobilized proteins were tested in some molecular-biological applications.

Key words: Dispersion polymerization, microspheres, protein immobilization, 2-hydroxyethyl methacrylate

Effect of Reaction Parameters on the Particle Size in the Dispersion Polymerization of 2–Hydroxyethyl and Glycidyl Methacrylate in the Presence of Ferrofluid. Horák D., Semenyuk N., Lednický F. *J. Polym. Sci., Polym. Chem. Ed.*, submitted.

Abstract Precipitation of Fe_3O_4 from aqueous solution using ammonium hydroxide produced nanoparticles which were coated with a layer of oleic acid (in some cases poly(ethylene oxide), or poly(vinylpyrrolidone)) prior to their dispersing into the organic phase. Encapsulation of magnetite nanoparticles in poly(2-hydroxyethyl methacrylate) or poly(2-hydroxyethyl-*co*-glycidyl methacrylate) microparticles was achieved by dispersion polymerization in toluene/2-methylpropan-1-ol. Magnetic poly(glycidyl methacrylate) microparticles were obtained in the presence of poly(ethylene oxide) (PEO) at the magnetite/monomer interface. The particles containing up to 20 wt.% of iron maintained their discrete nature and did not aggregate.

The effect of the reaction medium polarity, concentrations of monomer, initiator and stabilizer and temperature on the particle size and distribution, iron and the oxirane group content was studied.

Key words: Dispersion polymerization, magnetite, ferrofluid, 2-hydroxyethyl methacrylate, glycidyl methacrylate, magnetic microspheres

Review

Poly(2-Hydroxyethyl Methacrylate) Hydrogels. Preparation and Properties. Horák D., Jayakrishnan A., Arshady R. *In: Arshady R., Ed., Polymers in Medicine and Biology Series, Vol. 1, Citus Books, London 2003, in press.*

Abstract This chapter presents a systematic overview of poly(2-hydroxyethyl methacrylate) (PHEMA) hydrogels, their permeation and properties, with references to their bio- and hemocompatibility and biomedical application. Preparation of PHEMA by free radical and ionic mechanisms, and different polymerization processes (solution, bulk, suspension, emulsion and dispersion) are outlined. Copolymerization of HEMA with hydrophilic and hydrophobic comonomers including N-vinyl-2-pyrrolidone, (meth)acrylates, styrene and acrylamides are highlighted. Numerous PHEMA block and graft copolymers and interpenetrating networks are also discussed. Properties of PHEMA are discussed in terms of physicochemical (T_g, crosslinking, porosity, stability), mechanical (strength, modulus), swelling (matrix, water structure), permeability and transport behavior (diffusion, adsorption, osmotic, partition, drug release). Surface properties, various aspects of bio- and hemocompatibility and medical purity are also described including the influence of chemical composition and microdomain structure on protein sorption and implant biocompatibility. Includes 160 references, 21 illustrations and tables.

Recent publications

Characterization of Deoxyribonuclease I Immobilized on Magnetic Hydrophilic Polymer Particles. Rittich B., Španová A., Ohlashenyy Yu., Lenfeld J., Rudolf I., Horák D., Beneš M.J. *J. Chromatogr. B 774, 25-31 (2002).*

Abstract Magnetic bead cellulose particles and magnetic poly(HEMA-*co*-EDMA) microspheres with immobilized DNase I were used for degradation of chromosomal and plasmid DNAs. Magnetic bead particles were prepared from viscose and magnetic powder. Magnetic poly(HEMA-*co*-EDMA) microspheres were prepared by dispersion copolymerization of 2-hydroxyethyl methacrylate and ethylene dimethacrylate in the presence of magnetite. Divalent cations (Mg^{2+}, Ca^{2+}, Mn^{2+} and Co^{2+}) were used for the activation of DNase I. A comparison of free and immobilized enzyme (magnetic bead particles) activities was carried out in dependence on pH and activating cation. The maximum of the activity of immobilized DNase I was shifted to lower pH compared with free DNase I. DNase I immobilized on magnetic bead cellulose was used 20 times in the degradation of chromosomal DNA. Its residual activity was influenced by the nature of activating divalent cation. The immobilized enzyme with decreased activity was reactivated by Co^{2+} ions.

Keywords: Magnetic bead cellulose particles, magnetic poly(HEMA-*co*-EDMA), deoxyribonuclease I

Oriented Immobilization of Galactose Oxidase to Bead and Magnetic Bead Cellulose and Poly(HEMA-*co*-EDMA) and Magnetic Poly(HEMA-*co*-EDMA) Microspheres. Bílková Z., Slováková M., Lyčka A., Horák D., Lenfeld J., Turková J., Churáček J. *J. Chromatogr. B, Biomed. Sci. Appl. 770, 25-34 (2002).*

Abstract In order to obtain an active and stable oxidation reactor for daily use in biochemical laboratory we decided to immobilize galactose oxidase through a carbohydrate chain to magnetic carriers. We used hydrazide derivatives of non-magnetic and magnetic bead cellulose and of magnetic and non-magnetic poly(HEMA-*co*-EDMA) microspheres. Activation of the enzyme molecules was done by sodium periodate in the presence of supplements (fucose, $CuSO_4$, catalase). Orientedly immobilized galactose oxidase presents high storage stability and lower susceptibility to inappropriate microenvironmental conditions. Reactor reactivated by three pulses of *D*-galactose retained practically 100% of its native activity after 6 months. The positive properties of both magnetic carriers were entirely confirmed.

Keywords: Oriented immobilization, magnetic sorbents, enzymes, galactose oxidase

Enzymes Immobilized on Magnetic Carriers: Efficient and Selective System for Protein Modification. Bílková Z., Slováková M., Horák D., Lenfeld J., Churáček J. *J. Chromatogr. B, Biomed. Sci. Appl. 770, 177-181 (2002).*

Abstract In order to obtain an economical, efficient and selective system for glycoprotein modification, we prepared reactors with immobilized neuraminidase and/or galactose oxidase. High storage and operational stability of the enzyme reactors was obtained by their immobilization through the carbohydrate parts of the enzyme molecules to hydrazide-modified supports. Magnetic and non-magnetic forms of bead cellulose and poly(HEMA-*co*-EDMA) microspheres were used for immobilization. These reactors can be used almost universally for the activation of ligands and for labeling of substances having a carbohydrate moiety.

Keywords: Magnetic sorbents, neuraminidase, galactose oxidase, enzymes, glycoproteins

Poly(2-Hydroxyethyl Methacrylate-*co-N,O*-Dimethacryloylhydroxylamine) Particles by Dispersion Polymerization. Horák D., Chaykivskyy O. *J. Polym. Sci., Polym. Chem. Ed. 40, 1625-1651 (2002).*

Abstract Poly(2-hydroxyethyl methacrylate-*co-N,O*-dimethacryloylhydroxylamine) (poly(HEMA-*co*-DMHA)) particles were prepared by dispersion polymerization in the toluene/2-methylbutan-1-ol medium using cellulose acetate butyrate (CAB) and dibenzoyl peroxide (BPO) as steric stabilizer and initiator, respectively. The particle size was reduced with decreasing solvency of the reaction medium (more nuclei were generated), because the critical chain length of the precipitated oligomers decreased with increasing toluene content, which is a poorer solvent for the polymer than 2-methylpropan-1-ol. There is an optimum initiator concentration (2 wt.% BPO relative to monomers) for producing low-polydispersity particles under given conditions. At the same time, discrete spherical particles were obtained at a low monomer concentration and/or higher polymerization temperature.

Keywords: Dispersion polymerization, *N,O*-dimethacryloylhydroxylamine, 2-hydroxyethyl methacrylate, submicrometer-size range, crosslinked particles

Properties of RNase Immobilized on Magnetic Poly(HEMA) Microspheres. Horák D., Rittich B., Šafář J., Španová A., Lenfeld J., Beneš M.J. *Biotechnol. Prog. 17, 447-452 (2001).*

Abstract: Magnetic hydrogel particles 1.5 μm in size were prepared by dispersion copolymerization of 2-hydroxyethyl methacrylate and ethylene dimethacrylate in the presence of magnetite, which formed the core of the particles. RNase A was coupled to the particles by the cyanuric chloride method. Gel electrophoresis of plasmid DNA pUC 19 (contaminated by bacterial RNA) confirmed RNA degradation with the immobilized enzyme. The effect of temperature and pH on the relative activity of immobilized RNase was estimated after incubation of the samples at different temperatures (30-80 ºC) and pH (4.0-8.0). Maximum relative activity was observed at 70 ºC and pH 6.5. The matrices based on magnetic poly(HEMA) had a low tendency to adsorb RNA.

Contribution to the Newsletter, IPCG, February 2003

by Norio Ise

Manuscript submitted for publication.

Gravitational, Vertical Compression of Colloidal Crystals as Studied by the Kossel Diffraction Method

Tadatomi Shinohara(1), Hisashi Yamada(1),
Ikuo S. Sogami(1), Norio Ise(2), and Tsuyoshi Yoshiyama(1),

(1) *Department of Physics, Kyoto Sangyo University*
(2) *Professor Emeritus, Kyoto University*

Abstract

Availing of pillar-shaped crystals formed in dilute aqueous dispersions of colloidal silica particles (density: 2.2 gcm^{-3}), we photographed the Kossel diffraction patterns systematically at various heights and found that body-centered-tetragonal (bct) crystallites grew with the (110) plane in parallel to the cuvette surface and the colloidal crystal was contracted vertically. The lattice constants of the crystal decreased with decreasing height and the lattice constant in the vertical direction in the lower part of the dispersion was larger than that in the upper part. The gravitational effect is thus two-fold, namely sedimentation of particles causing isotropic contraction of crystals and vertical compression due to the small elastic constants.

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

Reporter: D. Sunil Jayasuriya

Contribution #1

AN APPLIED APPROACH TO FILM FORMATION FOR WATERBORNE INDUSTRIAL COATINGS *

J. W. Taylor, and T. D. Klots, Johnson Polymer, P.O. Box 902
Sturtevant WI 53177-0902

Presented at the International Waterborne, High Solids, and Powder Coatings Symposium
(February 6-8, 2002), New Orleans, LA, USA

Symposium Sponsored by
The University of Southern Mississippi
Department of Polymer Science

ABSTRACT

The commercialization of latexes in 1946 created a need for understanding film formation from discrete polymeric particles. Aided by technological advances and pushed by environmental considerations, there has since been a steady shift from solvent-borne to water-borne polymers. Early film formation theories focused on solvent-free waterborne latexes. However, significant levels of filming aid are used to optimize the performance of industrial and maintenance coatings. Better understanding of the role filming aids play in the film formation process will aid in the selection of the most efficient filming aid combination for optimizing coating performance.

In this work important parameters such as the glass transition temperature of filming aids and polymers, the volatility of filming aids in the presence of water and polymeric particles, the distribution coefficients of filming aids, and the Fox-Flory equation are used to predict the MFT of latex particles at deformation. A new experimental method that obtains the activity coefficients of filming aids during the drying process of latex films is demonstrated. These activity coefficients are used to predict the total solvent loss during the wet evaporation stage of the film formation process. Additionally, the clear film composition is modeled for the ensuing "volatility-controlled" stage that defines the time line where solvent evaporation is not diffusion controlled. The ability of the model to predict or follow the Tg of a "drying system" is demonstrated. The model presented can assist in the selection of filming aids for water-borne latex-based formulations and can provide important criteria for optimizing particle composition and morphology.

*** This paper was awarded the Shelby F Thames best paper prize at the 2002 International Waterborne, High Solids and Powder Symposium**.

International Polymer Colloids Group Newsletter

Haruma Kawaguchi
Faculty of Science & Technology, Keio University
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January 2003

Submitted Papers

1. **Hydrogel microsphere-enhanced surface plasmon resonance for detection of a K-ras point mutation employing peptide nucleic acid**

   Yasunobu Sato, Koji Suzuki and Haruma Kawaguchi

   Detection of point mutation was challenged by sandwich method on SPR using peptide nucleic acid (PNA) probe on SPR chip and DNA probe immobilized on microspheres. This sandwich system enhanced the detection sensitivity by 100 times compared with the conventional direct SPR method.

2. **Preparation of colored latex with high dye content by miniemulsion polymerization**

   Mayuko Takasu, Toshifumi Shiroya, Kimiya Takeshita, Nunehiro Sakamoto, and Haruma Kawaguchi

   Phthalocyanine dyes- and styryl dyes-carrying colored latexes were obtained by miniemulsion polymerization. Some dyes played a role of hydrophobe to prevent Ostwald repelling. The content of dye exceeded 40wt% when two kinds of phthalocyanine dyes were blended in miniemulsions although a part of dye molecules formed aggregates by π-π stacking in the particles. The colored latex gave brilliant color because the diameter was less than 100 nm.

3. **Dansyl fluorescence and local structure of dansyl-labeled core-shell and core-chair type microspheres in solution**

   Kazuyuki Horie, Sadakazu Yamada, Shinjiro Machida, Satoshi Takahashi, Yoko Isono, Haruma Kawaguchi

   Accepted for publication in Macromol. Chem. Phys.

   Core-shell type microspheres with fluorescent dansyl groups at random sites in crosslinked poly(N-isopropylacrylamide) (PNIPAM) shell chains and core-hair type microspheres with dansyl groups at terminal sites of PNIPAM hair chains graft-polymerized with living radical mechanism were prepared. Dansyl groups at the chain ends of PNIPAM hairs of core-hair type microspheres in water are located on the surface of hydrophobic cores.

4. **Particle Forming Precipitation Polymerization under Unusual Conditions**
   Toshio Takahashi, Hiroko Fukasawa and Haruma Kawaguchi
   Prog. Colloid Sci., in press.
   Summary: Presented in the previous newsletter.

5. **Synthesis of Functional Polymer Particles**
   Haruma Kawaguchi
   To appear in a monograph on "Single Organic Nanoparticles"
   Summary: Presented in the previous newsletter.

6. **Thermally sensitive poly(N-isopropylacrylamide) based colloidal particles: Proteins interactions**
   H. Kawaguchi, D. Duracher, A. Elaissari
   To appear in "Colloid Polymers: Preparation and Biomedical Applications" ed .by A. Elaissari.

Recent Publications

1. **Thermo-sensitive Amphoteric Microspheres and Its Potential Application as a Biological Carrier**
   Shi-Jiang Fang and Haruma Kawaguchi, Colloid Polym. Sci., 280, 984-989 (2002)

2. **Structure Characterization of Hairy Nanoparticles Consisting of Hydrophobic Core and Thermo-sensitive Hairs**
   Shinichi Takata, Mitsuru Shibayama, Reiko Sasabe and Haruma Kawaguchi
   Polymer, Polymer 44, 495-501 (2002)

3. **Colloidal properties and protein adsorption of amphoteric microspheres.**

   Shi-Jiang Fang, Haruma Kawaguchi, Colloids Surfaces A, 211, 79-84 (2002)

4. **Detection of K-ras point mutation employing peptide nucleic acid at the surface of a SPR biosensor.**

   Sato, K. Suzuki and Haruma Kawaguchi, Colloids and Surfaces B, 27, 23-31 (2003)

Contribution to IPCG newsletter from the

Laboratory of Physical Chemistry, Delft University of Technology
and the
Leiden Colloid and Interface Science group

A complete list of published material is available on
http://www.dct.tudelft.nl/lfc/persons/gkoper/Publ.htm

Relevant recent publications

- Mezzasalma S.A. and Koper GJM, *Semiclassical approach to electrorheological fluids. Influence of solid volume fraction on the suspension yield stress*, Colloid and Polymer Science **280** (2002) 160-166.
- Chassagne C, Bedeaux D, Koper GJM, *The interpretation of dielectric spectroscopy measurements on silica and hematite sols*, J Colloid Interf Sci **255** (2002) 129-137.
- Haemers S, van der Leeden MC, Koper GJM, Frens G, *Cross-linking and multilayer adsorption of mussel adhesive protein*, Langmuir **18** (2002) 4903-4907.
- Chassagne C, Bedeaux D, van der Ploeg JPM, and Koper GJM, *Theory of Electrode Polarization. Application to Parallel Plate Cell Dielectric Spectroscopy Experiments*, Colloids and Surfaces A **210** (2002) 137-145.
- Bouchama F, Estramil G, Autin AJE, and Koper GJM, *Film formation from concentrated emulsions studied by simultaneous conductometry and gravimetry*, Colloids and Surfaces A **210** (2002) 129-135.
- Borkovec M, Brynda M,Koper GJM, and Spiess B, *Resolution of microscopic protonation mechanisms in polyprotic molecules*, Chimia **56** (2002) 695-701.
- Chassagne C, Bedeaux D, and Koper GJM, *Dielectric response of colloidal spheres in non-symmetric electrolytes*, Physica A **317** (2003) 321-344.

Relevant preprints:

Synthesis and Protonation Behavior of Comb-Like Poly(Ethylene Imine)

Ger J.M. Koper, René C. van Duijvenbode, Danny D.P.W. Stam, Michal Borkovec

Comb-like poly(ethylene imine) (PEI) with -(CH_2CH_2N)($CH_2CH_2NH_2$)- as the repeating unit has been synthesized employing a protecting group strategy, and analyzed by potentiometric titration. Plotted the degree of protonation as a function of pH, the titration curve shows three protonation steps separated by two intermediate plateaus, namely one at degree of protonation of 1/2 and a second one at 3/4. The first protonation step occurring at pH around 9.5 corresponds to the protonation of the primary amine groups on the side chains. During the second protonation step at pH around 4.5 every second tertiary amine protonates, while the final protonation step, where the remaining tertiary amines protonate, probably occurs at pH near 0. The titration curve can be quantitatively predicted to a good degree of accuracy using a site binding model, which has been independently calibrated on titration data of low weight molecular amines.

Dielectric Spectroscopy Measurements on Latex Dispersions

C. Chassagne, D. Bedeaux, J.P.M v.d. Ploeg, and G.J.M. Koper

Experimental data on the dielectric response of latex dispersions for a large variety of particle sizes, surface charge densities and ionic strengths are interpreted using an analytical theory developed previously
(Chassagne, C., Bedeaux, D. and Koper, G.J.M., J.Phys.Chem B **105**, 11743 (2001) and Physica A, to be published). It is found that the conductivity increment is a crucial variable in the discussion about the need of a Stern layer conductance. Both the dielectric permittivity and the conductivity increments are fitted using the zeta potential and a Stern layer conductance.

