IPCG

INTERNATIONAL POLYMER COLLOIDS GROUP

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NEWSLETTER

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FROM THE EDITOR'S DESK

Membership

The recent activities response sheet has revealed that two longstanding members of the IPCG have ceased to be active in the area and wish to have their names removed from the membership list. Dr Melvin Croucher of Xerox Canada, who published much seminal work in nonaqueous dispersions, has, so I understand, become more active in commercial areas and so leaves the Group with our best wishes for future success in those areas. Dr Frank Saunders, a true pioneer in so many areas of applied colloid and polymer science, has retired from the Dow Chemical Company; again our best wishes for a long and happy retirement are extended to Frank. Do Ik Lee will, of course, continue to serve as Dow's representative on IPCG. Both Frank and Mel are thanked for their many fine contributions to the area and their departure from our membership ranks is tinged with sadness.

International Symposium on Polymeric Microspheres

The Fukui Symposium, which was attended by many of our members, has come and gone. The scientific agenda was both intense and highly stimulating. Professor Nomura is to be congratulated for the excellence of the program and his brilliant organization of all aspects of the Conference. The level of hospitality shown to the delegates at the official banquet, with its wonderful combination of Japanese food and music, and at other evening functions and on the tours had to be experienced to be believed. I seem to recall, however, Mohammed El-Aasser and Archie Hamielec, with official approval, attacking a wooden vat of sake with axes, which I hope is recorded for posterity.

Next NEWSLETTER

Please forward contributions to reach me by 30 April, 1992.

DHN

CONFERENCE

1992

CONFERENCE	LOCATION	DATE
Polymer Colloids	Bristol	30 March–1 April
203rd ACS National Meeting	San Francisco	5–10 April
66th Colloid & Surface Science	Morgantown, WV	15–18 June

SYMPOSIUMS

34th International Symposium on Macromoledules	Prague	13–18 July
10th International Conference on Surface Forces	Moscow	17–22 August
204th ACS National Meeting	Washington, DC	23–28 August
European Gordon Conference	Irsee, Baveria	13–18 September

1993

205th ACS National Meeting	Minneapolis	18–23 April
206th ACS National Meeting	Chicago	22–27 August

IPCG Membership FAX (Telecopier) Numbers

J M	Asua	34-43-21-2236
D R	Bassett	1-304-747-5570
DC	Blackey	44-1-700-4272
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FK	Hansen	47-2-45-5441
H	Kast	49-621-609-2505
Do Ik	Lee	1-517-638-7510
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S	Muroi	81-462-21-7212
DH	Napper	61-2-692-3329
M	Nomura	81-776-8767
RH	Ottewill	44-272-25-1295
R	Pelton	1-416-521-1350
C	Pichot	33-72-72-8080
I	Piirma	1-216-972-5290
GW	Poehlein	1-404-894-3120
G	Riess	33-89-59-9859
WB	Russel	1-609-258-6744
FL	Saunders	1-517-636-6558
PR	Sperry	1-215-592-3377
VT	Stannett	1-919-737-3465
PJ	Stenius	46-820-8998
DC	Sundberg	1-603-862-3564
K	Tukamura	1-519-332-5933
RE	Uschold	1-302-695-3645
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IPCG MEETING – 4 July, 1991

Chair: M. El–Aasser

1. Future Meetings

(a) European Gordon Conference: To be chaired by A. German. Following discussions and negotiations with Criukshank after the meeting, it is now confirmed that this will be held at IRSEE in Bavaria (easy access to Murich and Zurich) on 13th – 18th September (the week preceding the European Colloids Conference).

(b) The next (New Hampshire) Gordon Conference will be chaired by Bassett at Tilton; dates to be finalized. The 1995 gordon Conference will be chaired by van de Ven. Pelton had been asked by the convenors of the 1993 Colloid symposium in Toronto to organize a polymer colloid session, but duplication and hence clash with Gordon Conference participants and material should be avoided. 1994 Polymer Colloids to held in conjunction with the National Colloid & Surface Science Symposium at "Stanford" to be organized by Alice Gast. The 1996 meeting in Spain (Asua) should be a NATO one–Asua to check with the NATO Secretariat.

2. New Members

The following will be invited to join the IPCG: Okubo, Ise, Fryd and Daniel (Rhone-Poulenc).
The following should be strongly encouraged to attend the European Gordon Conference with a view to possible future membership: Storti and Cara (Italy), Jim Baker (3M, USA), Harry Ploehm (Texas A & M, USA), Hagioel and Donescu C Roumaria – Dimonie can supply details).

3. Newsletter

Ottewill needs updated list.

Members are to be asked to send their email addresses.

4. Any other business

It was decided to ask the Secretary to write on behalf of the IPCG to Langmuir to request a Polymer/Colloid section.

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

Reported by José.M. Asua

Kinetics of High Solids Content Emulsion Terpolymerization

(Agustin Urretabizkaia, María J. Unzué, Gurutze Arzamendi, Aranzazu Zamora and José. M. Asua)

The kinetics of the high solids content emulsion terpolymerization of butyl acrylate, methyl methacrylate and vinyl acetate was investigated. Polymerizations were carried out under starved conditions in a semicontinuous reactor. A seeded system was used to minimize the variations of the number of polymer particles in the reactor. The effect of the solids content, feed flow rate, total amount of emulsifier, distribution of the emulsifier between the initial charge and the feed, initiator concentration and reaction temperature on the overall conversion, terpolymer composition and number of polymer particles was investigated. It was found that the polymerization proceeded under Smith-Ewart Case 3 conditions with negligible aqueous phase termination. Under these circumstances, the kinetics of the process is independent of both the solids content and the number of polymer particles. In addition, it was found that the terpolymer formed under starved conditions was rather heterogeneous and the molar fraction of vinyl acetate in the terpolymer ($\cong 8\text{-}10\%$) was less than that in the feed (15%). A mathematical model for the process was developed. The model included the material balances for the initiator and the three monomers but the population balance for the polymer

particles was not included because the polymerization rate was independent of the number of polymer particles. The parameters of the model were estimated based on the best fit of the experimental data.

In the case of emulsion copolymerizations of monomers with widely different reactivity ratios we were able to obtain homogeneous copolymers using special monomer feeding strategies (Arzamendi and Asua: J. Appl. Polym. Sci., 38, 2019 (1989); Makromol. Chem., Macromol Symp., 35/36, 249 (1990): Ind. Eng. Chem. Res., 30, 1342 (1991)). In this work, the approach to calculate the monomer addition policies has been extended to emulsion terpolymerization. In the calculation, the mathematical model developed for the process was used. The minimum-time strategy to form a homogeneous terpolymer is obtained by charging in the reactor a reaction mixture including all of the least reactive monomer and some amounts of the other monomers. Then, the remaining monomers were added using a time dependent flow rate profile. 55 wt% solids content polymerizations following this strategy were carried out in a 2 L lab reactor and an almost homogeneous terpolymer was obtained. However, when this strategy was used in a reactor with limited capacity for heat removal, a thermal runaway, and sometimes latex coagulation, was observed.

In order to overcome this problem the feed rate profile was calculated taking into account the cooling capacity of the reactor. This resulted in a feeding strategy in which some fractions of the three monomers were included in the initial charge of the reactor and the rest of the monomers were fed following a time dependent profile. Polymerizations carried out according to this strategy showed that both the terpolymer composition and the reactor temperature were controlled.

POLYMER COLLOIDS GROUP NEWSLETTER

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

Reported by J. Bartoň

Emulsion Polymerization of Methyl Methacrylate and Styrene Initiated by Ammonium Peroxodisulfate and Dibenzoyl Peroxide in the Presence and/or Absence of Fremy's Salt.

J. Bartoň, V. Juraničová (submitted for publication)

The emulsion polymerization of styrene and methyl methacrylate initiated by dibenzoyl peroxide (DBP) in the presence of potassium nitrosodisulfonate, Fremy's salt (FS) starts without any inhibition period. The rate of emulsion polymerization of methyl methacrylate in the absence of FS is higher than that in the presence of FS. The difference between these rates for these two systems sharply increases beyond the conversion of 10% . For emulsion polymerization of styrene initiated by DBP polymerization rates in the presence as well as in the absence of FS are practically the same. The rates of DBP initiated emulsion polymerization of both monomers in the presence of FS are practically equal to the rates of dibenzoyl peroxide initiated bulk polymerization of styrene and methyl methacrylate. When using ammonium peroxodisulfate as initiator, distinct inhibition periods were observed for methyl methacrylate and styrene emulsion polymerization in the presence of Fremy's salt. After inhibition periods conversion curves show no retardation of polymerization with regard to the conversion curves of methyl methacrylate and styrene emulsion polymerizations in the absence of Fremy's salt.

The experimental results point at the mechanism of homogeneous bulk polymerization in monomer droplets, i.e. one polymerization locus present in the system (styrene, initiator DBP) and simulteneously occuring mechanism of homogeneous bulk polymerization in monomer droplets and in monomer-swollen polymer

particles, i.e. two polymerization loci are present in the system (methyl methacrylate, DBP). In case of ammonium peroxodisulfate and FS containing styrene and methyl methacrylate emulsion polymerization systems the results obtained confirmed the supposed homogeneous polymer particle nucleation mechanism for both monomers (J. Bartoň, V. Juraničová, Z. Hloušková, Makromol.Chem., 189, 501 (1988)).

Inverse Microemulsion Polymerization of Acrylamide Initiated by Ammonium Peroxodisulfate and Dibenzoyl Peroxide in the Presence and/or Absence of Fremy's salt.

J. Bartoň, (submitted for publication)

Ammonium peroxodisulfate (APS) initiated acrylamide microemulsion polymerization is characterized with very high polymerization rate. However, in the presence of Fremy's salt (FS) inhibition period was observed. After inhibition period, the rate of polymerization is remarkably retarded. If dibenzoyl peroxide (DBP) was used for initiator of acrylamide microemulsion polymerization the presence of FS does not affected the course of acrylamide inverse microemulsion polymerization. This means that FS does not interfere in the initiation reaction of acrylamide polymerization in this system. In the case of APS as initiator the locus of initiation is water pool of the inverse micelle. For DBP initiator the polymerization of acrylamide starts in the continous (toluene) phase. The acrylamide oligomer radicals after reaching their limit of solubility in toluene precipitate and form aggregates or are captured by inverse AOT (Aerosol OT, sodium bis(2-ethylhexyl) sulfosuccinate) micelles. The propagation of acrylamide oligomer radicals continues in acrylamide rich region in the shell of water pool of the inverse micelle (F. Candau et al.: J.Polymer Sci.., Polym.Chem.Ed., 23, 193 (1985)). This mechanism support the results found with percolating inverse microemulsion acrylamide polymerization systems (J. Bartoň : Paper submitted for International Symposium "Polymeric Microspheres", Fukui, 1991).

Effect of divinylbenzene on the emulsion polymerization and copolymerization of butyl acrylate and acrylonitrile.

I. Capek, P. Potisk

The kinetics of batch emulsion polymerization and copolymerization of butylacrylate (BA) and acrylonitrile (AN) in the presence of divinylbenzene (DVB) has been investigated using peroxodisulfate as the initiator and sodium dodecyl sulfate as the emulsifier. In system without or with a small amount of DVB conversion curves held their sigmoidal shape. The presence of a larger amount of DVB (> 0.7 mol.dm^{-3}) in the BA system leads to the shape of the conversion curves typical for the polymerization involving limited coagulation. DVB was found to decrease strongly the rate of polymerization of BA and mildly the rate of copolymerization of BA and AN. A crosslinking agent depresses the growth of polymer particles over the whole range of conversion, and the final particle size and shifts the nucleation period and the depletion of monomer droplets to higher conversions. The rate reduction in the presence of DVB is caused by the decrease of the equilibrium monomer concentration in the particles and the number of radicals per particle. The interior of crosslinked polymer particles is supposed to play a dominant role in the deactivation of entered radicals.