Polarization between Concentric Cylindrical Electrodes

C. Chassagne, D. Bedeaux, J.P.M v.d. Ploeg, and G.J.M. Koper

We consider an asymmetric electrolyte between two cylindrical concentric electrodes that are uncharged in the absence of an applied voltage difference. We calculate the dielectric response of this capacitor to an alternating voltage difference. The problem is solved using both classical boundary conditions and the new boundary conditions using excess densities to describe the charge build-up near the condensator plates as given in a previous article (C. Chassagne, D. Bedeaux and G.J.M. Koper , Colloid and Surfaces A). We verify that both boundary conditions give the same results. The advantage of the new boundary
conditions lies in the possibility to extend, in the future, the analysis to real electrodes including reactions and specific ion adsorption. A comparison of the model predictions, involving no adjustable parameters,
with experimental dielectric spectroscopy data is performed and excellent agreement is found.

Trapping agitated emulsions in non-preferred morphology

F. Bouchama, G.A. van Aken, and G.J.M. Koper

This paper reports on the mechanism of catastrophic phase inversion. Experiments were carried out in a stirred vessel where phase inversion was detected by a jump in emulsion conductivity. The system studied contained paraffin oil, water and Triton X-100. The position of the phase inversion has been compared between two emulsification routes of phase inversion, namely the direct emulsification route and the wash-out route. The locus of phase inversion was found to be strongly different for both cases. In particular for the wash-out route the way of dilution appeared to be an important parameter, which to our knowledge has never been studied in detail before. Our experiments show that the locus of catastrophic phase inversion is determined by the added volume of the dispersed phase at each step of the dilution rather than the addition rate. This observation is explained on the basis of the role of multiple emulsion formation in catastrophic phase inversion.

Entropy production for cylinder drying of linerboard and newspaper

G.J.M. Koper, S. Kjelstrup, M. Sadeghi, M. Douglas, and T.G.M. van de Ven

The entropy produced during paper drying has been calculated for five different cylinder dryer machine runs, three for linerboard and two for newsprint. Entropy produced by evaporation of water and by heat transfer from the cylinders to the paper constitute the largest contributions. Three drying regimes can be distinguished. The initial "free" water evaporation regime, with the largest entropy production, may last until the so called "fiber saturation point" of moisture content is reached. The second regime seems to be the regime where capillary water escapes the fibers. The third regime, with the lowest entropy production, starts when the sorption enthalpy of water to fiber becomes a significant contribution to the enthalpy of evaporation of (bulk) water. Possibilities for large improvements of the second law efficiency of the dryers were demonstrated: The lost exergy of two newsprint machines differed by 0.1 GJ per ton of paper produced.

Professor Peter A. Lovell

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UK Polymer Colloids Forum

The 9th Meeting of the Forum will be held from 11-12 September 2003 at UMIST. The plenary session speakers will be Terry Cosgrove, Bernadette Charleux and Hamid Elaissari. Enquiries should be made by e-mail to: ukpcf@umist.ac.uk

Polymer Colloids Research at the Manchester Materials Science Centre

My administrative commitments at UMIST changed during 2001 and 2002, culminating in my taking on the role of Dean of Teaching and Learning for UMIST in Summer 2002. This rather limited my output during this period, including contributions to the newsletter. Hence, this is something of a catch-up contribution.

In February 2002, Dr. Brian Saunders joined the Manchester Materials Science Centre from the University of Adelaide in Australia. The principal theme of his research concerns intelligent polymer colloids and he is now beginning to establish his research group in Manchester. You will hear more of Brian's work in the future.

Current Research Projects in the Field of Polymer Colloids

Studies of Alkali-Soluble Resins and their use in Emulsion Polymerisations

Research Student: Robert Blanchard

Sponsor: Avecia and the Engineering & Physical Sciences Research Council

Chain Transfer to Polymer in Free-Radical Polymerisations

Research Associate: Ian Gray

Collaborator: Frank Heatley (Chemistry Department, University of Manchester)

Sponsor: The Engineering & Physical Sciences Research Council

Novel Latent Crosslinking Monomers Designed for One-Part Crosslinkable Water-Borne Coatings

Research Student: Jihwan Yoon

Collaborators: David Berrisford (Chemistry Department, UMIST) and
Andy Whiting, (Chemistry Department, Durham University)

Sponsor: The Engineering & Physical Sciences Research Council

Recent Theses related to Polymer Colloids

Studies of Rubber-Toughened Acrylic Materials by Pranee Thongnoi, PhD Thesis, UMIST, graduated 2001

Structure-Property Relationships in Water-Borne, Crosslinked Pressure-Sensitive Adhesives by Nikki Errington, PhD Thesis, UMIST, graduated 2002

Grafting of Acrylic Monomers to Hydroxyethylcellulose During Emulsion Polymerisation by Ian Gray, PhD Thesis, UMIST, graduated 2002

Preparation and Applications of Polymer-Encapsulated Carbon Blacks by Parnia Navabpour, PhD Thesis, UMIST, graduated 2002

Recent Papers related to Polymer Colloids

"Viscoelastic Properties of Branched Polyacrylate Melts", N.M. Ahmad, P.A. Lovell and S.M. Underwood, *Polymer International,* **50**, 849-857 (2001)

The viscoelastic properties of poly(n-butyl acrylate), poly(ethyl acrylate) and poly(methyl acrylate) melts have been studied using samples that varied in both molar mass and the mol% branched repeat units, these properties having been previously determined by gel permeation chromatography and ^{13}C NMR spectroscopy, respectively. Poly(n-butyl acrylate) was studied most extensively using seven samples; one sample of poly(n-butyl acrylate), two samples of poly(ethyl acrylate) and one sample of poly(methyl acrylate) were used to study the effect of side-group size. Storage and loss moduli were measured over a range of frequency (1×10^{-3} rad s^{-1} to 1×10^{2} rad s^{-1}) at temperatures from T_g+20 °C to T_g+155 °C and then shifted to form master curves at T_g+74 °C through use of standard superposition procedures. The plateau regions were not distinct due to the broad molar mass distributions of the polyacrylates. Hence, the upper and lower limits of shear storage modulus from the nominal 'plateau' region of the curves for the seven poly(n-butyl acrylate) samples were used to calculate the chain molar mass between entanglements, M_e, which gave the range 13.0 kg mol^{-1}< M_e < 65.0 kg mol^{-1}. The Graessley-Edwards dimensionless interaction density and dimensionless contour length concentration were calculated for poly(n-butyl acrylate) using the mean value of plateau modulus (1.[illegible] Pa) and three different methods for estimation of the Kuhn length; the data fitted closely to the Graessley-Edwards universal plot. The Williams-Landel-Ferry C_1 and C_2 parameters were determined for each of the polyacrylates; the data for the poly(n-butyl acrylate) samples indicate an overall reduction in C_1 and C_2 as the degree of branching increases. Although the values of C_1 and C_2 were different for poly(n-butyl acrylate), poly(ethyl acrylate) and poly(methyl acrylate), there is no trend for variation with structure. Thus the viscoelastic properties of the polyacrylate melts are similar to those for other polymer melts and, for the samples investigated, the effect of molar mass appears to dominate the effect of branching.

"^{13}C NMR Spectroscopy Studies of Branching and Sequence Distribution in Copolymers of Vinyl Acetate and *n*-Butyl Acrylate Prepared by Semibatch Emulsion Copolymerization", D.J. Britton, F. Heatley and P.A. Lovell, *Macromolecules,* **34**, 817-829 (2001)

^{13}C NMR spectroscopy has been used to study branching and sequence distributions in copolymers of vinyl acetate (VAc) and n-butyl acrylate (BA) prepared by semi-batch emulsion copolymerization. All copolymerizations proceeded via a seed stage that was carried out under monomer-flooded conditions, followed by a growth stage that operated under monomer-starved conditions. The ^{13}C NMR spectra of the copolymers have been fully interpreted both in terms of the structural features arising from chain transfer to polymer and the repeat unit sequence distributions. The sequence distributions for copolymers formed in the seed stage are in reasonable agreement with predictions from the standard terminal-unit first-order Markov statistical model, showing that normal copolymerization kinetics operate under monomer-flooded conditions. However, the sequence distributions for copolymers produced in the growth stage are closely represented by a random Bernoullian distribution, showing that copolymers with random repeat unit sequence distributions are formed under monomer-starved conditions. The only reasonable explanation of this observation is that propagation is subject to diffusion control under monomer-starved conditions.

The branching data reveal a synergistic effect in which the inclusion of only small amounts of either monomer leads to disproportionate increases in the level of branching. This is a consequence of the efficacy of H-abstraction at BA backbone tertiary C–H bonds by the highly-reactive VAc-ended chain radicals. The results indicate that radicals with VAc end units abstract hydrogen atoms from BA repeat units about 7-8× times more rapidly than from VAc repeat units and that radicals with VAc end units are about 3× as effective in abstracting hydrogen atoms from BA repeat units than are radicals with BA end units. Copolymer composition drift occurs in the seed stage due to the monomer-flooded conditions and results in virtually all of the BA being consumed before the conversion is high enough for chain transfer to polymer to become significant; hence, branching arises almost exclusively from H-abstractions by radicals with VAc end units. However, in the monomer-starved growth stage, radicals with BA end units and radicals with VAc end units both contribute to chain transfer to polymer in proportions that correspond to the composition of the comonomer feed; this observation again is consistent with diffusion control of propagation under monomer-starved conditions.

"Chain Transfer to Polymer in Emulsion Copolymerizations", D.J. Britton, F. Heatley, P.A. Lovell and R. Venkatesh, *Macromolecular Symposia,* **175**, 95-104 (2001)

Chain transfer to polymer in emulsion copolymerizations of (i) vinyl acetate (VAc) with n-butyl acrylate (BA) and (ii) BA/acrylic acid with (a) methyl methacrylate (MMA) and (b) styrene (S) has been studied using ^{13}C NMR spectroscopy to quantify the level of branching in the copolymers produced. The results reveal synergistic effects in which the inclusion of a small amount of comonomer leads to disproportionate changes in the level of branching. The data from the VAc/BA copolymerizations show that radicals with VAc end units abstract hydrogen atoms from BA repeat units more frequently than from VAc repeat units and that radicals with VAc end units are more effective in abstracting hydrogen atoms from BA repeat units than are radicals with BA end units. These effects lead to higher levels of branching in

VAc/BA copolymers than results from the corresponding homopolymerizations and are a consequence of the efficacy of hydrogen abstraction at BA backbone tertiary C–H bonds by the highly-reactive VAc-ended chain radicals. In contrast, the effect of introducing MMA or S to an acrylate polymerization is to disproportionately reduce the level of branching, with S being more effective than MMA in moderating chain transfer to polymer. These effects arise because propagating radicals with MMA or S end-groups have longer lifetimes compared to those with acrylate end groups and have a very much lower tendency to abstract hydrogen atoms from acrylate repeat units.

"Chain Transfer to Polymer in Free-Radical Solution Polymerization of 2-Ethylhexyl Acrylate Studied by NMR Spectroscopy", F. Heatley, P.A. Lovell, and T. Yamashita, *Macromolecules*, **34**, 7636 (2001)

The effects of initial monomer concentration, $[M]_O$, and percent conversion on the extent of chain transfer to polymer in free-radical solution polymerization of 2-ethylhexyl acrylate (EHA) have been studied. The polymerizations of EHA were carried out in cyclohexane at 70 °C using 2,2'-azobis(2-cyanopropane) at 0.1 wt% to monomer as initiator. ^{13}C NMR spectra of the PEHA show that branching resulted from hydrogen abstraction at backbone C–H bonds, with no evidence for chain transfer in the side-group. The branching levels were determined from unique resonances of branch-point carbons and ranged from 3 to 8 mol%, increasing as the conversion increased and as $[M]_O$ decreased. The trends for variation of branching level with $[M]_O$ and conversion are comparable to those for solution and bulk homopolymerizations of other acrylate monomers and vinyl acetate, though the branching levels for PEHA are much higher than those for poly(*n*-butyl acrylate) prepared under the same conditions.

"Influence of Concentration on the Particle Size Analysis of Polymer Latexes using Diffusing Wave Spectroscopy", P. Navabpour, C. Rega, C.J. Lloyd, D. Attwood, P.A. Lovell, P. Geraghty and D. Clarke, *Colloid and Polymer Science*, submitted

The use of a Diffusing Wave Spectroscopy (DWS) technique for the particle size analysis of a series of suspensions of polymer latexes with diameters in the range between 90 and 1300 nm and volume fractions from 0.02 to 0.18 has been investigated. Particle sizes from DWS were in reasonable agreement with those from transmission electron microscopy and disc centrifuge photosedimentometry. Photon correlation spectroscopy was applicable only to the latexes with particle sizes less than 500 nm. For polymer latexes with volume fractions (V_f) up to 0.09, the decay of the autocorrelation function from DWS was related to the particle size over the range of particle sizes examined. At the highest volume fraction ($V_f = 0.18$) it was possible to distinguish between particles with diameters of 740 and 1300 nm from their autocorrelation functions, but not between particles with diameters of 90 and 430 nm.

“Degradation and Grafting of Hydroxyethylcellulose During Emulsion Polymerization”, T. Annable, I. Gray, P.A. Lovell, S.N. Richards and G. Satgurunathan, *Progress in Colloid and Polymer Science*, submitted

Degradation of hydroxyethylcellulose (HEC) in aqueous solution at 80 °C has been studied with the observations that degradation is rapid in the presence of ammonium persulfate (APS), but slow with 4,4'-azobis(4-cyanopentanoic acid), and that hydrolytic degradation is insignificant. Acrylic emulsion polymerizations performed at 80 °C with HEC as the principal colloid stabilizer and APS as initiator have also been studied. In the presence of acrylic monomers, the dominant reaction leads to grafting of HEC chains to the latex particles. However, during periods when monomer is absent the HEC chains degrade and those that are grafted to latex particles release free HEC chain fragments to the aqueous phase. These observations are discussed in relation to a proposed mechanism for degradation and grafting of HEC.

Contributions to the IPCG Newsletter
February 2003-01-20

CNRS-LCPP/ESPCE-Lyon

Characterisation of Polymer Colloids

Guyot, A., M. Schneider, T.F. McKenna,

Chapter 2 in Microspheres, Microcapsules and Liposomes, Vol. 4: Functional Polymer Colloids, A. Guyot et A. Arshady (eds), (Citus Books).

High solid content (HSC) latexes are of growing interest for many reason, but making this type of product entails many difficulties. Increasing the solid content (fraction of polymer relative to the continuous phase) in a reproducible manner entails the strict control of a complex particle size distribution (PSD). The PSD must be either quite broad, or multimodal in order to obtain solids contents much above 55 or 60% by volume. In addition, the viscosity of a latex is highly sensitive to the PSD near the upper limit of solids content, however it is still not possible to predict à priori how a complex PSD will effect the viscosity. This article presents an overview of the rheology of concentrated latexes, followed by a discussion of the state of the art in the area of high solids latex production.

High Solids Content Emulsions.

Part I: A study of the influence of the particle size distribution and polymer concentration on viscosity

M. Schneider, J. Claverie, C. Graillat, T.F. McKenna

J. Appl. Polym. Sci., **84**(10), 1878-1896 (2002)

An experimental and modelling study has been carried out to understand the relationship between the viscosity of a multimodal latex, and its particle size distribution and polymer concentration. The study illustrates the inadequacy of existing models in predicting the viscosity of complex latexes. It is shown that the latex viscosity at a fixed shear rate is very sensitive to the polymer concentration at high solids content, and to the PSD.

High Solids Content Emulsions.

Part II: Preparation of Seed Latexes

M. Schneider, C. Graillat, A. Guyot, T.F. McKenna

J. Appl. Polym. Sci., **84**(10), 1897-1915 (2002)

A systematic study of the synthesis of large and medium sized monomodal seed latexes for use in preparing highly concentrated, multipopulated emulsions was presented. The viscosity of these latexes is fairly low, which is important since they will be blended and further grown in order to modify the PSD in a subsequent stage. Low viscosity will ensure that mixing of the different seeds and/or added monomer, initiator and surfactant will be dispersed as uniformly as possible in the final product. These recipes also yielded stable emulsions. In effect, the average particle size and polydispersity of the medium-sized particles remained unchanged after several months of storage at ambient temperature.

It was demonstrated that the rate of reaction during the semi-batch step can be significantly increased through the use of an organo-soluble initiator, and that the stabilisation of homogeneously nucleated particles can be reduced if a non-ionic water soluble initiator is used in place of the more traditional persulphate initiators.

These products and concepts will be put to use in Part III of this series for the production of latexes with low viscosity, and with solids contents on the order of 65%

High Solids Content Emulsions.

Part III: Synthesis of Concentrated Latexes via Classic Emulsion Polymerisation

M. Schneider, C. Graillat, A. Guyot, T.F. McKenna

J. Appl. Polym. Sci., **84**(10), 1916-1934 (2002)

Two different methods of producing bi- and trimodal latexes of a mixture of methyl methacrylate, butyl acrylate and small amounts of acrylic acid were tested. It is shown that a combination of concentrating blends of seed particles via semibatch reaction, followed by a nucleation of small particles plus a second semibatch phase allowed us to obtain stable latexes with solids contents over 65% and viscosities of below 2500 mPa·s, with little coagulum formation. The key parameter in determining latex stability, coagulum formation and viscosity appears to be the the particle size distribution, and especially its modification due to secondary nucleation. Since it is not possible to eliminate water soluble monomers from the polymerisation recipe, secondary (homogeneous) nucleation must be minimised by careful addition of the free radical initiator, and choice of monomer feed flow rates. The nucleation of the third population in the trimodal latexes is best accomplished with a mixed surfactant system, since renucleation by anionic surfactant alone leads to detrimental changes in the PSD due to excessive flocculation of particles. In addition, it was found that the viscosity of the final products was not sensitive to small changes in the ionic strength of the latex, but neutralisation to a pH of 6 effectively doubles the final latex viscosity.

High Solids Content Emulsions.