The addition of a high water-soluble AN to the reaction system was found to supress the effect of DVB on the rate and particle size reduction and on the formation of particles by the micellar mechanism. On the contrary, in the presence of AN the homogeneous nucleation mechanism is opperative from which a water-insoluble DVB monomer is most probably excluded.

Associative Polymers with Novel Hydrophobe Structures

Richard D. Jenkins, Brijnaresh R. Sinha, and David R. Bassett
Union Carbide Chemicals and Plastics Company, Inc.
Technical Center, P.O. Box 8361, South Charleston WV 25303

Introduction

Due to the complex nature of the interactions among associative polymers and standard latex paint ingredients, a growing body of literature has developed around model associative polymers to understand, from fundamental first principles, the relationships among associative polymer structure, dispersion rheology and stability, and formulation. (For example, see references 1,2). This knowledge has not only aided paint formulation, but has also aided associative polymer design. Key parameters (among many) that influence the thickener's ability to control dispersion rheology include associative polymer molecular weight, the structure of the hydrophobe, and its mode of incorporation into the associative polymer.

Thus, we have developed novel hydrophobic structures for use in associative polymers, and in other applications. We have prepared linear end-capped and comb nonionic urethane based associative polymers, and alkali-soluble hydrophobically modified emulsion polymers with these novel hydrophobic structures. Polymers made with the new hydrophobes have enhanced efficiency in increasing the viscosity of a aqueous solution or latex dispersion, have enhanced adsorption to latex particles, and have enhanced interaction with surfactants as compared to thickeners made with traditional hydrophobes. This paper details some of the rheological properties achieved with associative polymers that contain the first in a series of new hydrophobic structures.

Experimental

Materials and Synthesis

Linear nonionic associative polymers were made by chain extending linear poly(oxyethylene) (Carbowax® 8500, Union Carbide Corporation) with isophorone diisocyanate (Aldrich) in a toluene solution that had been dried by azeotropic distillation. The chain extended polymer was subsequently terminated with conventional (hexadecane, Aldrich; nonylphenol, Union Carbide Corporation) and novel hydrophobic groups. Nonionic associative polymers with comb architecture were synthesized following the method of Hoy et al. (3). The molecular weight of the nonionic associative polymers were determined from intrinsic viscosity measurements in 40/60 solvent mixture of Butyl Carbitol/water by weight at 25°C, as calibrated with poly(oxyethylene) standards (Pressure Chemical Company). Previous rheological studies indicated that these conditions correspond to molecular dispersion (4). Table I summarizes the molecular weights of the associative polymers that we refer to in the subsequent figures.

Table I: Viscosity Average Molecular Weights of Linear Associative Polymers

End-Group	$[\eta]$	M_v
Hexadecane	.79	92,900
Nonylphenol	.76	87,200
New	.80	94,800

Hydrophobically modified alkali-swellable associative polymers were made by emulsion polymerization following the method of Shay et al. (5). The alkali-swellable polymers reported here are 50/40/10 ethyl acrylate/methacrylic acid/hydrophobic macromonomer by weight, and can be considered as models of the Polyphobe® brand of alkali-swellable associative polymers (Union Carbide Corporation). To convert the resulting latex into a solution, the latex was diluted to the desired concentration and neutralized to a pH of 9 with 2-amino 2-methyl 1-propanol (AMP-95, Angus chemical company). Tergitol® and Triton® (Union Carbide Corporation) ethoxylated nonylphenol and octylphenol surfactants were used as supplied as 100% active ingredient.

Apparatus

Aqueous solutions of the model associative polymers were made using double distilled deionized water that contained about 5 ppm of hydroquinone inhibitor. The solutions were equilibrated for at least two days before measurement with a Rheometrics RMS-605 rheometer using a cone and plate geometry (72 mm diameter, 1.14 degree angle cone), and with a Brookfield viscometer. All measurements were carried out at ambient temperature near 27 °C, and the steady shear viscosity was obtained by averaging measurements made in both rotational directions. The strain amplitudes in dynamic mode were less than the limit of linear

viscoelastic response. In fact, these solutions exhibited linear viscoelastic behavior up to 100% strain (corresponding to 500 mrad strain amplitude). The steady shear viscosity, and the shear rate corresponding to the onset of shear-thinning, did not depend on the cone diameter. A NIST 1490 standard sample of polyisobutylene in cetane was used to calibrate the instrument.

Results and Discussion

Solution Rheology

Figures 1 and 2 show the effect that the hydrophobic end-group exerts on the concentration dependence of the viscosity of linear end-capped associative polymers of similar molecular weight, and of alkali-swellable emulsion associative polymers whose composition differ only in the structure of the hydrophobe group, respectively. The thickener that has been terminated with the new hydrophobe is much more efficient than either the hexadecane or nonylphenol terminated thickeners. As expected for linear end-capped polymers, the solution viscosity decreases as molecular weight increases for a given concentration by weight because the number density of hydrophobic groups decreases as molecular weight increases (4,6). Like its hexadecane terminated counterpart, the thickeners terminated with the new hydrophobe are also linearly viscoelastic with a well defined characteristic relaxation time (Figure 3).

Figure 4 shows that solutions of the associative polymer that has been terminated with the new hydrophobe thins under shear from a low shear plateau, thickens at moderate Weissenberg numbers (i.e., when γ/β is between 1 and 10, where $1/\beta$ is the relaxation time constant of the material), and thins at larger Weissenberg numbers. Paradoxically, solutions of the polymer that has been terminated with the new hydrophobe show a comparatively larger degree of shear-thinning as compared to solutions of the hexadecane terminated polymer, even though the solution viscosity of the polymer with the new hydrophobe is much larger. This suggests that a solution of the polymer with the new hydrophobe contains a network with a relatively larger number of weaker network junctions as compared to the hexadecane terminated polymer. Experiments that probe the effect of shear on the density of network junctions are in progress.