Part IV: Improved Strategies for Producing Concentrated Latexes

M. Schneider, C. Graillat, A. Guyot, I. Betrémieux, T.F. McKenna

J. Appl. Polym. Sci., **84**(10), 1935-1948 (2002)

A new means of producing high solids content latexes with low viscosity is presented. The replacement of water soluble initiators that decompose to give charged free radicals are shown to perturb the stability of highly concentrated latexes. Their replacement by an oil soluble inititator during particle growth, then by an activated, water soluble system to remove residual monomer has been shown to help significantly reduce the number of stable particles generated by homogeneous nucleation. Latexes with 73% (v/v) solids have been produced with a bimodal PSD consisting of 900 and 110 nm particles. The viscosity of these latexes can be as low as 300 mPa·s at 20 s^{-1}. Despite the presence of water soluble monomers, excellent control over the evolution of the PSD allows one to obtain highly reproducible results. In addition, latexes produced with the new initiator system have a much lower water uptake and their viscosity is much less sensitive to changes in pH than is the case for latexes produced using standard emulsion polymerisation techniques.

On-Line Monitoring of the Evolution of Number of Particles in Emulsion Polymerization by Conductivity Measurements. I. Model Formulation

A.F. Santos, E.L. Lima, J.C. Pinto, C. Graillat and T. McKenna
To Appear, J. Appl. Polym. Sci.

The conductivity meter is an inexpensive instrument that can be easily installed in polymerization reactors. This instrument can be used to monitor ionic species without time-consuming calibrations. A probe is inserted into the media providing in-situ measurements of conductivity in real-time. In the case of emulsion polymerization reactions, the conductivity meter can respond to changes of ionic surfactant concentration, allowing for determination of surfactant dynamics in the media. Surfactant concentration can then be related to the changes in the surface area of the polymer particle phase, which can be linked to the nucleation or coagulation phenomena.

In this work, a conductivity meter device was coupled to a calorimetric reactor in order to provide *in-situ* and on-line measurements of conductivity during the emulsion polymerization of styrene, using sodium dodecyl sulfate as an anionic surfactant, and potassium persulfate as the free radical initiator. A semi-empirical model was built to describe the conductivity signal as a function of the latex composition and of the reactor temperature. The model was inverted and combined with the available conductivity signal, conversion and temperature measurements, being able to accurately predict the number of polymer particles in the latex and also the surfactant concentration in the many phases, without need of on-line measurements of particle size.

Continuous Tubular Reactor as a Seed Reactor for Emulsion Polymerisation,

Ouzineb, K., C. Graillat, T.F. McKenna,
7th International Workshop on Polymer Reaction Engineering, Hamburg, Germany, 8-10 October, 2001.

Economics favour a continuous process over a batch process when product volumes are large enough or when product grades differ slightly, and a continuous process improve quality by eliminating batch to batch variations. In addition, tubular reactors are tempting to use for a number of reasons, including: the large surface area of the tube is advantageous for the strongly exothermic polymerization, their flexible geometry allows us to change the shape and to control temperature profiles rather easily, the narrow residence time distribution suggests that a narrow particle size distribution could be obtained, and its greatly reduced backmixing also permit stable operation.

In this study, a tubular reactor was used as a seed reactor for the continuous production of styrene seeds via mini-emulsion for use in other applications in the laboratory (e.g. study of emulsion in a CSTR). The apparatus is built with 0.4 cm ID Teflon tube and is up to 84 m in length (total volume of approxiamtely 1L). The tube is divided into different parts, each one being immersed in a bath which imposes the desired temperature. Sampling valves are located at positions along the tube. The objectives were to have continuously large volume of styrene latex with constant characteristics: N_p, d_p, surface coverage, 30% of solid content and the elimination of fouling problems. In miniemulsion nucleation occurs only in the small monomer droplets which leads to a slightly broader particle size distribution as compared to conventional emulsion, and a broader distribution shows a lower viscosity.

Miniemulsion polymerizations were carried out at laminar flow rate (Re = 35, Q = 5ml.min^{-1}, residence time = 212 min) with styrene as monomer (35 % solid contents), sodium dodecyl sulfate (SDS, 0.4*CMC), Triton X-405 (2.6*CMC) as surfactants and stearyl methacrylate (SMA, 9 g/L-water) as cosurfactant to stabilize the monomer droplets against Ostwald ripening. Potassium persulfate as initiator. Previous experiments in batch allowed us to select SMA as the optimal cosurfactant for our operatives conditions. We succeeded in polymerising all of the initial droplets dispersed in the aqueous phase ($N_p/L = 3*10^{16}$). Complete conversion were obtained after two residence time with an average particle size of 300 nm and a surface coverage of 90 %.

The feasibility of miniemulsion polymerization as a strategy to eliminate problem of mixing and fouling in the tubular reactor has been demonstrated, in addition the control over the number of particle is ensured. So the CSTR reactors can be feed continuously which represent a large gain of time compared to the usual processes.

On-Line Monitoring of the Evolution of Number of Particles in Emulsion Polymerization by Conductivity Measurements. II. Model Validation

A.F. Santos, E.L. Lima, J.C. Pinto, C. Graillat and T. McKenna

To Appear, J. Appl. Polym. Sci.

A model to describe the evolution of conductivity measurements in emulsion polymerizations was presented in the first part of this work [Santos et al., 2002, *J. Appl. Polym. Sci.*, submitted]. The model was built on the assumption that surfactant is partitioned among the three principle phases of the polymerizing latex. Model parameters were estimated by fitting the model responses to experimental conductivity data obtained in different runs performed with similar solids content, reactor temperature and initiator concentration. A soft-sensor strategy was then proposed for monitoring of the number of polymer particles (N_p) by combining the conductivity model with the available conversion, temperature and conductivity signals. The main objective of the current work is to validate the conductivity model in a broader range of operation conditions, in order to follow the evolution of N_p (nucleation/coagulation) on-line under different reaction conditions. A series of batch and semi-batch polymerization runs were carried out aiming to evaluate the model performance when different solids content, surfactant concentration and reactor temperatures are used. Additionally, simulation studies were performed in order to assess the model sensitivity to the fluctuations of the conversion and temperature signals. Results showed that the model is able to perform accurate predictions of N_p even when disturbances of +/- 2°C in temperature and +/- 0.03 in monomer conversion take place during the polymerization process.

Stabilization and Compartmentalization in Miniemulsions Polymerization

K. Ouzineb, C. Graillat, T.F. McKenna

Submitted to J. Appl. Polym. Sci.

Different surfactant and co-stabilization systems were studied for the miniemulsion polymerizations of styrene and of butyl methacrylate. It was found that the combination of sodium dodecyl sulfate (SDS), Triton X-405 and octadecyl acrylate (ODA) yielded excellent results. With this system all of the droplets initially present in the reactor polymerized. This stabilization system was then used in the study of compartmentalization of the monomer droplets in miniemulsion polymerization.

Blends of butyl methacrylate (BMA) and styrene miniemulsions were prepared separately and polymerized together to study mass transfer in this system. It was observed that no matter is exchanged between the different phases. This compartmentalization was also demonstrated and exploited by producing a bimodal molecular weight distributions latex. It was achieved with a semi-continuous process the lower MWD was created by adding a second miniemulsion containing transfer agent.

On-line Reaction Calorimetry. Applications to the monitoring of emulsion polymerization without samples or models of the heat transfer coefficient

S. BenAmor, D. Colombié and T. McKenna
Ind.Eng.Chem.Res.2002,41,4233-4241

A high gain non-linear cascade state estimator is presented in this work, and used to monitor conversion and polymer composition in an emulsion copolymerization process. The advantage of this cascade observer is that it requires neither occasional on-line samples, nor prior knowledge of the dependence of the overall heat transfer coefficient with the solids content of latex. A simple test is used to ensure that the results are robust to process noise and to rapid changes in conditions during the semi-batch phase. Applications of this technique are presented in both laboratory scale and industrial pilot scale reactors.

Polymer composition control in emulsion co- and terpolymerizations

Nida Othman[1], Gilles Févotte[2], Timothy .F. McKenna[1*]
Ind. Eng. Chem. Res., **41**(5), 1261-1275, 2002

A new strategy for the composition control in emulsion copolymerization and terpolymerization processes, based on the use of nonlinear estimation and control techniques is presented in the current work. The strategy uses the estimation of the concentration of monomers in the reactor, and the manipulated variables used for the composition control are the flow rates of the most reactive monomers, calculated in such a way as to account for the reaction rate, thereby allowing us to anticipate changes

in the polymer composition. The controllers are experimentally validated for several composition set-points and systems. It was found that the controllers maintain the composition at the desired value even for monomers with a wide difference in their reactivity ratios.

A new approach to the joined estimation the the heat generated by a semicontinuous emulsion polymerization and the overall heat exchange parameter, UA,

F. B. Freire, T. F. McKenna, S. Othman, R. Giudici
To Appear Brazil J. Chem. Eng.

This work is concerned with the coupled estimation of the heat generated by the reaction (Qr) and the overall heat transfer parameter (UA) during the terpolymerization of styrene, butyl acrylate and methyl methacrylate from temperature measurements and the reactor heat balance. By making specific assumptions about the dynamics of the evolution of UA and Q_R, we propose a cascade of observers to successively estimate these two parameters without the need for additional measurements of on-line samples. One further aspect of our approach is that only the energy balance around the reactor was employed. It means that the flow rate of the cooling jacket fluid was not required.

A contribution to modelling of emulsion polymerisation: A Physical APproach

M. Fortuny, T.F. McKenna
Proceedings (Poster Presentation)
3rd World Congress on Emulsions, Lyon, France, 24-27 September 2002.

The fact that a great deal of work on the modelling of emulsion polymerisations can be found in the open scientific literature attests to the importance of this subject, and to the lack of satisfactory physical descriptions of emulsion polymerisation. Some of the reasons for this, situation are the complexity of the physical systems, and the fact that different systems can behave in very different manners.

We are developing a physically realistic model of the polymerisation of a copolymer of butyl acrylate and methylmethacrylate (BA and MMA) – a product used as a model pressure sensitive adhesive. The product has a bimodal particle size distribution (PSD) to enable us to make a high solid content latex. This poses a number of physical problems since particles of different sizes grow at different rates. The physically realistic models presented here are based on a reasonable understanding of polymerisation kinetics under industrial conditions (obtained experimentally). Particle nucleation can take place by both micellar and homogeneous nucleation. Discrepancies between model predictions and experimental data are used to highlight the weak points in current understanding of system behaviour and to propose new means of describing the polymerising system.

Formulation of High Solid Content Latexes with Low Viscosity

Salima Boutti, Keltoum Ouzineb, Timothy F. McKenna, Christian Graillat,

Oral presentation at
Polymer Colloids: Preparation and Properties of Aqueous Polymer Dispersions,
July 14-19, 2002
Swabian Conference Centre, Kloster Irsee, Germany

For many reasons high solid content latexes (in the current content with solids contents above 65%) are attracting more and more attention. While this is not a high value when we are talking about caulks, sealants or non-polymeric latices, it is very high when the products we are interested are paints or adhesives and must be applied in thin films very quickly. In these cases, we must achieve the double objective of increasing the solid content while maintaining relatively low viscosity for a number of reasons. To make HSC latexes, one needs to create a well-defined bi- or trimodal particle size distrubtions (PSD). By well-defined, we mean that the ratio of small to large particle diameters and the relative quantities of small to large particles are within fixed limits. This requires us to develop specific recipes for polymerisation, and in particular for the the formation of the second, and eventualy third, population of particles.

This paper explored some of the different routes tested by our research group to make HSC latexes. These include the use of both batch and continuous reactors, as well as of classic and miniemulsion polymerisation. With classic emulsion polymerisation, we have achieved solids contents of well over 70% with very low viscosities through an improved formulation of the initiators used at different stages in the polymerisation. It seems that this is the key to producing a well defined PSD – more so even than the choice of surfactant. By correctly formulating the initiator type and addition rate we can eliminate the stabilisation of homogeneously nucleated particles (even in the presence of water soluble monomers such as MMA or acrylic acid). Very promising results have also been obtained using miniemulsion systems in semi-batch and tubular reactors.

A One-Step Process for the Synthesis of High Solids-Content Latexes.

Salima Boutti, Timothy F. McKenna, Christian Graillat
Oral presentation at
Polymer Colloids: Preparation and Properties of Aqueous Polymer Dispersions,
July 14-19, 2002
Swabian Conference Centre, Kloster Irsee, Germany

Emulsion polymerization is generally used to make monomodal Particle Size Distribution (PSD) latexes. However, the choice of a polymodal PSD allows us to obtain high solids-content (> 60%) while maintaining relatively low viscosity. This explains the increasing interest for bi- or trimodal PSD latexes. Some recent studies have underlined important links between PSD, solid content and viscosity. Moreover, numerous ways of synthesis of polymodal PSD latexes have been explored, but most of those processes implies the use of a seed.

The use of a one-step process to synthesize polymodal PSD latexes would enable us to avoid the need to synthesize and store seeds, making the process more effective. Thus, our aim is to synthesize a bimodal PSD latex by a one-step process. Our reasoning is as follows.<P>

For polymodal PSD latex synthesis, the purpose is the PSD control throughout all the process. It is obviously essential to nucleate a first particle population corresponding to some well-defined criteria. This initial population must be concentrated, and the size increased, while control is maintained over secondary nucleation. This had been made possible by controlling radicals flux.

The third stage of the envisaged process is the in-situ nucleation of the second population. Nucleation is a complex phenomenon and the presence of the first population redefines the problem. Thanks to conductivity measurements we acquired a better understanding of molecular dynamic in the medium. Thus, the second population granulometry can be controlled.

Finally, the fourth and last stage of the envisaged process is the relative growth of both populations. For this part of the study several ways can be explored in order to increase the solid content and maintain the defined ratio between each population diameter.

Butyl Acrylate/Methyl Methacrylate Latexes: Adhesive Properties

Keltoum Ouzineb, Renata Jovanović*, Timothy F. McKenna and Marc A. Dubé*
*Univeristy of Ottawa

Submitted to Polymer.

In this study, high solids content butyl acrylate/methyl methacrylate (BA/MMA) latexes of bimodal molecular weight and particle size distribution were prepared by conventional emulsion and miniemulsion polymerization. For one case, a first stage BA/MMA batch emulsion polymerization was conducted and in the second stage, a BA/MMA pre-emulsion was added to generate a second particle population. For another case, the first stage BA/MMA copolymerization was carried out in miniemulsion and a BA/MMA miniemulsion was added at the second stage to generate a bimodal particle size and molecular weight distribution. The final latexes were coated onto a polyethylene terephthalate carrier, dried and their performance as pressure-sensitive adhesives was evaluated. Tack, peel and shear adhesion were investigated. The structure-property relationships between the adhesive properties and the weight-average molecular weight and average particle size were examined. Both latexes showed high tack, moderate peel and low shear adhesion.

Modélisation de Procédés de Synthèse de Latex Multipopulés

Montserrat Fortuny

Ph.D. Thesis, Defended November 21, 2002,

University Claude Bernard Lyon I,

Lyons, France

This work concerns the development of mathematical models that describe the production of polymer latexes with multimodal particle size distributions (PSD), obtained by emulsion polymerisation. These models allow us to better understand how to control the PSD, which in turn allows us to optimise the rheological properties for the final latex, and the production of high solids content latexes with controlled viscosity.

The emulsion polymerisation processes studied in this thesis involved several stages with different experimental conditions. Hence, the understanding of the physical and chemical mechanisms underlying these very different stages is critical for the development of robust mathematical models. First of all, experimental kinetic studies were performed to ensure am adequate description of the butyl acrylate/methyl methacrylate emulsion copolymerisation reactions, and of related phenomena such as secondary particle nucleations and the formation of polymer particles with high molecular weight and high gel contents.

Additional experimental studies were carried out in order to understand some important features of our latexes, such as the properties of mixed surfactant systems, monomer partitioning, and the electrostatic stabilisation of the polymer particles. The description of these phenomena required the use of different experimental techniques, and, in some cases, new ones were developed. Afterwards, mathematical models were derived aiming to describe each phenomenon separately. The, these individual mathematical models were incorporated into a complete mathematical model for the PSD.

The PSD evolution was described through the population balances approach, which involve highly complex integro-differential equations. The model was successfully applied to the description of the particle coagulation provoked by electrolytes, the competitive growth of particles during semibatch operations and particle nucleation during batch reactions. These latter systems are very important to the multimodal latexes production.

EMULSION AND MINIEMULSION POLYMERIZATION : STABILIZATION, TUBULAR REACTOR AND PRACTICAL APPLICATIONS

Keltoum Ouzineb,

Ph.D. Thesis, to be defended February 20, 2003,

University Claude Bernard Lyon I,

Lyons, France

Most of the time, the main processes employed for the production of polymers are evaluated (in an industrial context) in terms of basic economics: volume and cost of production, energy consumption, simplicity of execution. It is clear that these considerations are intimately related to the polymer characteristics and quality. Emulsion polymerization processes are therefore generally adjusted to tailor the properties of the final polymer, which will include the polymer composition, number of particles and particle size distribution, viscosity, molecular weight distribution, solids content, etc. The choice of the recipe, reactor configuration and the process conditions will of course have a great influence on the quality of the final polymer product.

Emulsion polymerization has been widely studied in batch and semi-batch reactors, but to a much lesser extent in continuous stirred tank reactors (CSTRs) and tubular reactors. Economics will favor a continuous process when product volumes are large enough, when product grades differ slightly, or by eliminating batch-to-batch variations. Tubular reactors appear to be an interesting tool for emulsion polymerization for several reasons: (i) the large surface area of the tube is advantageous for exothermic polymerizations, (ii) in laminar or turbulent flow narrow residence time distributions (RTD) are easily obtained, which suggests that narrow particle size distribution could be obtained, (iii) the kinetics can be directly transposed from batch reactors if the RTD is well adjusted, and the mixing sufficient to prevent phase separation. The main obstacle to their use appears to be the fouling or the plugging of the tube.

For the past several years, miniemulsion polymerization had been proposed for many applications, essentially as an alternative to “classic” emulsion polymerization because of the way in which the particles are formed. A non-exhaustive overview of this process is presented in Chapter 1. Most of the studies were dedicated to understanding particle stabilization and formation, as well as to looking at reaction kinetics. Also, given the fact that the droplets are very small (100-300 nanometers), and that particles are formed by mechanically agitating an organic dispersion means that miniemulsions are very interesting in terms of producing hybrid materials such as acrylic resins, and encapsulated pigments or liquids, just to name a couple. The objective in terms of particle formation is to create a dispersion of very small but stable droplets, and to nucleate (i.e. polymerize) all of these bodies. In this sense, we are polymerizing in the monomer droplets and do not have the particle nucleation stage inherent to emulsion polymerization (see also Chapter 1 for more details).