The shear-thickening region in the viscosity profile is not surprising, because the shear-thickening occurs at nearly the same shear rate as in the data for other nonionic associative polymers (4,6). Our previous experimental data with hexadecyl end-capped polymer solutions that exhibit shear thickening show that the number density of network junctions do not increase with shear, as is expected for an increase in the number of intermolecular junctions due to a shear induced association. Our data are consistent with those of Richey et al. (7), whose fluorescence measurements for solutions of pyrene end-tagged poly(oxyethylene) model associative polymers showed that the number of junctions were independent of shear up to 1500 sec^{-1}. Also, the complex viscosity of these solutions do not exhibit a shear thickening region; shear-thickening results only when large strains have been applied. Thus, the shear-thickening comes from another mechanism rather than from shear-induced association.

In our previous theoretical analysis (4), we generalized Yamamoto network theory to apply to a network composed of polymer chains that had a non-Gaussian free energy, and whose junction breakage potential depended on the conformation of the network chains. This model successfully simulated the steady shear viscosity profiles of the model associative polymer solutions. According to this model, and to measurements on the effect of shear on the concentration of intermolecular network junctions, the shear-thickening results from the finite extensibility of the network chains under shear rather than from a shear-induced increase in the concentration of intermolecular junctions. Thus, the shear-thickening in the viscosity profiles of our model associative polymer solutions is a natural consequence of the stretching of an association network under large strains.
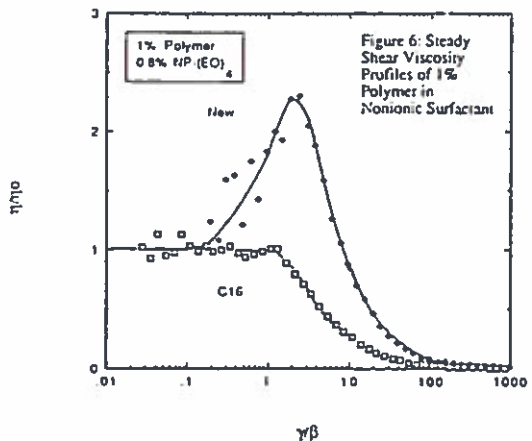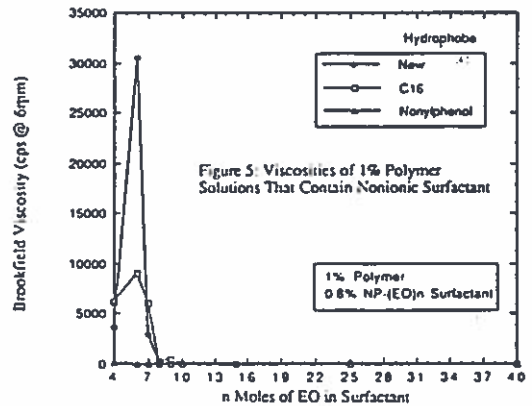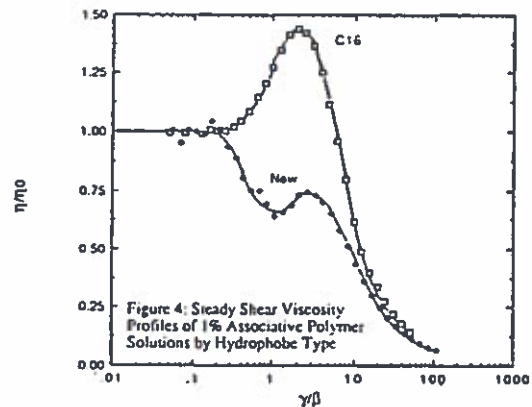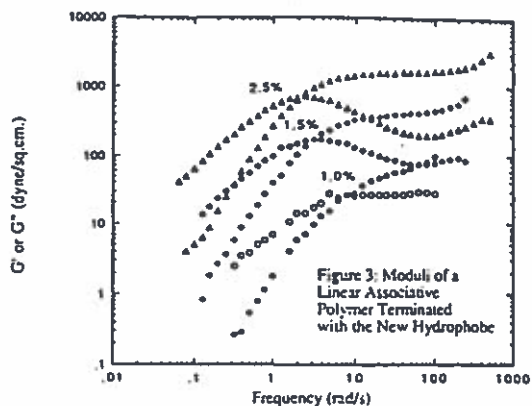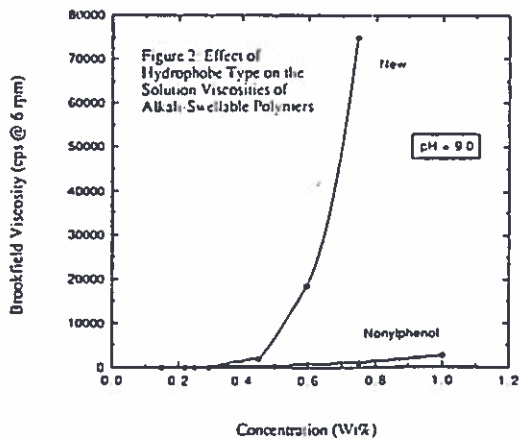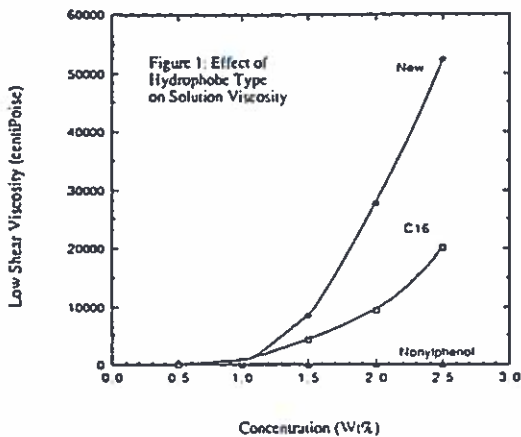
Interaction With Nonionic Surfactants

The synergistic interactions of anionic and nonionic surfactants (4,8,9) with both linear and comb (3) associative polymers, are well known. Figures 5 shows the effect of the degree of ethoxylation of nonionic surfactants on the viscosities of 1% aqueous solutions of linear end-capped nonionic associative polymers. As expected, the solution viscosity shows a maximum at 5-6 moles of ethoxylation for both nonylphenol and octylphenol based surfactants. The associative polymer that has the new hydrophobe shows a larger relative increase in the solution viscosity maximum as compared to that of a hexadecane or nonylphenol terminated polymer. The effect of nonionic surfactant on hydrophobically modified alkali - swellable polymers is analogous. Similar to data reported for other systems, the viscosity of the associative polymer solution depends on surfactant concentration as well.

The network becomes more viscoelastic at the viscosity maximum: a dramatic increase in relaxation time constant (i.e., pseudo-equilibrium modulus) at the degree of surfactant ethoxylation that corresponds to the viscosity maximum indicates that the surfactant increases the number density of network junctions. That the rheological properties of solutions of the associative polymer with the new hydrophobe are more sensitive than the properties of solutions of the hexadecane terminated polymers is consistent with the conclusion that the new hydrophobe forms a larger number of domains in solution. The steady shear viscosity profiles of solutions of the associative polymer with the new hydrophobe exhibit a dramatic shear-thickening region when nonylphenol surfactant with 6 moles of ethoxylation is added (Figure 6); this is in contrast to steady shear viscosity profiles for solutions of the hexadecane terminated polymer. These data indicate that the nonionic surfactant increases both the strength and number of network junctions of the associative polymer with the new hydrophobe in solution.

Cited Literature

1. Shultz,D.N.; Glass,J.E., ed., Symposium Series Number 462; American Chemical Society: Washington D.D., 1991.
2. Glass, J.E., ed., Advances in Chemistry Series Number 228; American Chemical Society: Washington D.D., 1989.
3. Hoy, K.L.; Hoy, R.C., U.S. Patent 4 426 485, 1984.
4. Jenkins, R.D., Ph.D. Dissertation, Lehigh University, 1990.
5. Shay, G.D.; Rich, A.F., J. Coat. Tech., 1986, 58(732), 43-53.
6. Jenkins,R.D.;Silebi,C.A.; El-Aasser,M.S., Proc. PMSE, 1989, 61, p. 629-633.
7. Richey,B.;Kirk,A.B.;Eisenhart,E.K.;Fitzwater,S.;Hook,J.W., J. Coat. Tech., to appear, 1991.
8. Lundberg, D.J.; Zeying,M.; Glass,J.E.; Proc. PMSE, 1990, 63, p.440-444.
9. Lundberg, D.J.; Glass,J.E.; Proc. PMSE, 1989, 61, p.533-538.

Figure 3: Moduli of a Linear Associative Polymer Terminated with the New Hydrophobe

Figure 4: Steady Shear Viscosity Profiles of 1% Associative Polymer Solutions by Hydrophobe Type

Figure 1: Effect of Hydrophobe Type on Solution Viscosity

Figure 5: Viscosities of 1% Polymer Solutions That Contain Nonionic Surfactant

1% Polymer
0.8% NP-(EO)n Surfactant

Figure 2: Effect of Hydrophobe Type on the Solution Viscosities of Alkali-Swellable Polymers

pH = 9.0

Figure 6: Steady Shear Viscosity Profiles of 1% Polymer in Nonionic Surfactant

1% Polymer
0.8% NP (EO)6

FURTHER COMMENTS CONCERNING THE EFFECTS OF POLYVINYLMETHYL ETHER UPON LATICES

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Possible mechanisms whereby water-soluble polymers, notably polyvinylmethyl ether, impart heat-sensitivity to ammonia-preserved natural rubber latex were summarised in a previous contribution to this newsletter. The ability of polymers such as polyvinylmethyl ether to heat-sensitise latices is almost certainly associated with their inverse solubility behaviour in water. However, notwithstanding this, the temperature at which the colloidal destabilisation of ammonia-preserved natural rubber latex containing polyvinylmethyl ether is first observed is considerably higher than the temperature at which polyvinylmethyl ether first precipitates out of solution in water. Possible heat-sensitisation mechanisms fall under two broad headings, namely, mechanisms which depend upon the presence of water-soluble polymer dissolved in the aqueous phase of the latex, and mechanisms which depend upon the presence of water-soluble polymer adsorbed at the polymer-aqueous phase interface of the latex. The results which have been obtained in the experimental investigation of the effects of polyvinylmethyl ether upon various latices, reported in our previous contribution to this newsletter, are consistent with the heat-sensitisation of ammonia-preserved natural rubber latex being primarily a consequence of the effect of increased temperature upon polyvinylmethyl ether which is adsorbed at the surface of the latex particles, rather than of precipitation of polyvinylmethyl ether in the aqueous phase of the latex as the temperature is raised. Interparticle bridging by adsorbed polyvinylmethyl ether molecules as the temperature of the latex is raised could well be an important factor in the mechanism.

In the previous contribution, reference was made to an interesting question which arises from this investigation, namely, why ammonia-preserved natural rubber latex should behave so differently from carboxylate-stabilised synthetic latices when polyvinylmethyl ether is present. Ammonia-preserved natural rubber latex which contains polyvinylmethyl ether appears to be colloidally stable at ambient temperatures, but gels rapidly when the temperature is raised above a certain critical value, whereas carboxylate-stabilised synthetic latices are either unaffected by the presence of polyvinylmethyl ether or undergo pronounced thickening at ambient temperatures. No definite reason for this difference in behaviour can be given at present, but it is of interest to speculate concerning possible reasons. The principal differences between ammonia-preserved natural rubber latex and the various carboxylate-stabilised synthetic latices used in our investigation fall under three broad headings, namely, differences which pertain to the polymer contained in the latex, differences which pertain to the interfacial region between the polymer particles and the aqueous phase, and differences which pertain to the aqueous phase.