An efficient miniemulsion polymerization (efficient in terms of particle formation) is very useful as it allows us to control the number and size of particles being formed in a manner very different from particles formed by micellar or homogeneous nucleation. In principle, it also offers many of the advantages of emulsion polymerization, including relatively rapid kinetics (with respect to bulk or suspension), high molecular weights, etc. The fact that the droplets are the main locus of polymerization also offer many other advantages, especially in continuous processes like CSTRs (no oscillation of particle number and size at the reactor outlet), and in obtaining high solids contents.

However, it is no small matter to polymerize the entirety of the droplets formed at the outset, and droplet nucleation is greatly influenced by the stabilization system employed to counteract both coalescence and degradation diffusion (also referred to as Ostwald ripening).

The main objectives of the present thesis are therefore to propose practical applications of emulsion and miniemulsion polymerization. We will therefore begin by comparing batch and tubular reactors under similar operating conditions in Chapter II. The experimental conditions in the continuous tubular reactor (solids content, surfactant system…) will be selected from batch runs. We will attempt to clearly identify limitations on the operation of tubular reactors for classical emulsion polymerization, and then in Chapter V, will look at how to overcome these by using miniemulsions.

In chapter III, we will identify a suitable stabilization system for different miniemulsions, and conduct a study that will allow us to better understand droplet formation and stabilization. Different homogenization methods will be examined in Chapter IV to elucidate main parameters influencing droplet formation, and to see if we cannot propose advantageous means of making miniemulsions on an industrial scale. Finally, we will also look at compartmentalization and mass transfer in miniemulsion systems.

Chapter V will deal with different means of using miniemulsions, including making systems with high solids contents, and with complex molecular weight distributions. As mentioned above, we will also look at polymerizing miniemulsions in continuous tubular reactors.

Contribution to Polymer Colloids Group Newsletter

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News on Polymer Colloids in Japan:

The 12th Polymeric Microsphere Symposium was held in Fukui in November 6-8, 2002 with 73 presentations and 230 participants. The preprints, although written in Japanese, is available by direct request to M. Nomura. The titles of the papers presented are shown below, The 13th Polymeric Microsphere Symposium will be held in 2004 in Yonezawa, Yamagata.

Recent Research Activity on Polymer Colloids in Fukui University:

We are interested mainly in the kinetic role of oil-soluble initiator including redox initiator systems in the microemulsion and conventional emulsion polymerizations. The following are recent publications from our group.

(1) Emulsion Copolymerization of Vinylidene Chloride and Methyl Methacrylate. I. Effects of Operating Variables othe Kinetic Behavior, M. Nomura, H. Sakai, Y. Kihara and K. Fujita, *J. Polym. Sci., Part A: Polym. Chem.* **40**, 1275-1284 (2002)

Synopsis: The effects of operating variables on the kinetic behavior of the emulsion copolymerization of vinylidene chloride (VDC) and methyl methacrylate (MMA) were examined at 50°C by using sodium lauryl sulfate as emulsifier and potassium persulfate as initiator, respectively. The number of polymer particles produced increased in proportion to the 1.0 power of the initial emulsifier concentration and to the 0.3 power of the initial initiator concentration and decreased with increasing the content of MMA in the initial monomer charge. The rate of copolymerization was proportional to the 0.4 power of the initial emulsifier concentration and to the 0.5 power of the initial initiator concentration and increased with increasing the content of MMA in the initial monomer charge. The molecular weight of copolymer produced was found to decrease drastically with increasing the content of VDC in the initial monomer charge.

(2) Kinetics and Mechanisms of O/W Microemulsion Polymerization of Styrene
K. Suzuki and M. Nomura, *Macromol. Symp.* 179, 1-12 (2002)

Synopsis: To clarify the kinetics and mechanisms of o/w microemulsion polymerization, the o/w microemulsion polymerizations of styrene were carried out with different kinds and types of initiators and surfactants. The number of polymer particles and the molecular weight of polymer formed were not affected by the kinds and types of initiators and surfactants. The rate of polymerization with different kinds of azo-type oil-soluble initiators with widely different water-solubility was almost the same, but was much lower than that with KPS. A kinetic model proposed by us could mostly explain the kinetic behavior except for the difference in the polymerization rate with KPS and that with oil-soluble initiators.

(3) Continuous Emulsion Polymerization of Vinyl Acetate. I. Operation in a Single Continuous Stirred Tank Reactor using Sodium Lauryl Sulfate as Emulsifier, Mamoru. Nomura, *J. Appl. Polym. Sci.,* **86**, 2748-2754 (2002).

Synopsis: In order to compare to CCTVFR, old data with CSTR were published.

(4) Continuous Emulsion Polymerization of Vinyl Acetate. II. Operation in a Single Couette-Taylor Vortex Flow Reactor using Sodium Lauryl Sulfate as Emulsifier, X. Wei, I. Yokota, M. Nomura, *J. Appl. Polym. Sci.*, **86**, 2755-2762 (2002).

Synopsis: Continuous emulsion polymerizations of vinyl acetate were conducted at 50°C in a single continuous Couette-Taylor vortex flow reactor (CCTVFR) using sodium lauryl sulfate as emulsifier and potassium persulfate as initiator, respectively. It was found that the polymerization can be carried out very smoothly and stably, but the steady-state monomer conversion attained in a CCTVFR is not so high as that in a plug flow reactor (PFR), but only slightly higher than that in a continuous stirred tank reactor (CSTR), even if the Taylor number is adjusted to an optimum value. It was also found that the effects of operating variables such as the emulsifier, initiator and monomer concentrations in the feed and the mean residence time on the kinetic behaviors are almost the same as those observed in a CSTR.

The titles of the 10th Polymeric Microsphere Symposium:

01Particle Nucleation in Emulsion Polymerization of Methyl Methacrylate. S.Kawaguchi, et al. (Ymagat Univ.)
02 Kinetic Behavior of Styrene Emulsion Polymerization Initiated by Redox Initiator Cumene Hydroperoxide and Fe^{2+}., K.Suzuki, et al. (Fukui Univ.)
03 Kinetic Behavior of Methyl Metacrylate Emulsion Polymerization with Mixture of Anionic and Nonionic Surfactants., K.Suzuki,et al. (Fukui Univ.)
04 Emulsion Polymerization of Styrene using Butyl Acrilate-Acrilic Acid Reactive Polymeric Emulsifier, S.Kato, et al. (Fukui National College of Technology)
05 Emulsion Polymerization of Vinyl Acetate Using Hydroxymethyl Cellulose as a Protective Colloid, T.Okaya, et al. (University of Shiga Prefecture)
06 Kinetic Study of Seeded Emulsion Polymerization in the Presence of Poly(styrene/α-methyl styrene/acrylic acid), J.-H. Kim, et al. (Yonsei Univ., Korea)
07 Bimodal Molecular Weight Distribution Formed in Emulsion Polymerization., H.Tobita (Fukui Univ.)
08 Effect of Additives on the Emulsion Polymerization of Vinyl Acetate (VAc) using Poly(vinyl alcohol) as a Protective Colloid., A.Suzuki, et al. (University of Shiga Prefecture)
09 Emulsion polymerization of AN using PVA as a protective colloid., Y.Yagi, et al., Asahi Kasei Co.
10 Study on the Initial Stage of Emulsion Polymerization of Styrene using Poly(vinyl alcohol) as a Protective Colloid, A.Suzuki, et al. (University of Shiga Prefecture)
11 Study on the Emulsion Polymerization of Styrene using Poly(vinyl alcohol) as a Protective Colloid., T.Masuda,et al. (University of Shiga Prefecture)
12 Emulsion Polymerization of Styrene Stabilized by Poly(vinyl alcohol)., M.Nomura,et al. (Fukui Univ.)
13 Aqueous Solution Behaviors of Amphiphilic Block Polyelectrolyte and Application to Emulsion-Dispersion Polymerization. A.Nishimura, et al., (Yamagata Univ.)
14 Kinetic Behavior of Polymerizable Emulsifiers in the Emulsion Copolymerization with Styrene., K.Kusunoki, et al. (Tokyo University of Agriculture and Technology)
15 Chain Length Enlargement in Emulsion Polymerization of Allyl Monomers., T.Matsuura, et al. (Kansai Univ.)
16 Characterization of Crosslinked Polymer Microspheres Obtained by Emulsion Crosslinking Allyl Methacrylate/Alkyl Methacrylate Copolymerizations., H.Hayashi, et al. (Kansai Univ.)
17 In-Situ Kinetic Pursuit of Emulsion Crosslinking Polymerization of Allyl Methacrylate by Means of ReactIR., Y.Yuki, et al. (Kansai Univ.)
18 Dispersion Polymerization of Vinyl Acetate in Mixture of Water and Ethanol., T.Okaya, et al., (University of Shiga Prefecture)
19 Preparation of Polystyrene Microspheres with Anionic Poly(amino acid)., H.Yoshizawa, et al., (Okayama Univ.)
20 Synthesis of PEO Macromonomers by Initiation Method and Their Application to Emulsion and Dispersion Polymerizations., K.Ito, et al., Toyohashi (University of Technology)
21 Dispersion Polymerization Using Polyamic Acid as a Stabilizer., S.Watanabe, et al. (Kitami Institute of Technology)
22 Dispersion Polymerization Using Macromonomer Having Carboxyl Groups Synthesized by High Temperature polymerization., H.Matsuzaki, et al. (Toagosei Co.)
23 Synthesis of Monodisperse Polystyrene Particles having more than 5μm Diameter by Dispersion Polymerization using Chain Transfer Polymer as a Steric Stabilizer., N.Yabuuchi, et al., (Nippon Paint Co., & Kobe Univ.)
24 Microencapsulation of Dye by Mini-Emulsion polymerization., S.Kobayashi, et al. (Niigata Univ.)
25 Preparation of Microcapsules from(W/O)/W Emulsion by Glass Membrane Emulsification Technique and Suspension Polymerization., Y. Uno, e t al, (Tokyo University of Agriculture and Technology)

26 Preparation of Hydrophilic Core/Hydrophobic Shell Composite Particles via W/O/W Multiple Phase Emulsion by using SPG Membrane., H.Sone, et al., (Tokyo Univ. of Agriculture and Technology)

27 Preparation of Hydrophilic Microspheres from W/O Emulsion by PTFE Membrane Emulsification,. K.Naganuma, et al. (Tokyo University of Agriculture and Technology)

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<Publications 2002-2003>

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<Recently works>

1. **Production of hollow polymer particles by suspension polymerizations for ethylene glycol dimethacrylate/toluene droplets dissolving styrene-methyl methacrylate copolymers**
   M. Okubo, Y. Konishi, T. Inohara, H. Minami, *J. Appl. Polym. Sci.*, **86** (5), 1087-1091 (2002)
   Suspension polymerizations for ethylene glycol dimethacrylate (EGDM)/toluene droplets dissolving styrene-methyl methacrylate copolymers with different compositions were carried out. Hollow particles were obtained independent of the copolymer composition. In suspension copolymerizations for EGDM/divinyl benzene/toluene droplets dissolving poly(methyl methacrylate), hollow particles were produced at high EGDM content, but not at low EGDM content. Preferential adsorption of the polymer formed by the suspension polymerizations at the interfaces of the droplets over the (co)polymers preliminarily dissolved therein was one of key factors for the formation of the hollow structure.

2. **Estimation of adsorption state of nonionic emulsifier molecules onto styrene-methacrylic acid copolymer particles by *in situ* ^{1}H NMR measurement**
   M. Okubo, T. Suzuki, R. Shinohara, N. Fukami, *Colloid Polym. Sci.,* **280** (11), 1053-1056 (2002)
   Adsorption behavior of polyoxyethylene nonylphenylether nonionic emulsifier molecules onto polystyrene (PS) and styrene-methacrylic acid copolymer {P(S-MAA)} particles dispersed in D_2O were evaluated by in situ ^{1}H NMR measurement at room temperature. The resonance due to the protons of the emulsifier molecules was only observed. Normalized NMR integrals of the resonance due to the protons of hydrophobic groups (nonyl and phenyl groups) and hydrophilic group (polyoxyethylene chain) at a certain concentration of the emulsifier decreased with an increase in the total surface area (At) of the PS particles dispersed in the system. The decrease for the hydrophobic groups was much larger than that for the hydrophilic groups. In the dispersion system of P(S-MAA) particles, ionized carboxyl groups at the particle surface were decreased the amount of the emulsifier adsorbed.

3. **Production of polydivinylbiphenyl particles by precipitation polymerization in supercritical carbon dioxide**
   M. Okubo, S. Fujii, H. Maenaka, H. Minami, *Colloid Polym. Sci.,* **280** (12), 1084-1090 (2002)
   Polydivinylbiphenyl particles were produced by precipitation polymerization of

divinylbiphenyl without any stabilizer in supercritical carbon dioxide as polymerization medium at ca. 30 MPa for 24 h at 65°C at different initiator concentration (0.5-58.1 mmol/L). The conversions in all polymerization systems were relatively high, and the increase in the initiator concentration led to the increases in the degree of coagulation and the amount of low molecular weight byproducts and to the decrease in the amount of vinyl groups in the particle.

4. **Preparation of micron-sized, monodisperse poly(methyl methacrylate)/polystyrene composite particles having a large number of dents on their surfaces by seeded dispersion polymerization in the presence of decalin**
   M. Okubo, R. Takekoh, A. Suzuki, *Colloid Polym. Sci.,* **280** (11), 1057-1061 (2002)
   Seeded dispersion polymerization of styrene with 1.77-µm-sized, monodisperse poly(methyl methacrylate) seed particles was carried out in a methanol/water medium (8/2, w/w) in the presence of decalin droplets. The monodisperse poly(methyl methacrylate)/polystyrene composite particles produced had a large number of dents on their surfaces. The effects of the amount of decalin in the polymerization system on the number, the diameter, and the depth of the dents on the surface of the composite particles were clarified.

5. Production of polystyrene/poly(ethylene glycol dimethacrylate) composite particles encapsulating hinokitiol, M. Okubo, H. Minami, Y. Jing, *J. Appl. Polym. Sci.*, *in press*

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7. Preparation of micron-sized, monodisperse, magnetic polymer particles, M. Okubo, H. Minami, T. Komura, *J. Appl. Polym. Sci.*, *in press*

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11. Estimation of heterogeneous surface structure of blend polymer film consisting of hydrophobic and hydrophilic polymers in water by atomic force microscope, M. Okubo, T. Suzuki, Y. Fukuhara, *Progr. Colloid Polym. Sci.*, *in press*

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13. Production of micron-sized, monodisperse polysytyrene/poly(n-butyl methacrylate) composite particles having "hamburger-like" morphology by seeded polymerization, M. Okubo, H. Yonehara, T. Kurino, *Progr. Colloid Polym. Sci.*, *in press*

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18. Estimation of heterogeneous surface structure of submicron-sized, composite polymer particles consisting of hydrophobic and hydrophilic components by atomic force microscopy, M. Okubo, T. Suzuki, Y. Fukuhara, *Colloid Polym. Sci.*, *in press*

Contribution to the IPCG Newsletter January 31, 2003

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Main activities of our group are on colloidal crystals, their morphology, crystal structure, crystal growth kinetics and effect of external fields such as a gravitational field, an electric field, and a centrifugal field. Microgravity effect on colloidal dispersions has been studied systematically using dropping, aircraft and rocket techniques. Dissipative structures of colloidal dispersions, alternate multi-layered complexation of colloidal spheres with macroions, and seed polymerization of TEOS are also included in our recent research fields.

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Colloidal Crystals and Colloidal Liquids

(1)"**Rheological Properties of Sodium Montmorillonite in Exhaustively Deionized Dispersions and in the Presence of Sodium Chloride**", H. Kimura and T. Okubo, *Colloid Polymer Sci.*, **280**, 579-583 (2002).

(2)"**Kinetics Analysis of Colloidal Crystallization of Silica Spheres Modified with Polymers on Their Surfaces in Acetonitrile**", T. Okubo, H. Ishiki, H. Kimura, M. Chiyoda and K. Yoshinaga, *Colloid Polymer Sci.*, **280**, 290-295 (2002).

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(16)”**Dissipative Structures Formed in the Course of Drying the Colloidal Crystals of Silica Spheres on a Cover Glass**”, T. Okubo, S. Okuda and H. Kimura, *Colloid Polymer Sci.*, **280**, 454-460 (2002).

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Colloid-Macroion Complexation

(18)”**Synchronous Multi-layered Adsorption of Macrocations and Macroanions on Colloidal Spheres. Influence of Foreign Salt and Basicity or Acidity of the Macroions**”, T. Okubo and M. Suda, *Colloid Polymer Sci.*, **280**, 533-538 (2002).

(19)”**Multi-layered Adsorption of Macrocations and Macroanions on Colloidal Spheres as Studied by the Dynamic Light-scattering Measurements**”, T. Okubo and M. Suda, *Colloid Polymer Sci.*, in press.

Seed Polymerization

(20)”**Seed Polymerization of Tetraethylorthosilicate in the Presence of Anionic and Cationic Polystyrene Colloidal Spheres**”, *Colloid Polymer Sci.*, in press.