As regards the contained polymers, the glass-transition temperature of natural rubber is very low (ca. -72°C), being lower than that of the styrene-butadiene copolymers and acrylic polymers in the latices of other rubbery polymers which we have investigated, and much lower than that of polymer in the polystyrene latices which were used in most of our work on synthetic latices. It may be that T_g affects the ease with which polyvinylmethyl ether molecules are adsorbed at the surface of the latex particles, even if the polymer surfaces themselves are similar as regards polarity. However, this seems unlikely as the principal cause of the difference in behaviour between natural rubber latex and carboxylate-stabilised synthetic latices containing polyvinylmethyl ether. Our results suggest that in all cases the polyvinylmethyl ether molecules are able to adsorb at the particle

surface provided that there are sufficient vacant adsorption sites available, or that sufficient vacant sites can be created by displacement of other molecules which are weakly adsorbed.

There are marked differences between the polymer particle/aqueous phase interfacial region in ammonia-preserved natural rubber latex and that in the carboxylate-stabilised synthetic latices used in our investigation. The latter latices were stabilised by carboxylate anions adsorbed at the particle surface. The predominant stabilisation mechanism was presumably electrostatic, possibly augmented by a contribution from hydration stabilisation due to water molecules bound to the adsorbed anions. Ammonia-preserved natural rubber latex is believed to be stabilised partly electrostatically by adsorbed carboxylate anions (some of which are associated with soaps and some with anionic proteinaceous residues), and partly sterically by adsorbed proteinaceous residues. Again, hydration of the adsorbed molecules may make a significant contribution to the colloid stability, but the extent of this contribution is at present unknown. One possible reason for the difference in behaviour between ammonia-preserved natural rubber latex and carboxylate-stabilised synthetic latices when polyvinylmethyl ether is present may be that the steric stabilisers in natural rubber latex provide a mechanical (or perhaps entropic) barrier between the latex particles at ambient temperatures, thereby preventing the particles from coming into sufficiently close contact to form a coherent network. It may be that, as the temperature of the latex is raised, the adsorbed proteinaceous residues become less hydrophilic, and so are less hydrated and extend less into the aqueous phase, their effectiveness as steric stabilisers being thereby reduced. In the case of the carboxylate-stabilised synthetic latices, steric stabilisation is largely absent, and thus coherent interparticle structures can form even at ambient temperatures. The principal objection to this hypothesis is that it makes the heat-sensitisation of ammonia-preserved natural rubber latex by polyvinylmethyl ether depend on the effect of temperature upon the solubility behaviour of the proteinaceous stabilisers, rather than upon that of the polyvinylmethyl ether itself. This seems to be inherently incorrect.

As regards the aqueous phases of the two types of latices, there are again marked differences. The aqueous phases of the carboxylate-stabilised synthetic latices were relatively simple, containing only ions derived from the polymerisation initiator and the carboxylate-soap stabiliser. The aqueous phase of ammonia-preserved natural rubber latex is far more complex, containing various inorganic ions together with a wide variety of organic species derived by hydrolysis of constituents of the cells of which the fresh latex was the sap. It seems likely that the reason for the difference in behaviour between ammonia-preserved natural rubber latex and carboxylate-stabilised synthetic latices when polyvinylmethyl ether is present lies in these differences in the aqueous phases of the two types of latex. It is possible that, in the case of the carboxylate-stabilised synthetic latices, the polyvinylmethyl ether molecules adsorbed on contiguous latex particles are able to associate with each other at ambient temperature, thereby causing the development of interparticle structures within the latex. This can occur at ambient temperatures because the solubility of polyvinylmethyl ether in water at such temperatures is borderline and can be adversely affected by a change in environment such as that brought about by adsorption at a polymer surface. In the case of ammonia-preserved natural rubber latex, the solubility of polyvinylmethyl ether molecules in the aqueous phase may be enhanced by association with, say, some of the dissolved proteinaceous residues present in the aqueous phase, so that colloidal destabilisation requires elevation of the temperature. If this is so, then we have an explanation as to why the temperature at which the colloidal destabilisation of ammonia-preserved natural rubber latex containing polyvinylmethyl ether is first observed is considerably higher than the temperature at which polyvinylmethyl ether first precipitates out of solution in water.

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

Françoise CANDAU

EFFECT OF THE MICROEMULSION POLYMERIZATION PROCESS ON COPOLYMER STRUCTURE
(in collaboration with J.M. Corpart, J. Selb)

In the previous Newsletter, we have reported on some characteristics of polyampholytes formed by copolymerization of methacryl-oyloxyethyltrimethylammonium chloride (MADQUAT) and sodium-2-acrylamido-2-methylpropanesulfonate (NaAMPS) in microemulsions.

The reactivity ratios values calculated from various methods (Kelen-Tüdos, Fineman-Ross and Tidwell-Mortimer) were found to be $r_{MADQUAT}$ = 1.97 and r_{NaAMPS} = 0.81 (see previous report). This shows that the monomer sequence distribution is almost random ($r_1 . r_2$ = 1.6). On the contrary, the reactivity ratios of NaAMPS and MADQUAT for copolymers prepared in homogeneous aqueous solution are found to be : $r_{MADQUAT}$ = 0.64 and r_{NaAMPS} = 0.07 in favor of a monomer sequence distribution close to alternative ($r_1 . r_2$ = 0.045).[1] (Fig.1).