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Contribution to Polymer Colloids Groups Newsletter

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Functionalized Thermally-sensitive Polymer Latex Particles: Useful Tools for Diagnostics

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Abstract: This paper aims at reviewing recent works dedicated in this lab to the elaboration and applications in the biomedical domain of hydrophilic stimuli-responsive latex particles based on the use of various polyalkyl(meth)acrylamides together with functional monomers bearing bioreactive groups. At first, a brief description is provided on the synthesis of such particles, differing in their surface and internal morphology, through radical-initiated polymerization processes in heterogeneous media. Then, it is showed that several colloidal properties of these particles drastically changed, not only as a function of temperature, but also versus pH and salinity. The good knowledge of these characteristics is a prerequisite for an optimal control of the immobilization of various biologically-active macromolecules, mostly by covalent binding. Finally, some applications of these particles are described, especially for improving the sensitivity in genic diagnostic or for the separation and concentration of biomolecules. (*Journal of Dispersion Science & Technology, special issue concerning Particles 2002 congress in Orlando, april 2001).*

Preparation and characterization of narrow sized (o/w) magnetic emulsion

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Abstract: The preparation of well-defined (o/w) magnetic emulsions from an organic ferrofluid is reported. The ferrofluid synthesis is first described and a complete characterization is achieved by using numerous techniques. The ferrofluid is found to be composed of superparamagnetic maghemite nanoparticles, with a diameter below 10 nm, stabilized in octane by a surrounding oleic acid layer. This magnetic fluid is then emulsified in aqueous media in order to obtain stable ferrofluid droplets. The use of a couette mixer and a size sorting step under magnetic field allowed to produce magnetic emulsion with a narrow size distribution. Morphology and chemical composition of the magnetic emulsion are investigated. Magnetic properties of both ferrofluid and magnetic emulsion are also compared and discussed. In particular, it is showed that the superparamagnetic behavior is still observed after the emulsification process. (*Journal of Magnetism and Magnetic Materials, 250, 2002, 302-312*)

Thermally Sensitive, Hydrophilic, and Reactive Latex Particles as Versatile Supports for Biomolecules Immobilization

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Abstract: This article is a short review of recent laboratory work devoted to stimuli-responsive polyalkyl(meth)acrylamide based hydrophilic colloidal particles and their potential applications in biomedical diagnostic and molecular biology. After a brief introduction and presentation of the main criteria required to design suitable particles for biological purposes, the first part describes shortly several aspects related to synthesizing different types of stimuli-responsive latex particles by radical polymerization of alkyl(meth)acrylamide derivatives. Secondly, the colloidal properties of these colloids are presented. The last part briefly mentions several potential applications of these particles in the biological field. (*Progress in Colloid & Polymer Science, in press*)

Biorelevant Latexes and Microgels for the Interaction with Nucleic acids

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Abstract: This chapter is a review of recent work devoted to polymer colloids in nucleic acids domain and principally in biomedical diagnostic, in which latex particles are used as carrier. After a brief introduction concerning the applications of latex particles in the biomedical field, the first part describes the routes leading to the elaboration of reactive latexes using radical-initiated polymerization in heterogeneous media. Secondly, the adsorption and the chemical grafting of nucleic acids are presented as a function of pH, ionic strength, surface charge density and cationic and anionic nature of particles surface. The good knowledge of the colloidal properties of latex latexes particles permits the well control of the immobilization process (adsorption and covalent binding) of functionalized single stranded DNA fragments (oligonucleotides). Finally, the last part briefly describes some fine applications based on latex-oligonucleotides in the specific capture of target DNA or RND and also on colloidal particles for separation and concentration nucleic acid molecules. (*Current Chemistry, in press*)

Adsorption/Desorption Behavior and Covalent Grafting of an Antibody onto Cationic Amino-Functionalized Poly(Styrene-N-Isopropylacrylamide) Core-Shell Latex Particles

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Abstract: The adsorption of anti-□-Feto protein onto polystyrene-core-poly(N-isopropylacylamide)-shell particles was investigated as a function of temperature, pH and salinity. The influence of various physico-chemical parameters onto the colloidal and surface properties of such stimuli-responsive particles was first studied. Then, the adsorption of anti-□-Feto protein antibody was investigated in order to point out the driving forces involved in the adsorption process. The effects of salinity, pH and temperature demonstrated that adsorption was mainly governed by electrostatic interactions. In addition, the adsorption isotherms were analyzed on the basis of a Langmuir model leading to the determination of affinity constants. Finally, based on this adsorption study, various covalent coupling methodologies of the antibody were compared by using two different copolymers as a reactive spacer arm. The amount of chemically grafted antibody was obtained after performing the desorption step (by lowering the temperature, changing the pH or raising ionic strength). The grafted quantity of antibody was found to be related to the adsorbed amount as a function of pH and ionic strength. (Colloids & surfaces, B: Biointerfaces, in press).

Surface functionalization of oil-in-water nanoemulsion with a reactive copolymer: colloidal characterization and peptide covalent coupling

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Abstract: Cationic emulsion droplets were prepared using medium chain triglyceride (MCT), phosphatidylcholine / phosphatidylethanolamine phospholipid mixtures (Lipid E-80), pluronic F68 and poly[N-acryloylmorpholine-co-N-acryloxysuccinimide] (poly[NAM/NAS]) copolymer functionalized with N-(acetyl)spermine and decylamine through chemical modification of succinimide groups. In addition, 2-(2-pyridyldithio)ethylamine was grafted onto copolymer in order to target the covalent binding of a peptide model. At first, the obtained emulsion was colloidally characterized by investigating the particle size and size distribution. A relatively narrow droplet size distribution was revealed by quasi-elastic light scattering analysis. Electrokinetic study and colloidal stability were performed as a function of both pH and salinity, revealing the marginal effect of the pluronic used as stabilizing agent. Secondly, immobilization isotherm on droplet surface of Influenza hemagglutinin HA-2 derived peptide was carried out and highlighted the contribution of covalent binding to the fixation process. (*Collois & Surfaces, B: Biointerfaces, in press*)

Polymer mediated peptide immobilization onto amino-containing N-isopropylacrylamide-styrene core-shell particles

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Abstract: Monodisperse cationic core-shell latex particles have been prepared using a shot polymerization process, with N-(3-aminopropyl)-methacrylamide) hydrochloride (APMH) as the functional monomer. The final latexes were characterized with respect to final polymerization conversion, water soluble polymer formation, particle size and size distribution, surface charge density and electrokinetic properties. Then, the covalent grafting of maleic anhydride-alt-methyl vinyl ether (MAMVE) copolymer onto aminated latex particles was investigated. The most efficient conditions to obtain derivatized particles with no alteration of the colloidal stability were to control both polymer amount/latex particles concentration ratio and the mixing methodology of both species. The charge inversion of the hydrolyzed MAMVE functionalized particles was evidenced by measuring the electrophoretic mobility as a function of pH. Finally, the covalent binding approach was implemented with peptide-MAMVE conjugates, confirming the great potential of this promising methodology for elaborating reactive latex particles bearing peptides. (*Colloid Polymer Science, in press*)

Surface functionalization of poly(D,L-lactic acid) nanoparticles with poly(ethylenimine)-Interactions with plasmid DNA

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Abstract: The layer-by-layer approach was used for the elaboration of nanosized DNA carriers. Poly (D, L lactic acid) (PLA) particles obtained by the emulsification-diffusion process were surface modified by electrostatic interactions with cationic poly(ethylenimine) (PEI). The charge inversion was evidenced by zeta-potential measurements and the adsorption isotherms of PEI were established. The mean diameter of the cationized particles were measured by Quasi Elastic Light Scattering (QELS) and visualized by Scanning Electron Microscopy (SEM). No flocculation was observed so long as the PEI amount in the adsorption medium was close the surface saturation. The amount of immobilized PEI was affected by the ionic strength of the medium. In the absence of salt, lower loading levels were achieved and the modified colloids displayed a quasi-neutral zeta-potential, due to the charge-to-charge neutralization. Hence, a flat conformation of the polymer was deduced. When salt was added to the adsorption medium, higher amounts of polymer were immobilized at the

surface of the PLA particles. Moreover, the colloids were highly positively charged (+ 20-30 mV), which suggested a loops and tails conformation of the PEI at the inteface. Onto the cationized PLA particles, a model plasmid was adsorbed. The two main parameters controlling this step were the pH of the adsorption medium and the interfacial conformation of the polycation. With a decrease in pH, resulting in the reduction of the surface potential of the particles, the DNA was less efficiently attracted by the colloidal carrier. Hence, lower saturation levels were observed.When the PEI was adsorbed flat at the interface, low amounts of plasmid were adsorbed and a poor compaction of the DNA molecules was observed by the Ethidium Bromide displacement method. With the highly positively charged particles obtained by adsorption of PEI in thepresence of salt, the amounts of immobilized DNA were higher than in the previous conditions and, moreover, the compaction of the plasmid on forming polyelectrolyte complexes with the particles was as efficient as with the free PEI in solution. *(in press Colloids and Surfaces: Part A: Physicochemical and Engineering aspects)*

Preparation of Magnetic Polymeric Particles via Inverse Microemulsion Polymerization Process

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Abstract: Hydrophilic submicron magnetic polymer particles were prepared using inverse microemulsion polymerization process. Firstly, the magnetic properties of iron oxide nanoparticles elaborated were examined using X-ray diffraction and magnetization analysis of the chemical structure and the magnetic properties respectively. The results obtained using stoechiometric precipitation of $FeCl_2$ and $FeCl_3$ revealed the magnetite iron oxide properties. Secondly, various magnetic latexes were prepared by investigating the effect of surfactant (AOT) concentration, the amount of cross-linker (MBA), the initiator nature and the microemulsion elaboration methodology. The colloidal characterization of the final magnetic latexes revealed to be submicronic in size, spherical in morphology, containing 5 to 23 wt% iron oxide amount and superparamagnetic in character. (*Journal of Magnetism and Magnetic Materials, in press*)

Preparation of low size monodisperse charged poly(methyl methacrylate) latexes

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Narrowly size distributed poly (methyl methacrylate) (PMMA) latexes with diameters between 80-120 nm and bearing carboxylic groups were prepared via emulsion polymerization using 4,4'-azobis(4-cyanopentanoic) acid (ACPA) as initiator and sodium dodecyl sulphate (SDS) as surfactant. Polymerization conversions and kinetics were followed by gravimetry. All final latexes were fully characterized with respect to particle size and particle size distribution as well as electrophoretic mobility behaviour. The influence of SDS concentration on the production of low size particles was clearly evidenced *(in press, Progress in Colloid Polymer Science)*

THESIS:

Thomas Trimaille: Elaboration of colloids functionalized by reactive polymers: New potential vectors for nucleic acids (UCB Lyon, December 2001)

Franck Montagne: Preparation and characterization of functionalized magnetic latexes by polymerization of ferrofluid emulsions - Surface forces between oligonucleotides-particles conjugates (UCB Lyon, December 2002)

Arnaud Favier: Synthesis of architectured copolymers controlled by RAFT process for applications in biological diagnostic and gene transfer (UCB Lyon, December 2002)

REVIEW

ENCYCLOPEDIA OF NANOSCIENCE AND NANOTECHNOLOGY

(www.aspbs.com/enn)

Organic–Inorganic Nanocomposite Colloids

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Organic/inorganic (O/I) colloids with diameters ranging from ten nanometers up to several hundred nanometers are important class of nanocomposite materials with potential applications in a variety of domains ranging from the encapsulation and controlled release of active substances (drugs, dyes) to their utilization as fillers for the paint and coating industries. Owing to their major technological interest, much efforts have been done over the last two decades to develop processing techniques based on either physicochemical routes or polymerization methods. Details of preparation of organic/inorganic colloids with core-shell, multinuclear, raspberry and hairy-like morphologies are reported and discussed in this article. The physicochemical route mainly involves adsorption of preformed macromolecules and/or nanoparticles onto colloidal templates, whereas in the chemical route, the mineral and organic phases are generated in-situ onto latex seeds or inorganic particles, respectively. The simultaneous reaction of organic and inorganic moities to produce single-phase hybrid nanoparticles will also be considered. We present in this chapter a general overview of the different techniques and briefly report on the potentials of organic/inorganic colloids in various fields of material science including the paint industry and the medical field.

Keywords : Organic, Inorganic, Colloids, Hybrid, Latexes

ARTICLES

Pigment Encapsulation by Emulsion Polymerization, Redispersible in Water

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ABSTRACT: Emulsion polymerization was carried out in the presence of inorganic pigments such as TiO_2, black Fe_xO_y, yellow Fe_xO_y, and red Fe_xO_y, and NP_{30} as surfactant, and water soluble azo compounds or KPS as initiator. Monomers with specific hydrogen bonding interaction must be used in the initial steps of polymerization, methylmethacrylate and vinyl acetate being the most convenient. Then a semi continuous feed of a mixture of monomers was carried out in starved conditions. In order to make the covered pigments water-redispersible, a mixture of hydrophobic and hydrophilic monomers should be chosen with proper pH conditions. The amount of surfactant has to be chosen so that no agglomeration of the covered pigments take place. The covered pigments were dried upon lyophylisation, then formulation of powder paints was carried out using commercial powder binders and other additives. Good properties of the paints, such as brightness were obtained in that way.

Macromol. Symp. 2002, *187*, 651-661.

Latex Particles Bearing Hydrophilic Grafted Hairs with Controlled Chain Length and Functionality Synthesized by RAFT

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Robert G. Gilbert, *Key Centre for Polymer Colloids – Chemistry School F11, University of Sydney NSW 2006, Australia*

Abstract: Controlled radical polymerization of the bi-substituted acrylamide derivative N-acryloylmorpholine (NAM) has the potential to yield telechelic polymers, one end of which can subsequently be grafted to latex particles using a "grafting onto" strategy. The controlled polymerization of NAM using reversible addition-fragmentation chain transfer (RAFT) was performed using two new chain transfer agents S=C(Z)–SR bearing the same functional propanoic acid group (R) and two different Z groups, benzyl (CTA 1) and phenyl (CTA 2). The structure of the RAFT agents used (propionic acid R group) was designed such that the resulting polyNAM chains could be able to react with the surface of amino-functionalized particles. RAFT polymerization of NAM mediated by CTA 1 was very fast (>80% conversion in less than half an hour at 65°C). The linear evolution of $\overline{M}_n$ and the low polydispersity indices ($\overline{M}_w/\overline{M}_n < 1.2$) were in accord with the expected characteristics of a controlled polymerization. CTA 2 leads to broader $\overline{M}_w/\overline{M}_n$s (< 1.4). The resulting CTA-capped polymers were further used to yield an amphiphilic polyNAM-block-polystyrene. These □.□-functionalized polyNAM chains were characterized by ^1H NMR and MALDI-ToF mass spectrometry. Amino-functionalized particles were obtained by emulsion free radical polymerization of styrene with an hydrophilic functional comonomer (aminoethyl methacrylate hydrochloride) and grafting reactions between -NH_2 bearing polystyrene particles and polyNAM chains were performed. Well-controlled hairy particles were obtained and characterized by SEC chromatography of the resulting dry extract or by ^1H NMR analyses performed either on the resulting dry extract or directly on the latex itself.

D'Agosto (*), F., Hughes, R., Charreyre, M.-T., Pichot, C., and Gilbert, R.G., *Macromolecules*, **2003**, 36, in press.
D'Agosto, F., Charreyre, M.-T., Pichot, C., and Gilbert, R.G., *J. Polym. Sci.* **2003**, in press.

(*) Franck D'Agosto did his phD in Dr. C. Pichot's group (UMR CNRS-bioMérieux, Lyon France, 1997/2000) under the supervision of Dr. M.T. Charreyre. His research work was devoted to the synthesis of multifunctional polymers with controlled architectures for the binding of biological molecules. He then joined Prof. R. Gilbert's group (Key Center for Polymer Colloids- University of Sydney-Australia (2001/2002) to develop the synthesis of latex particles bearing hydrophilic grafted hairs with controlled chain length and functionality synthesized by RAFT. He is now further investigating new strategies in the same area in R. Spitz's group (LCPP, CPE/CNRS, Villeurbanne, France) as a CNRS research scientist since april 2002.

Contribution to the International Polymer Colloids Group Newsletter

Gérard RIESS

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The review article "Micellization of block copolymers" submitted to Progress in Polymer Science has been accepted by the Editor.

Another feature article "Emulsion and dispersion polymerization in the presence of block copolymers" will be submitted shortly to Macromol. Rapid Comm.

The PhD thesis "Synthesis and characterization of acrylic latexes prepared with PMMA-PEO diblock copolymers" was submitted by Helene GRAFTIEAUX-BLAISE on December 18th 2002.

The paper "Industrial application of disinfectant containing non-aqueous emulsions stabilized by block copolymers" by G. RIESS, A. CHEYMOL, P. HOERNER, R. KRIKORIAN was presented at the 3rd World Congress on Emulsions (Sept. 24-27, 2002) Lyon. Manuscript reference 1-A-137.

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On the measurement of ``tack" for adhesives [submitted to *Physics of Fluids*]

One of the tests for determining the bond strength of adhesives involves measuring the force or the work required to pull apart two surfaces separated by a thin film of adhesive. The pull-off force is measured via the bending of a cantilever that connects one of the surfaces to a motor controlled vertical traverse. Although such tests are routinely performed, little attention has been paid to the understanding of force measurements and their relation to the dynamics of the instrument. Specifically, the measured force versus gap profile for the pull-off process is different from that measured when the same adhesive is compressed between two approaching surfaces. Through experiments on Newtonian liquids and a simple analysis involving lubrication analysis of thin liquid films, we show that the hysteresis in measurements results from a combination of an instrument-related instability and the nucleation and collapse of cavitation bubbles in the flow field.

Measuring the ``tack" of waterborne adhesives
[to be submitted to *Journal of Rheology*]

Recent ``tack" experiments on Newtonian liquids have shown that the force versus gap measurements obtained by pulling apart two surfaces separated by a thin liquid film results from a complex and dynamic balance between the viscous force resisting the separation and the spring force exerted by the compliant load cell of the instrument\cite{paper-1}. Here, we present similar experiments with waterborne adhesives that are colloidal dispersions of soft polymer spheres dispersed in water. By employing a simple power-law to describe the complex rheology of the waterborne adhesives and a lubrication approximation for the viscous force, we predict pull-off forces in close agreement with those observed experimentally. However, experiments with high particle concentration adhesive and/or large separation rates cause cavitation in the gap, resulting in forces that are lower than predicted. Finally, a simple analysis for adhesives of two different rheologies shows that the tack test may result in contradictory conclusions, since the forces are sensitive to small variations in the instrument settings.

Contribution to IPCG Newsletter
Stan Slomkowski, Center of Molecular and Macromolecular Studies, Lodz, Poland

Recently published papers

1. A.Azioune, M.M.Chehimi, B.Miksa, T.Basinska, S.Slomkowski
   The hydrophobic protein-polypyrrole interactions: the role of van der Waals and Lewis acid-base forces as determined by contact angle measurements

   Langmuir, 18, 1150-1156 (2002)

2. S.Slomkowski, T.Basinska, B.Miksa
   New types of microspheres and microsphere related materials for medical diagnostics
   Polym. Adv. Technologies, 13, 905-918 (2002)

3. Anamika Gambhir, Arun Kumar, Bansi D. Malhotra, Beata Miksa, Stanislaw Slomkowski
   Covalent immobilization of urease to polypyrrole microspheres for application to urea biosensor

   E-Polymers, 052, 1-9 (2002)

Papers in press

Immobilization of urease (Urs) onto poly(styrene/acrolein) microspheres. Comparison of activities of immobilized and free urease from jack beans (*Canavalia ensiformis*) and from pigeonpea (*Cajanus cajan*)

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Journal of Bioactive and Compatible Polymers, in press

Abstract

Poly(styrene/acrolein) microspherers P(S/A) were synthesized by emulsifier-free emulsion-dispersion radical copolymerization of styrene and acrolein. Particles with number average diameter $\overline{D}_n = 373$ nm, narrow diameter distribution ($\overline{D}_w / \overline{D}_n = 1.008$) and surface concentration of aldehyde groups from polyacrolein units equal $2.51 \cdot 10^{-6}$ mol/m^2 were obtained. Ureases from jack beans (Urs-JB) and from pigeonpea (Urs-PP) were immobilized onto these microspheres. Activity of free and immobilized urease was determined using a standard phenol method. Surface concentration of attached enzymes

was varied in the range from 0.06 to 1.6 mg/m^2. Specific activity of Urs-JB in solution was 1.9 times higher that that of Urs-PP, however, upon immobilization of enzymes onto P(S/A) microspheres the reverse was true. Due to very high denaturation activity of immobilized Urs-JB was 10 times lower than in solution. In the case of Urs-PP denaturation of the enzyme upon immobilization was much lower and possibly due to cooperative effect resulting from local high concentration of immobilized enzyme its specific activity was from 3 to 9 times higher that that of immobilized Urs-JB.

Structure and properties of surface layer of poly(styrene/α-*t*-butoxy-ω-polyglycidol) microspheres

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J.Polym.Sci., Polym.Chem. (A), in press

Composition and properties of surface layer of poly(styrene/α-*t*-butoxy-ω-polyglycidol) (poly(styrene/VB-polyGL)) microspheres synthesized by radical copolymerization of styrene and α-t-butoxy-ω-vinylbenzyl-polyglycidol macromonomers (VB-polyGL) (with $\overline{M}_n$ = 950 and 2700) were investigated by X-ray photoelectron spectroscopy (XPS), ^{13}C NMR and adsorption of human serum albumin and gamma globulins. Number average diameter of synthesized microspheres was 220 nm. Their surface layers were rich in polyglycidol with polyglycidol to polystyrene unit ratio 0.443 (VB-polyGL with $\overline{M}_n$ = 950) and 0.427 (VB-polyGL with $\overline{M}_n$ = 2700). In suspension of poly(styrene/VB-polyGL) particles in D_2O polymer chains in the polyglycidol rich surface layer were highly mobile allowing registration of the polyglycidol ^{13}C NMR spectra by using standard procedures for polymer solutions. In these spectra signals of the relatively immobile polystyrene segments were absent. Relaxation times (T_1) measured for polyglycidol in microsphere surface layer and for VB-polyGL macromonomers in solution were very close indicating similar degree of motion in bound (constituting particle surface layer) and in free (in solution) polyglycidol macromolecules. Studies of protein adsorption revealed that hydrophilic polyglycidol layer was a protein repellent. It was found that longer polyglycidol chains in particle surface layer were more mobile (higher values of T_1) and provided better protection against protein adsorption.

Synthesis, characterisation and biomedical applications of functionnalized polypyrrole-coated polystyrene latex particles

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Macromol. Symp., in press

N-hydroxysuccinimide-functionalised polypyrrole (PPy-NHS) coated onto polystyrene (PS) latex particles were prepared by the in-situ copolymerisation of pyrrole 1 and the active ester-functionalized pyrrole 3 (pyrrole-NHS) in the presence of bare PS substrates. The initial comonomer concentration was 25/75 and 50/50 for pyrrole and pyrrole-NHS. PS particles were prepared by two methods: emulsion polymerisation leading to particle size in the 450-500 nm range, and by dispersion polymerisation using poly(N-vinylpyrrolidone) (PNVP) as a steric stabiliser. The polypyrrole-coated PS particles (PS-PPy) were characterised in terms of particle size, surface charge, and surface chemical composition. For the "emulsion" PS coated with polypyrrole, the particles were evaluated as bioadsorbents of human serum albumin (HSA). It is believed that the proteins attach by covalent bonds at the surface of NHS-functionalised PPy-PS particles. It is shown that the maximum adsoroption levels off at 0.2 mg/m^2 in the case of the 50/50 initial concentration but only to 0.02 mg/m^2 in the case of the 25/75 ratio, an indication that a higher concentration of surface reactive groups decreases the amount of covalently attached HSA at the surface of polypyrrole particles.

Report from the Institute of Polymeric Materials, University of Pardubice

Reporter: Jaromir Snuparek

Activity of the group has been focused mainly on synthesis of binders for water-borne paints by emulsion polymerization. Acrylic monomers have been investigated predominantly. The investigation is focused on preparation of copolymers containing higher contents of functional comonomers as AA, MAA, HEMA, AAm, MAAm, on copolymerization of monomers with different polarity in semi-continuous process as well as on the particle growth. Structured core-shell particles with different degree of core and/or shell crosslinking and copolymer composition have been syntesized. Film-formation properties of binders, properties of cured films 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. The rheological behaviour of highly carboxylated copolymers and interaction of associative thickeners with different copolymer particles has been studied with support by Grant Agency of the Czech Republic and in collaboration with Institute of Macromolecular Chemistry CAS Prague.

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

Butyl Acrylate/Styrene/Methacrylamide Copolymer Latices - copolymerization, particle formation, properties.
(M. Kaska - finished 2002)

Binder – Pigment Interaction in Binders Based on Alkali-swellable Structured Particles.
(B. Kadrnka)

Recent papers

Horský J., Quadrat O., Porsch B., Mrkvičková L., Šňupárek J.:
Effect of Alkalinization of Carboxylated Latices Prepared with Various Amount of a Non-ionogenic Hydrophilic Comonomer 2-Hydroxyethyl Methacrylate.
Colloids Surf. A 180, 75 – 84 (2001).
ISSN 0927-7757.

Benda D., Šňupárek J., Čermák V.:
Oxygen Inhibition and the Influence of pH on the Inverse Emulsion Polymerization of the Acrylic Monomers.
Eur. Polym. J. 37, 1247 – 1253 (2001).
ISSN 0014-3057.

Quadrat O., Horský J., Mrkvičková L., Mikešová J., Šňupárek J.:
Thickening of Butyl Acrylate/Styrene/2-Hydroxyethyl Methacrylate/Acrylic Acid Latices with an HEUR Associative Thickener.
Progr. Org. Coat. 42, 110 – 115 (2001).
ISSN 0300-9440.

Socha F., Dobáš I., Šňupárek J.:
Cyclic Acetals: Synthesis and Polymerization.
J. Appl. Polym. Sci. 81, 2875 – 2880 (2001).
ISSN 0021-8995.

Quadrat O., Horský J., Šňupárek J., Baghaffar G.:
Thickening of Butyl Acrylate/Styrene/2-Hydroxyethyl Methacrylate/Acrylic Acid Latices with Crosslinked Ethyl Acrylate/Methacrylic Acid Copolymer.
Progr. Org. Coat. 42, 188 - 193 (2001).
ISSN 0300-9440.

Šňupárek J., Quadrat O., Horský J., Kaška M.:
The Effect of Hydrophilic Non-ionogenic Comonomers on Flow Properties of Carboxylated Latices in Polymer Colloids: Science and Technology of Latex Systems (E. S. Daniels, E. D. Sudol and M. S. El-Aasser, Eds.), ACS Symposium Series 801, American Chemical Society / Oxford University Press, Washington, D.C., Chapter 6, 71 – 79, 2001

J. Šňupárek, M. Kaška, G. Baghaffar, O. Quadrat:
Synthesis and Some Properties of Functionalized Film-Forming Latexes
in: Non-Conventional Polymer Dispersions, (I. Capek, Ed.) Willey - VCH Verlag, Weinheim 2002, pp. 89 – 103
ISBN 3-527-30469-X
Macromol. Symp. **179**, 89 – 103 (2002)
ISSN 1022-1360

J. Šňupárek, B. Kadrnka, P. Ritz, O. Quadrat:
Hydroplasticization Effect in Structured Latex Particles Film Formation
in: Quo Vadis – Coatings, (H.-J. Adler, K. Potje-Kamloth, Eds.) Willey – VCH Verlag, Weinheim 2002, pp. 367 - 376
ISBN 3-527-30477-0
Macromol. Symp. **187**, 367 - 376 (2002)
ISSN 1022-1360

A. Kalendová, J. Šňupárek:
Anticorrosive Pigments for Chemically and Thermally Resistant Coatings
in: Quo Vadis – Coatings, (H.-J. Adler, K. Potje-Kamloth, Eds.) Willey – VCH Verlag, Weinheim 2002, pp. 97 – 107
ISBN 3-527-30477-0
Macromol. Symp. **187**, 97 - 107 (2002)
ISSN 1022-1360

J. Huybrechts, P. Bruylants, K. Kirshenbaum, J. Vrána, J. Šňupárek:
New Applications of Catalytic Chain Transfer Polymerization to Waterborne Binders for Automotive Paint Systems
Progr. Org. Coat. **45,** 173 - 183 (2002).
ISSN 0300-9440.

Submitted papers:

THICKENING OF ACRYLIC LATICES WITH DISPERSIONS OF CROSSLINKED ETHYL ACRYLATE - METHACRYLIC ACID COPOLYMERS

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Running head: Thickening of acrylic latices

Key words: Acrylic latices - crosslinked ethyl acrylate-methacrylic acid copolymer dispersions - thickening - rheology

Summary

Thickening of three model latices of copolymers of ethyl acrylate and 0 - 2 wt.% of acrylic acid using dispersions of ethyl acrylate - methacrylic acid copolymer crosslinked with 0.25 - 5 wt.% of *N,N′*-methylenebisacrylamide was investigated. Measurement of the static light scattering revealed that the highest thickening effect occurred when, after alkalinization, a sufficient amount of highly swollen crosslinked particles arose from the thickener. Viscoelastic properties of this basic matrix are a decisive factor for the rheological behaviour of thickening material.

Submitted to Progr. Org. Coat.

THICKENING EFFECT OF COMMERCIAL ASSOCIATIVE THICKENERS ON THE LATICES OF COPOLYMERS OF ACRYLIC MONOMERS CARRYING HYDROPHILIC REACTIVE GROUPS

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Keywords: Latices of acrylic copolymers containing (2-hydroxyethyl)-methacrylate groups, Associative thickeners, Thickening efficiency.

Summary

Investigation of flow properties of butyl acrylate/styrene/2-hydroxyethyl methacrylate/acrylic acid latices thickened by commercial associative thickeners based on hydrophobic ethoxylated urethane (HEUR) or hydrophobically modified alkali-soluble emulsions (HASE) showed that the apparent viscosity at a constant medium shear rate increased with the increasing content of 2-hydroxyethyl methacrylate (HEMA). In contrast, the relative change in latex viscosity after the thickener addition (thickening efficiency) expressed as the ratio of viscosities of the thickened and untreated latices remained constant or even decreased. This indicates that the increase in viscosity of the thickened latex with a higher HEMA content is caused by the

increasing viscosity of the untreated latices due to rising hydrodynamic volume of alkalinized latex particles and not by higher particle bridging with the thickener macromolecules. The HEMA monomer increases hydrophilicity of the particle surface which may reduce adsorption of hydrophobic ends of the thickener on latex particles and decrease the thickening efficiency.

Submitted to Progr. Org. Coat.

VISCOELASTIC BEHAVIOUR OF BUTYL ACRYLATE/STYRENE/2-HYDROXYETHYL METHACRYLATE/ACRYLIC ACID LATICES THICKENED WITH ASSOCIATIVE THICKENERS

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Keywords: Latices; Thickening; Acrylic copolymers containing 2-hydroxyethyl methacrylate groups, Associative thickeners, Viscoelasticity.

Running head: Viscoelasticity of thickened latices

Summary

Rheological behaviour of butyl acrylate/styrene/acrylic acid latices thickened with a hydrophobically modified ethoxylated polyurethane (HEUR) or hydrophobically modified alkali-soluble polyacrylate emulsion (HASE) was investigated. While the pseudoplastic character of frequency dependence of complex viscosity was similar for both thickeners, viscoelastic behaviour, expressed as the ratio of loss and storage moduli, significantly differed indicating that the HEUR molecules, unlike swollen HASE particles, create a viscoelastic space structure. The increase in hydrophilicity of the particle surface, achieved by incorporation of 2-hydroxyethyl methacrylate (HEMA) monomer into latex copolymer reduced the viscoelasticity of latices thickened with HEUR but not those thickened with HASE. This confirms that adsorption of hydrophobic end-groups on particle surface is important for thickening of latices with HEUR and that a physical network of latex particles interconnected by the thickener macromolecules is formed.

Accepted to CR Acad.Sci.

International Polymer Colloids Group Newsletter

Eric S. Daniels, Victoria L. Dimonie, Mohamed S. El-Aasser,
Andrew Klein, Cesar A. Silebi, and E. David Sudol

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Recent Publications

Incorporation of Alkoxysilanes into Model Latex Systems: Vinyl Copolymerization of Vinyltriethoxysilane and *n*-Butyl Acrylate, I. Marcu, E. S. Daniels, V. L. Dimonie, C. Hagiopol, J. E. Roberts, and M. S. El-Aasser, *Macromolecules*, **36**(2), 328 - 332 (2003).

The increase in industrial interest in the incorporation of alkoxysilanes in organic polymer coatings arises from their ability to form self-crosslinkable films at room temperature. In the past few years, many patents were published, offering solutions for avoiding premature crosslinking of alkoxysilane-containing latexes and for obtaining good film-forming properties without using organic solvents. The present paper proposes a miniemulsion approach for the incorporation of alkoxysilanes into acrylate latex systems in order to protect the silane moieties from hydrolysis and premature crosslinking by reducing their contact with water. Vinyltriethoxysilane (VTES)/*n*-butyl acrylate (BA) copolymer latexes were synthesized by both conventional emulsion and miniemulsion procedures. The amount of coagulum and conversion were determined by gravimetry. Differences in coagulum levels were observed with respect to the copolymerization procedure (1.1 – 32.7 wt.% based on monomers in conventional systems vs. 1.2 – 5.5 wt. % on monomers in miniemulsion systems for a VTES feed of 1 to 50 mole %) and acrylate/alkoxysilane molar ratio. Gas chromatography was used to determine the reactivity ratios of VTES/BA pairs by analyzing the evolution of unreacted comonomers during copolymerization. The reactivity ratios between the alkoxysilane and acrylate differed by two orders of magnitude for VTES (monomer 1) and BA (monomer 2), where $r_1 = 0.044$ and $r_2 = 8.56$. These results were confirmed by FT-IR analysis of the copolymer composition ($r_1 = 0.086$; $r_2 = 8.51$).

Towards an Understanding of the Role of Water-Soluble Oligomers in the Emulsion Polymerization of Styrene-Butadiene-Acrylic Acid. Separation and Characterization of the Water-Soluble Oligomers, X. Y. Yuan, V. L. Dimonie, E. D. Sudol, and M. S. El-Aasser, *Macromolecules*, **35**(22), 8346 - 8355 (2002).

A series of techniques was developed to quantitatively characterize the free water-soluble oligomers found in the aqueous phase in a model styrene/butadiene/acrylic acid (St/Bu/AA) batch emulsion terpolymerization process. Particular attention was paid to the early stages of the polymerization. Ultracentrifugation was used to accomplish the separation of the aqueous phase from the particle phase. ^{1}H NMR, aqueous phase GPC, and GC techniques were used to determine the oligomer concentration as well as their composition and the surfactant concentration in the aqueous phase, the oligomer molecular weight, and the acrylic acid monomer conversion, respectively. The results were related to the overall conversion and the number of particles as a function of conversion. The oligomer concentration vs. conversion curves for the model system show a maximum at around 12% conversion. However, the position of this maximum with respect to conversion is related to the surfactant concentration. The sharp decrease in the oligomer concentration after micelles disappeared and the decrease in the number of particles was considered to have resulted from a strong interaction of these oligomers, which are rich in St and Bu units, with the polymer of the latex particle surface. Increasing the AA concentration in the recipe increased the water-soluble oligomer concentration and the number of particles, thereby increasing the rate of polymerization.

Towards an Understanding of the Role of Water-Soluble Oligomers in the Emulsion Polymerization of Styrene-Butadiene-Acrylic Acid. Mechanisms of Water-Soluble Oligomer Formation, X. Y. Yuan, V. L. Dimonie, E. D. Sudol, J. E. Roberts, and M. S. El-Aasser, *Macromolecules*, **35**(22), 8356 - 8370 (2002).

The mechanism of water-soluble oligomer formation during the emulsion terpolymerization of styrene/butadiene/acrylic acid differs depending on whether the surfactant concentration is above or below the cmc. A growth mechanism for the water-soluble oligomers involving reactions in both the aqueous and organic phases for polymerizations carried out above the cmc of SLS is proposed. This is used to explain why the fraction of butadiene (Bu) units in the water-soluble oligomer chains is the highest compared to the styrene or even the acrylic acid (AA), despite the low water solubility of Bu monomer relative to AA. The supporting evidence for this mechanism includes: (1) the increase in the oligomer molecular weight with increasing initiator concentration, as in the case of polymerization occurring in micelles, indicating that the oligomers had grown in an isolated organic phase; and (2) the much higher fraction of AA homo dyads found in the oligomers formed at an SLS concentration below the cmc compared to that above the cmc. These results indicate that, in the absence of micelles, the oligomers will grow in the aqueous phase and result in more AA block dyad sequence units in the oligomer chains owing to the higher AA monomer concentration there. When micelles exist, the water-soluble oligomers will grow in both the aqueous phase *and* the organic phase. In this case, fewer AA dyads will be noted.

Mechanical Properties of Films Prepared from Model High-Glass-Transition-Temperature/ Low-Glass-Transition-Temperature Latex Blends, J. Tang, E. S. Daniels, V. L. Dimonie, M. S. Vratsanos, A. Klein and M. S. El-Aasser, *J. Appl. Polym. Sci.*, **86**(11), 2788 - 2801 (2002).