These results confirm other studies of Candau et al.,[2] and Kozakiewicz and Lipp.,[3] which have shown that the reactivity ratios values of various pairs of water-soluble monomers are affected by the microenvironment, especially when the monomer(s) involved is ionogenic. As seen in Table 1, the reactivity ratios of monomer pairs depend upon whether the polymerization reaction medium is a homogeneous solution, emulsion or microemulsion. More precisely, the values found in solution and in emulsion correspond closely but strongly differ from those in microemulsion. An interesting finding is that the microemulsion polymerization seems to improve the structural homogeneity of the copolymers since in all the cases investigated, the reactivity ratios values tend towards unity. In this respect, the case of poly(acrylamide-co-sodium acrylates) is particularly remarkable. A careful ^{13}C NMR study[2] has shown that the monomer sequence distribution is perfectly random since it obeys Bernouillian statistics with reactivity ratios both close to unity. The average copolymer composition was also found to be independent of the degree of conversion.

These results can be qualitatively interpreted by considering the differences between microemulsion polymerization and the other processes, namely mechanism and microenvironment. With regard to polymerization mechanism, the copolymerization reactions quoted above were performed in bicontinuous microemulsions. However, the bicontinuous structure breaks up as soon as the polymerization starts because of an increase of the interfacial tension due to monomer consumption from the w/o interlayer. Therefore, at finite conversion, the system becomes similar to that obtained when the initial microemulsion is of globular type. Reactivity ratios close to one indicate that at any time, a growing chain does not show any preference for either one of the monomers. A

mechanism based on interparticular collisions followed by complete mixing of the particles content accounts fairly well for the data. In this case, the monomer proportions at the reactions sites would be maintained throughout the polymerization at their initial values, thus generating a homogeneous microstructure.

However, this explanation may be too simplistic, since some deviations from unity are observed. Various causes may be at the origin of these deviations. Some partial monomer diffusion through the organic phase could favor the reactivity of one monomer with respect to the other, because of different water solubilities. Also, some local monomer concentration variations can occur for example in the neighboring of the interface formed of nonionic surfactants owing to salting-out effects of different amplitudes. This would result in some preferential sequences of either one of the monomers along the copolymer backbone.

On the other hand, the microenvironment plays also a major role in the monomer sequence distribution. The high local monomer concentration (3-5 M) compared to that in solution ($\simeq$ 0.5-1 M) produces an increased screening of the polyions by the small ions in the solution. This would reduce repulsions for example between neighboring acrylate units (case of poly(acrylamide-co-sodium acrylates)) or attractions between NaAMPS and MADQUAT monomers (case of polyampholytes). In particular, in the latter case, the formation of associated monomer pairs which takes place in aqueous solution, as suggested by the almost alternated sequence distribution, should be strongly diminished. Thus, the intrinsic reactivity of the monomers could prevail over the electrostatic interactions.

Comparing the inverse emulsion and microemulsion data, it is not possible to only involve charge screening arguments to explain the differences because the local concentrations are similar. The difference in mechanism should also come into play. In the inverse emulsions, monomer diffusion from source droplets to the polymerization locus is thought to be an important step. Since the two monomers have different solubilities in the organic phase, their concentrations at the polymerization locus might be different from those in the source droplets. Reactivity ratios obtained by using the droplet concentrations as those of reacting monomers could be apparent rather than true reactivity ratios.

If the results obtained in microemulsions were confirmed for other monomer pairs, microemulsion polymerization would be an attractive method to produce copolymers of homogeneous composition.

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5) C. Pichot, C. Graillat, V. Glukikh and M.L. Llauro, *Polymer Latex II* (Plastic Rubber Institute, London, 1985) p.II/1.
6) D. Hunkeker, A.E. Hamielec and W. Baade, *Polymers in Aqueous Media*, J.E. Glass, Ed. (ACS Symposium, Series n° 223, 1989) Chap.10, pp.175-190.

Table I. Reactivity ratios values for some monomer pairs

Monomer Pair	Aqueous Solution r_A	r_B	Emulsion r_A	r_B	Microemulsion r_A	r_B
Acrylamide (A)	0.95	0.30	1.06	0.29	0.95	0.89
Sodium acrylate (B) (pH=9)	(ref.4)		(ref.5)		(ref.2)	
Acrylamide (A)	0.43	2.39	Values close to those in solution		0.74	1.23
MADQUAT (B)	(ref.6)		(ref.6)		(ref.3)	
NaAMPS (A)	0.07	0.64	-		0.81	1.97
MADQUAT (B) (pH = 7)	(ref.1)				(ref.1)	
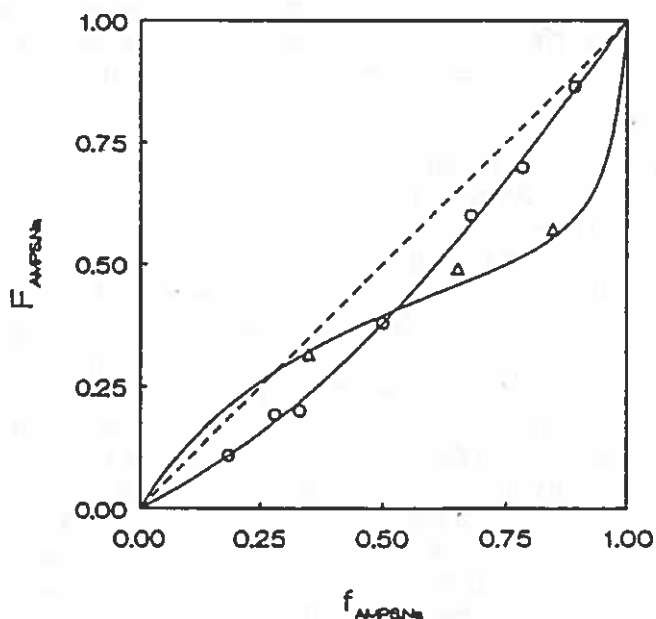
Figure 1 : Variation of average copolymer composition with feed composition for polyampholytes obtained at low degrees of solution : (Δ) : in solution
(O) : in microemulsion

Contribution to the International Polymer Colloids Group Newsletter

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The titles of our current research projects are given in the Contents of our Graduate Research Progress Reports, No. 36, July, 1991, which can be found at the end of this report. Summaries of progress in several research areas are presented here.