The mechanical properties of films prepared from model high T_g/low T_g latex blends were investigated using tensile testing and dynamic mechanical analysis. Polystyrene (PS; carboxylated and non-carboxylated) and poly(*n*-butyl methacrylate-co-*n*-butyl acrylate) [P(BMA/BA); non-carboxylated] were used as the model high T_g and low T_g latexes, respectively. Carboxyl groups were incorporated into the PS latex particles to alter their surface properties. It was found that the presence of carboxyl groups on the high T_g latex particles enhanced the Young's moduli and yield strength of the PS/P(BMA/BA) latex blend films, but did not influence the ultimate properties such as the stress at break and maximum elongation. These phenomena can be explained by the maximum packing density of the PS latex particles, the particle-particle interfacial adhesion, and the formation of the "glassy" interphase.

The Evaluation of the Size and the Structure of the Interphase in Composite Particles Containing a Macromonomer Studied by Solid-state NMR, K. Landfester, V. L. Dimonie, M. S. El-Aasser, *Macromol. Chem. Phys.*, **203**(12), 1772 - 1780 (2002).

The degree of coverage and the structure and thickness of interphases in composite latex particles consisting of a poly(butyl acrylate) (PBA) core incorporated with poly(methyl methacrylate) (PMMA) macromonomer of different molecular weight and a PMMA shell was analyzed by using solid-state NMR spin-diffusion measurements. By changing the temperature at a given filter strength or by adjusting the filter strength at a given temperature, the spin-diffusion experiment could be performed in such a way that the overall structure could be detected. At filter strengths softer than necessary for the detection of the overall structure, information regarding larger structures can be obtained, whereas for stronger filters detailed information about small structures in the interphase region can be extracted. The data obtained by NMR were related to previous TEM and dynamic mechanical studies on these particles.

Influence of Particle Surface Properties on Film Formation from Precipitated Calcium Carbonate/ Latex Blends, J. Tang, E. S. Daniels, V. L. Dimonie, A. Klein, and M. S. El-Aasser, *J. Appl. Polym. Sci.*, **86**(4), 891 - 900 (2002).

The surface properties of films prepared from a blend of precipitated calcium carbonate pigment (PCC) and poly(*n*-butyl methacrylate-co-*n*-butyl acrylate) [P(BMA/BA); T_g = 0 °C] latex were investigated in terms of the surface characteristics of the PCC and P(BMA/BA) latex particles. It was found that the presence of carboxyl groups on the P(BMA/BA) latex particles significantly improved the uniformity of the distribution of the PCC particles within the P(BMA/BA) copolymer matrix and the gloss of the resulting films. This phenomenon could be explained by an acid-base reaction between the PCC particles and the carboxylated P(BMA/BA) latex particles. Studies on the influence of the composition of PCC/P(BMA/BA) latex blends on the gloss and transparency of the films were also performed, which led to the determination of the critical pigment volume concentration (CPVC) of this system which was found to be 42 vol%.

Publications Accepted

A Miniemulsion Approach to the Incorporation of Vinyltriethoxysilane into Acrylate Latexes, I. Marcu, E. S. Daniels, V. L. Dimonie, J. E. Roberts, and M. S. El-Aasser, accepted by *Prog. Colloid Polym. Sci.*

The present work describes a miniemulsion approach for the incorporation of alkoxysilanes into acrylate latex systems in order to protect the silane moieties from hydrolysis and premature crosslinking by reducing their contact with water. Vinyltriethoxysilane (VTES) / *n*-butyl acrylate (BA) systems were analyzed. Copolymer latexes were synthesized by miniemulsion polymerization procedures using ammonium persulfate as initiator and sodium lauryl sulfate as surfactant. Silane moieties were successfully incorporated up to 50 mole % into poly(BA) latex systems by batch miniemulsion polymerization. An oil-soluble initiator, 2,2'-azobis(2-methyl-butyronitrile) (AMBN) was also employed. Gas chromatography was employed to monitor the VTES/BA miniemulsion copolymerization reactions. Swelling studies showed that the degree of crosslinking in the resulting copolymers and the molecular mobilities of silane vinyl groups depended on the initiation system; ^{1}H spin-diffusion NMR experiments allowed the inference of particle morphologies that were found to depend on the reaction pH (domains for pH 5.5 and core/shell for pH 1.5). Differential scanning calorimetry (DSC) measurements and FT-IR analyses of residual OH groups in cast films were employed to evaluate the capacity of crosslinking upon film drying. Quantitative ^{13}C NMR analysis found no difference in the amount of unreacted silane vinyl groups between the systems initiated by APS at pH 1.5 and AMBN at pH 5.5, respectively. The effect of the monomer hydrophobicity was studied using 2-ethylhexyl acrylate. Comparative kinetic studies (reaction calorimetry) on VTES/BA and VTES/2-ethylhexyl acrylate miniemulsion systems indicated that the silane hydrolysis is influenced by the hydrophobicity of the acrylic monomer and occurs at the droplet/water interface, the best silane protection from hydrolysis being achieved for the least hydrophobic monomer (BA).

Agitation Effects in Emulsion Copolymerization of *n*-Butyl Methacrylate and N-Methylol Acrylamide, S. Krishnan, A. Klein, M. S. El-Aasser, and E. D. Sudol, accepted by *Polym. React. Engng.*

The effects of agitation in emulsion copolymerization have been studied using a semi-batch emulsion copolymerization recipe that gave a latex with ca. 44 wt % solids. The two-stage polymerization process consisted of an in situ seed-formation step followed by copolymerization of the continuously added *n*-butyl methacrylate and N-methylol acrylamide monomers under monomer-starved conditions. A 2-dm^3 glass reactor and Rushton turbine agitators of different diameters (4, 6 and 8 cm) were used in the study. Agitation influenced the particle number at the end of the seed stage. This influenced properties like latex viscosity, the amount of water-soluble polymer, and the particle size in the final latex. Analysis of the water-soluble polymer using NMR spectroscopy showed that it was mostly a homopolymer of N-methylol acrylamide. With the 4 cm diameter agitator, the mixing of the pseudoplastic latex was poor during the feed stage. Formation of a zone of poor mixing could be observed on top of the fluid in the reactor, when the monodisperse particles in the latex formed an iridescent structure. Poor emulsification of the added *n*-butyl methacrylate monomer resulted in a greater amount of water-soluble polymer.

Relative Importance of the Effects of Feed Stage Agitation on Latex Properties in Semi-batch Emulsion Copolymerization of *n*-Butyl Methacrylate and N-Methylol Acrylamide, S. Krishnan, A. Klein, M. S. El-Aasser, and E. D. Sudol, accepted by *Polym. React. Engng.*

The effects of agitation in a ca. 24 % solids semi-batch emulsion copolymerization of *n*-butyl methacrylate and N-methylol acrylamide in a 2 dm^3 reactor are reported. A Rushton turbine with 8 cm tip-to-tip diameter was used as the agitator. The agitation speeds during the seed and feed stages of the semi-batch process were varied at two levels. The final latexes obtained from the four experiments were characterized for the size of the polymer particles, viscosity, amount of water-soluble polymer, and the amount of coagulum at the end of the reaction. A higher agitation speed nucleated a greater number of polymer particles during the in situ seed formation step (seed stage). In the absence of any secondary nucleation during the monomer-feeding stage, the final latexes had a higher number of particles when the agitation speed during the seed stage was higher. The amount of coagulum increased with an increase in the agitation power-input. The amount of water-soluble polymer was influenced mainly by the agitation during the seed stage of the process, through the effect of the latter on the number of polymer particles. However, the pooling of the BMA monomer during the feed stage, because of poor mixing and shear in the reactor, resulted in an increased water-soluble polymer formation. Latexes prepared using a higher agitation speed during the seed stage had a higher viscosity.

Recent Ph.D. Dissertations

Preparation of Urethane/Acrylic Hybrid Miniemulsion Nanoparticles
Mei Li

Nanosized polyurethane (PU)/poly(*n*-butyl methacrylate) (PBMA) hybrid latex particles (~50 nm) with various compositions were successfully prepared using a redox-initiated miniemulsion polymerization process. This process provides a new method to synthesize nanosize hybrid latex particles using a relatively small amount of surfactant.

Studies were performed ranging from fundamental research on the redox-initiated miniemulsion polymerization of *n*-butyl methacrylate (BMA) using a Mettler RC1 reaction calorimeter, the preparation of isocyanate-terminated urethane prepolymers using methylene-di-*p*-phenyldiisocyanate (MDI) or isophorone diisocyanate (IPDI) reacting with polypropylene glycol diol (PPG-diol; molecular weight = 2,000 g/mol) and a small amount of hydroxyethyl methacrylate (HEMA), miniemulsification and miniemulsion polymerization of PU/BMA droplets, chain extension of urethane in the obtained nanoparticles, film formation of the resulting hybrid latexes, and evaluation of the mechanical and surface properties of the resulting films. A suitable chain extension process was developed to introduce interparticle crosslinking while maintaining the original small-size of the obtained hybrid nanoparticles. DMA and stress-strain tests show that intimate mixing of the PU and PBMA chains was achieved at the molecular level in the PU/PBMA hybrid system, while typical two-phase composite behavior was observed in a PU-PBMA latex blend system. The presence of the non-crosslinked PU phase significantly increased the maximum strain of the PU/PBMA hybrid films with some sacrifice of the tensile strength and Young's modulus. However, in the PU-PBMA latex blend system, the presence of the PU decreased not only the maximum strain, but also the tensile strength and Young's modulus.

Fundamental research on the miniemulsion polymerization of BMA initiated by the hydrogen peroxide/ascorbic acid redox initiation system was carried out in terms of the order of addition, feed strategy, initiation mechanism, reaction temperature, surfactant concentration, and initiator concentration. The influence of the presence of ferrous ion (Fe^{2+}) on the redox initiation system was also studied. It was found that a low polymerization temperature and a fast initiation and polymerization rate are the key parameters needed to obtain small-sized particles via the miniemulsion process. The use of a redox initiator in the miniemulsion polymerization of BMA can result in the formation of nanoparticles as well as nearly 100% droplet nucleation.

Effects of Agitation in Emulsion Polymerization of *n*-Butyl Methacrylate and its Copolymerization with N-Methylol Acrylamide
Sitaraman Krishnan

Effects of agitation in emulsion polymerization were investigated using a 2 dm^3 stirred reactor and Rushton turbine agitators and a semi-batch mode of reaction. High-solids recipes giving monodisperse polymer particles with core-shell morphology were developed for monomer-starved, semi-batch emulsion copolymerization of *n*-butyl methacrylate (BMA) and N-methylol acrylamide (NMA). A larger agitator, or a higher agitation speed, resulted in higher particle concentration, more viscous latex, less water-soluble polymer, and higher mass of coagulum. Better incorporation of NMA in the polymer particles was because of greater particle-water interfacial area and more efficient macromixing in the reactor. A mechanism where the surface of the polymer particles is the most favorable site for copolymerization, is proposed for the incorporation of NMA. Nucleation of a greater number of particles at higher agitation intensity was a general observation for recipes with surfactant concentrations below the critical micelle concentration (cmc).

Effects of agitation on the kinetics of emulsion polymerization of BMA were studied using reaction calorimetry. At a reaction temperature of 70 °C, the molecular weight was higher at higher agitation speed, while at 50 °C, the converse was true. The order of dependence of the mass of coagulum on the agitation speed depended on the surfactant coverage of the polymer particles: the variation was almost two-fold (1.2 to 2.3). The coagulum mass was related to the surfactant coverage using results from DLVO theory. The volume-surface average diameter of the monomer droplets in the emulsion scaled to the 1.6 power of the agitation speed, and the droplet size distribution was log-normal.

Thermal crosslinking of the copolymer particles and films was investigated, and the effect of carbon tetrabromide on the gel content of the copolymer films was studied experimentally and theoretically. The increase in the gel content as a function of time during thermal curing was studied at temperatures of 90 °C, 120 °C, and 150 °C. The calculated time required for disentanglement of the polymer chains explained the observed induction periods for gel formation at 90 °C and 120 °C. Morphologies of copolymer particles and latex films were studied using transmission electron microscopy and atomic force microscopy. Unique surface features attributable to crosslinked shell and linear core of the copolymer particles, were observed by AFM.

International Polymer Colloids Group
January 2003 Newsletter Contribution
University of New Hampshire

Evaluating Transmission Electron Microscopy Techniques for the Determination of Latex Particle Morphology

Jeffrey M. Stubbs and Donald C. Sundberg

Transmission electron microscopy (TEM) has been one of our most relied upon and revealing methods for the determination of latex particle morphologies. From time to time we have obtained some confusing or questionable results from TEM which have led us to more closely investigate our sample preparation techniques. Discussions with other researchers experienced in the use of TEM for observing latex particles (Helen Hassander and Ola Karlsson at Lund Univ) revealed that they had also noticed similar results in certain samples. The major factor that we became concerned about was the embedding step during the preparation of a sample for microtoming. The method we have traditionally employed is to dry the latex to a powder (in cases where the latex is not film forming). A small amount of this powder is then mixed into an epoxy and cured, usually at 60C for several hours. The epoxy that has typically been used by many who employ TEM for the study of polymers is commonly referred to as EPON. An EPON embedding kit includes a bisphenol A – epichlorhydrin epoxy monomer, two different crosslinkers and an epoxy accelerator. It has become evident to us that during the embedding step this epoxy can plasticize the particles. This can result in either changes in the morphology or drastic changes to the sample in which the particles coalesce into much larger domains of polymer.

The microtomed TEM photos shown in Figure 1 illustrate this effect. The latex in these photos consists of a seed polymer of butyl acrylate and styrene (30wt%BA) and a second stage of PMMA. All of the photos shown in Figure 1 are taken at the same magnification level (20,000X), however it is clear that the size of the polymer domains vary from one photo to another. This clearly illustrates that the particles have been plasticized and coalesced with one another.

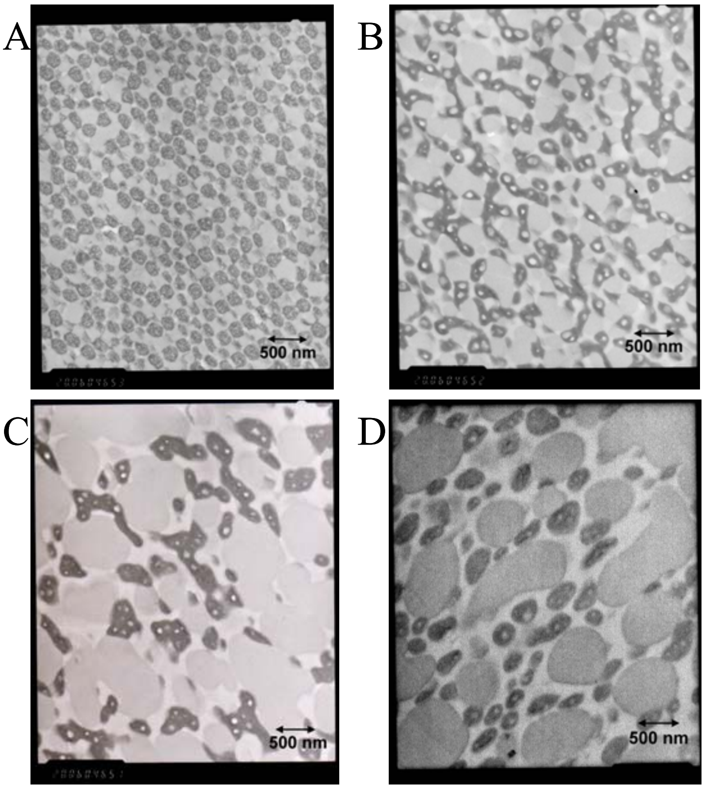

Figure 1: Microtomed TEM photos using EPON as the embedding epoxy.

Furthermore, the extent to which this plasticization occurs varies with the position within the sample where the photo was taken. When the latex polymer sample is crushed into a powder before embedding, it is not broken down into individual particles but rather larger agglomerates of many particles. The ability of the epoxy, which is highly viscous, to penetrate into an agglomerate seems to vary with the agglomerate size and position within the agglomerate. The progression from photos A to D in Figure 1 represents on in which the location in the sample changes from the interior of a large agglomerate (photo a) towards the outside (photo d). This clearly displays how the plasticization effect varies with position throughout the sample.

After noticing this effect in a number of samples, we were forced to search for a new epoxy that would not plasticize our samples and alter the particle morphologies. We began using a common epoxy that is used for building models. This is a two part epoxy that cures in 30 minutes at room temperature. Figure 2 shows the microtomed TEM photo of the same sample as in Figure 1, but using this new epoxy. It is clear that the particles appear very different than when using the EPON epoxy. They are clearly present as separate particles and this does not change with position throughout the sample, even in areas where the particles are finely dispersed in the epoxy. They now appear to display very little structure. This type of homogeneous structure is also suggested by DSC analysis, in which we find only one rather narrow Tg that is in between the Tg's of the pure seed and second stage polymer. Therefore, we believe that this new epoxy is not plasticizing our particles and allowing us to observe the true particle morphology in the TEM.

Having knowledge of the actual particle morphology (homogeneous structure) helps to further understand the plasticization effect of the EPON epoxy. In Figure 1a, although the particles have remained separate from one another it is clear that they are beginning to be plasticized. This is evident by the "necking" or "bridging" that is apparent between different particles. Also, separate domains of light and dark polymer are present within each, indicating that the seed and second stage polymers have been able to phase separate to a greater extent than in the "true" morphologies in Figure 2. The extent of this phase separation increases, and consolidation of the two polymer phases occurs within individual particles (Figure 1b) and then between separate particles (Figures 1c and 1d), showing how the extent of plasticization increases towards the outer regions of the particle agglomerate.

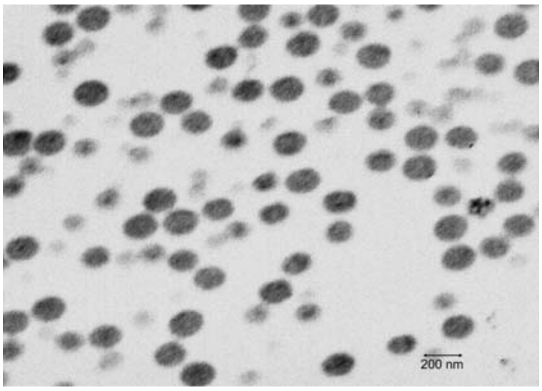

Figure 2: Latex sample from Figure 1 but using new epoxy for embedding

This study has shown the importance of the sample preparation methods in TEM analysis and the care that must be taken to avoid misleading results. Other effects have been noticed as well, such as the effect of staining with Ruthenium before embedding, and how this can affect the extent to which plasticization occurs. We are continuing to pursue this study, in conjunction with Ola Karlsson and Helen Hassander at Lund University, and working towards perfecting our electron microscopy techniques for the analysis of latex particle morphology.

Encapsulation of Fire-Retardant Agents in Latex Particles

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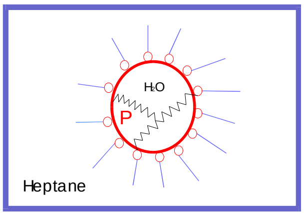
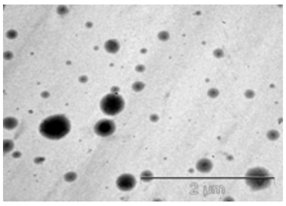
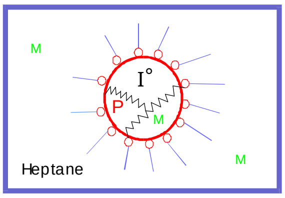
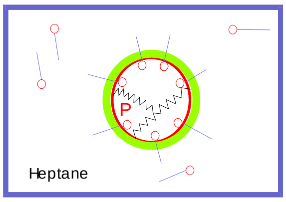
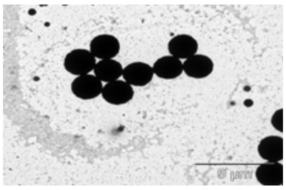
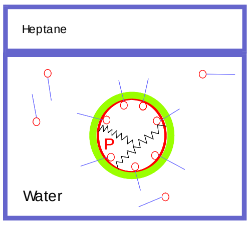
Encapsulation of water-soluble fire-retardant agents (FRA) in a latex particle allows for decreased FRA leaching under weathered conditions. FRA being usually not compatible with the polymer they protect, encapsulation prevents the occurrence of phase separation events. It also reduces the corrosion issues associated with the presence of FRA and improves the fire resistance due to better dispersion of the FRA.

We are currently encapsulating water-soluble phosphorous-based FRA in latex capsules. For this purpose, we start by an inverse emulsion polymerization of acrylamide in the presence of FRA (1). At the end of this first step, an inverse latex of polyacrylamide, swollen by as much as 40% FRA, is obtained. Then, an organosoluble monomer (typically, styrene, acrylonitrile, butyl methacrylate or MMA) is polymerized (2): because the polymer is neither soluble in water nor in the organic phase, a shell is formed around the polyacrylamide reservoir (3). Finally, the capsules are transferred into water, through a phase inversion process. The permeability of the capsules, and their capacity to impart fire protection are currently under scrutiny.

 1. Polyacrylamide latex containing phosphorous FRA (P)	 1. TEM of polyacrylamide latex	 2. Addition of an organosoluble monomer (M) and initiation of the polymerization by a water soluble initiator
 3. Formation of an interfacial layer of polymer	 3. TEM of the latex (outer shell = polyacrylonitrile)	 4. Phase transfer into water

Heterophase Polymerization

Co-workers: Klaus Tauer, Sophie Viala, Victor A. Khrenov, Hasan Ahmad, Rosemarie Rafler, Sylvia Pirok, Ursula Lubahn

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Heterophase polymerization techniques are a fascinating and attractive example of applied polymer colloid chemistry. Our main research topics of the last two years were *(a)* exploration of new ways to prepare block copolymers by radical heterophase polymerization, *(b)* mechanistic investigation of controlled radical polymerization with 1,1-diphenyleltylene (DPE) based precursor polymers, *(c)* further evaluation of poly(ethylene glycol)-azo-initiators, and *(d)* development of procedures to prepare μm-sized, monodisperse particles with surface poly(ethylene glycol) groups.

Preparation of block copolymers

The strategy employed consists of a multi-stage radical heterophase polymerization by utilizing the ceric ion redox initiation mechanism to generate radicals at preferably hydroxyl group substituted polymer chain ends that subsequently form polymeric micelles or particles during an aqueous heterophase polymerization as isolated reaction loci where the further block copolymer formation takes place after addition of another batch of monomer. This strategy allows the preparation of very unique block copolymers, which are not accessible by any other route. Examples are poly(ethylene glycol)-*b*-poly(N-isopropyl acrylamide)-*b*-poly(acrylamidopro-pane sulfonate), polystyrene-*b*- poly(N-isopropyl acrylamide)-*b*-poly-(styrene sulfonate), or poly-(styrene sulfonate)-b-poly(methacrylic acid) [1]. Besides the chemical distribution the block copolymer nanoparticles possess at least under wet conditions (in the dispersed state) also a characteristic density distribution which changes upon electrolyte addition and / or temperature changes. Moreover, particles of this kind exhibit interesting features which are not yet completely understood. For example, transmission electron microscopy (TEM) images of poly(ethylene glycol-*b*-poly(N-isopropyl acrylamide)-*b*-poly(methyl methacrylate) (PEG-PNIPAM-PMMA) triblock copolymer particles show a hairy morphology whereas atomic force microscopy (AFM) images reveal a rather tuber-like morphology (Figure 1). This polymerization strategy can also be used to prepare block copolymer particles with special core morphology such as PEG-*b*-PNIPAM-*b*-poly(styrene sulfonate) particles where the core consists of cross-linked poly(styrene sulfonate). These hydrophilic gel particles have been used to prepare redispersable polyelectrolyte surfactant complexes that are colloidal particles with anisotropic, crystalline cores. Figure 2 shows a TEM picture of cross sections of such colloidal complexes with tetradecyltrimethyl ammonium counterions. [2].

Control of radical polymerizations with DPE precursor polymers

Recently it was found that the use of (DPE) in conventional free radical polymerization allows a high degree of structural control [3]. The principle of this new method consists of a two - step polymerization. In the first step a DPE – containing precursor polymer is prepared, which in a second polymerization leads to the formation of block copolymers. The two steps can be carried out either sequentially and spatially separated or conducted like a one pot synthesis with consecutive addition of monomers. In contrast with all other methods of controlled radical polymerization, the DPE – based technique can be applied for all types of acrylate, methacrylate, vinyl and styrene monomers. Moreover, it can be applied in bulk, solution as well as heterophase polymerizations and the DPE-precursor polymer can be either hydrophilic or hydrophobic. In collaboration with the BASF Coatings AG the mechanism of this reaction was investigated. It turned out that the active species in the precursor polymer is the α,p-dimer unit which is formed by combination termination of two DPE – ended radicals (cf. Formula 1) [4, 5]. The results of comprehensive studies reveal that the semiquinoid structure of the precursor polymer is activated by the attack of free radicals and thus, in a second stage polymerization with a second monomer, block copolymers are formed. The block copolymer yield can be well above 90 % but depends strongly on the ratio between the amount of DPE-containing precursor polymer and the initiator and monomer concentration used in the second stage (cf. Figure 3). The mechanism proposed is able to explain at least qualitatively all experimental results including the restriction of this mode of control of radical polymerization to the formation of diblock copolymers only.

Poly(ethylene glycol)-azo-initiators in heterophase polymerizations

The use of nonionic poly(ethylene glycol)-azo-initiators (cf. Formula 2) instead of ionic initiators in emulsion polymerizations offers interesting possibilities to modify colloidal and polymeric properties of polymer dispersions. Experimental results have been obtained for various kinds of anionic, cationic, and nonionic stabilizers. For example, in a styrene emulsion polymerization with monomer to water mass ratio of 1 : 4 at a given concentration of 1 % with respect to monomer mass of either an anionic or a cationic surfactant the replacement of either peroxodisulfate or 2,2'-azobis(2-amidinopropane)-dihydrochloride, respectively, by PEGA200 leads to particles with considerably smaller size, polymers with higher molecular weight, and latexes with higher viscosity. These results indicate on the one hand a special interaction between the PEG-radicals and ionic surfactant and on the other hand the influence of the ionic strength on aqueous heterophase polymerization. [*6*].

Large, monodisperse poly(ethylene glycol) – coated latex particles

Polymer particles with polar functional groups such as poly(ethylene glycol) on the surface are widely utilized in biomedical applications particularly for protein immobilization and cell adhesion studies. Depending on the size and morphology, the particles prepared are also considered to be useful for use as size-exclusion HPLC packings. The objective of this project was to develop synthetic routes to prepare large monodisperse particles with a PEG shell. For this the following synthesis strategy was developed which is illustrated in Figure 4 by means of scanning electron microscopy (SEM) and light microscopy (LM) images. First, polystyrene seed particles have been prepared by dispersion polymerization in ethanol – water mixtures with poly(vinyl pyrrolidone) as stabilizer and 2,2'-azobisisobutyro-nitrile as initiator. These particles have been swollen with a large excess of styrene by activated swelling procedures (step A in Fig. 4) and subsequently polymerized (step B in Fig. 4). Finally, these particles were used as seed in a second seed copolymerization with styrene / PEG-mono methyl methacrylate with average molecular weights of PEG chains of 1000 g mol^{-1} and 4000 g mol^{-1} as monomer mixture and PEGA200 (cf. Formula 2) as initiator (step C in Fig. 4). The developed strategy allows the preparation of monodisperse polystyrene particles with PEG shells in the size range between 1 and 10 µm [*7* - *9*].

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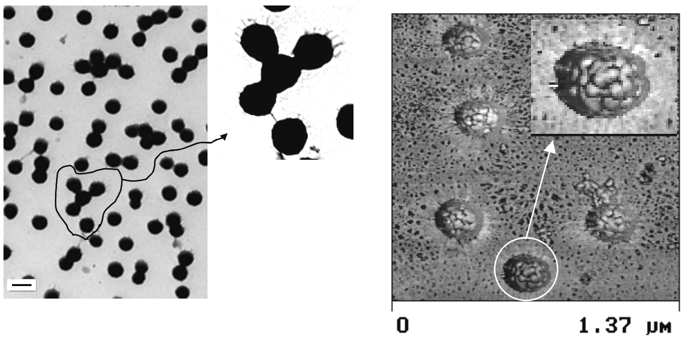


Figure 1 TEM (left) and AFM image (right) of PEG-PNIPAM-PMMA triblock copolymer particles; the bar indicates 20 nm

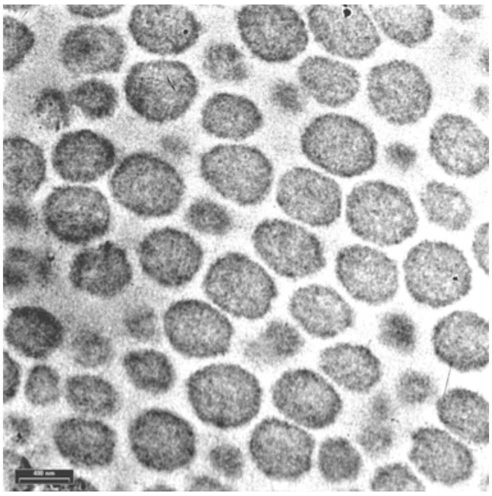
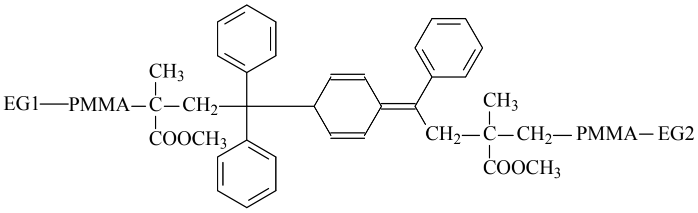


Figure 2 TEM picture of cross section of polyelectrolyte surfactant complex particles; the bar indicates 300 nm



Formula 1 Active semiquinoid structural unit (α,p-dimer) in DPE – PMMA precursor polymers; EG1 and EG" denote different end groups arising from initiating radicals

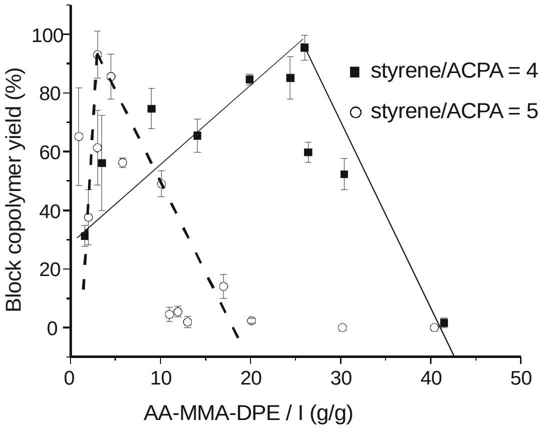
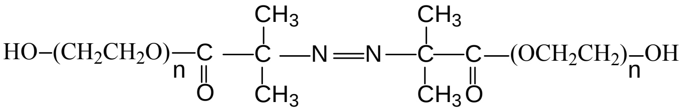


Figure 3 Block copolymer yield between a hydrophilic precursor polymer made of acrylic acid, methyl methacrylate and DPE (AA-MMA-DPE) and styrene during an aqueous heterophase polymerization with 4,4’-azobis(4 - cyanopentanoic acid) (ACPA) as initiator (I) in dependence on the precursor polymer to initiator ratio for two different monomer to initiator ratios (each experiment was repeated 4 times; lines are just for guiding the eyes)



$$HO{-}(CH_2CH_2O)_n{-}\underset{\displaystyle O}{\underset{\|}{C}}{-}\underset{\displaystyle CH_3}{\underset{|}{\overset{\displaystyle CH_3}{\overset{|}{C}}}}{-}N{=}N{-}\underset{\displaystyle CH_3}{\underset{|}{\overset{\displaystyle CH_3}{\overset{|}{C}}}}{-}\underset{\displaystyle O}{\underset{\|}{C}}{-}(OCH_2CH_2)_n{-}OH$$

Formula 2 Poly(ethylene glycol)-azo initiators (PEGA) (PEGA200 n~4.5)

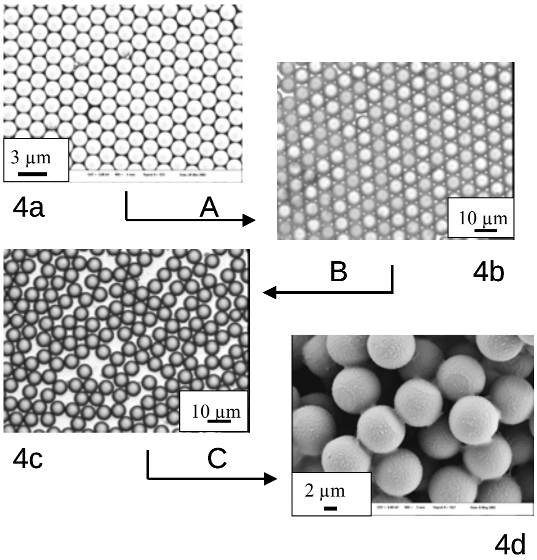


Figure 4 Images of monodisperse polymer particles: 4a – seed particles (polystyrene); 4b – swollen seed particles (styrene + polystyrene); 4c – polymerized swollen particles (polystyrene); 4d – composite particles PS/P(S-PEGMMA)

FILM FORMATION AND POLYMER DIFFUSION IN POLY(VINYL ACETATE-CO-BUTYL ACRYLATE) LATEX FILMS. TEMPERATURE DEPENDENCE

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(to *Macromolecules*)

Abstract

We describe the first polymer diffusion measurement in a poly(vinyl acetate) copolymer latex film by fluorescence decay measurements of nonradiative energy transfer (FRET). The base monomer is a 4:1 weight ratio copolymer of vinyl acetate and butyl acrylate P(VAc-*co*-BA) with a glass transition temperature of ca. 12 °C. P(VAc-*co*-BA) latex labeled particles with phenanthrene (Phe) as the donor and with 4'-dimethylaminobenzophenone (NBen) as the acceptor were prepared by semicontinuous emulsion polymerization. Latex films were cast from a 1:1 mixture of Phe- and NBen-labeled latex samples. First, a series of films containing NBen-labeled latex samples with different NBen levels were annealed at 45 °C, showing that NBen levels have no influence on the rate of polymer diffusion in P(VAc-*co*-BA) latex films. From the fully mixed solvent-cast films, the characteristic distance for energy transfer between Phe and NBen (the Förster radius R_0) was obtained as 2.44 nm. Then, polymer diffusion was monitored as a function of annealing temperature in latex film containing Phe-labeled latex with 1 mol % PheMA and NBen-labeled latex with 0.3 mol % of the NBen chromophore. The temperature dependence of the diffusion rate was characterized by an effective activation energy $E_a = 34 \pm 0.5$ kcal/mol. In parallel, an effective $E_a = 34$ kcal/mol was obtained from viscoelastic relaxation measurements over a range of temperature close to those of the diffusion experiments.

SYNTHESIS OF DYE-LABELED POLY(VINYL ACETATE-*co*-DIBUTYL MALEATE) FOR FLUORESCENCE RESONANCE ENERGY TRANSFER EXPERIMENTS

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(to *J. Polym. Sci. Part A Polym. Chem.*)

We examined the emulsion copolymerization of vinyl acetate (VAc) with dibutyl maleate (DBM) (VAc:DBM 4:1 w/w) in the presence of three dyes chosen for fluorescence resonance energy transfer (FRET) experiments. The donor dyes were 9-acryloxymethylphenanthrene (PheMA) and 9-methacryloxymethylphenanthrene (PheMMA), and the non-fluorescent acceptor dye was 2'-acryloxy-4'-methyl-4-N,N-dimethylaminobenzophenone (NBen). The presence of the DBM co-monomer significantly retards the rate of polymerization, which makes it hard to obtain monomer-starved feeding conditions for semi-continuous VAc-DBM emulsion polymerization. Under batch emulsion conditions, the polymer produced from the 4:1 wt ratio of VAc:DBM shows a composition by ^{1}H NMR throughout the polymerization that is very close to the monomer feed ratio. Other evidence, however, shows that there is microphase separation in the latex polymer. It appears that the nature of this phase separation remains constant as a function of monomer conversion. This copolymerization behavior allowed us to obtain dye-labeled latex particles with uniform dye labeling. In this way we synthesized latex particles with a diameter of ca. 100 nm containing 1 mol % PheMA or PheMMA, and similar particles containing 0.3 mol % NBen. We report preliminary non-radiative energy transfer experiments on these latex films and on their solvent-cast counterparts. These experiments provide further information about phase separation in the films and also about the rates of polymer diffusion in these P(VAc-*co*-DBM) latex films. We compare results obtained in films in which PheMA is the donor dye with those in which PheMMA is the donor dye.