1. Development of Particle Morphology in Artificial Composite Polymer Latexes
   (Yi-Cherng Chen)

Two artificial composite latexes were prepared by the method of direct emulsification using solutions of polystyrene (PS) and poly(methyl methacrylate) (PMMA) in toluene followed by removal of the solvent. The two latexes differed in that the polymers used had higher molecular weights in the first case (designated PS-1s/PMMA-1s) as compared to the second (PS-2s/PMMA-2s). The final particle morphology of the PS-2s/PMMA-2s composite latex particles showed the PMMA domains to be partially covered by the PS. However, the PS-1s/PMMA-1s particles showed a reverse morphology where the PS was partially engulfed by the PMMA. These observed morphologies were found to be consistent with the interfacial tensions measured between individual polymer solutions and the surfactant containing aqueous phase as determined by the drop volume method. The phase with the higher polymer/aqueous phase interfacial tension is engulfed by that with the lower interfacial tension.

Extended mixing of the swollen composite latex particles prior to solvent removal produced different results for the PS-1s/PMMA-1s latex. Subjecting the latex (polymer concentration in toluene = 0.35 gm/cm^3) to 30 days end-over-end mixing at room temperature resulted in the formation of individual PS and PMMA particles. This did not occur in the second latex. This phenomenon could be due to the differences in molecular weights of the polymers used in the preparations. The use of the the lower molecular weight polymers is expected to result in a lower polymer/polymer interfacial tension (i.e., for the PS-2s/PMMA-2s system) and an increase in the thickness of the interfacial mixing zone between the two polymers preventing complete phase separation. The PS-2s/PMMA-2s latex was further treated by removing the toluene and reswelling with cyclohexane which is a good solvent for PS and a nonsolvent for PMMA. After mixing for 30 days at room temperature some individual PS and PMMA particles were observed coexisting with composite particles which showed varying sizes and shapes of the PMMA domains. These results indicated that the formation of PS and PMMA individual particles was mainly due to the shear forces and milling action encountered during the mixing of the swollen particles. The degree of phase separation between polymers in composite particles can therefore be affected by agitation depending on the viscosity of the polymer phases and the interfacial tension or degree of mixing at the polymer/polymer interface.

2. Dynamic Stability Studies of Miniemulsion Droplets Using Capillary Hydrodynamic Fractionation (Chris Miller)

Miniemulsions are made up of stable, submicron (50 - 500nm), oil-in-water droplets stabilized by use of a surfactant and "co-surfactant". When a monomer such as styrene is used as the oil phase, these emulsions can be polymerized creating a latex. Nucleation has been shown to occur chiefly in the small monomer droplets. It is thus expected that the size and size distribution of the miniemulsion droplets before and during the polmerization has a great effect on the observed polymerization kinetics. Therefore, a systematic study of the effects of important preparative variables on the size of miniemulsion droplets should provide useful information for understanding various mechanistic aspects of the polymerization, particularly during the nucleation stage of the reaction.

Preliminary experiments were conducted in an effort to find an accurate and rapid means of determining miniemulsion droplet sizes. Established techniques, such as light scattering and electron microscopy, proved to be deficient, requiring much dilution or time for sample preparation. Capillary Hydrodynamic Fractionation (CHDF), a relatively new technique for sizing colloidal particles, was considered a viable alternative for the rapid determination of the size of miniemulsion droplets. CHDF was applied to the measurement of droplet sizes of minemulsions prepared with toluene as the oil phase and sodium dodecyl sulfate/cetyl alcohol as the stabilizer system. An example of a fractogram for a miniemulsion is given in Figure 1 relative to a marker species.
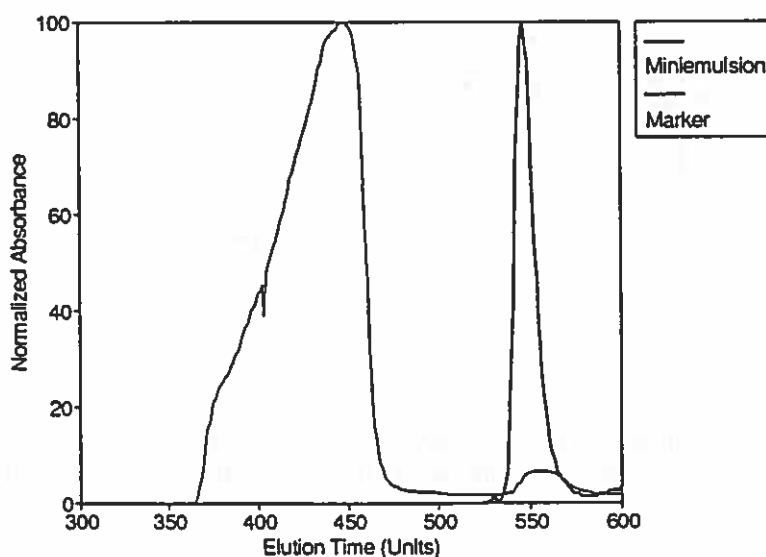
Figure 1. *CHDF Fractogram obtained for a miniemulsion prepared with 10mM sodium lauryl sulfate, 30mM cetyl alcohol (both based on the aqueous phase), and 20% toluene as the oil phase.*

The work performed thus far has focused on the determination of the stability of miniemulsion droplets prepared varying the amount and type of co-surfactant and the means of shearing the system. The stability of these systems is followed by observing the change in the volume average size of the droplets as a function of time for periods of up to four hours, typically the maximum lifetime of droplets from the moment of preparation until the final disappearance in a miniemulsion polymerization. Several important pieces of information may be dervived from such

a study. First, the optimum conditions for preparing miniemulsions with a specific droplet size may be determined directly, as opposed to secondary methods such as the determination of the free surfactant or the observation of the polymerization kinetics and the resulting particle size. Second, by comparing the size changes with time for different systems, a more fundamental understanding of the stabilization mechanism might be obtained. Figure 2 shows the time evolution of the average droplet diameter (determined from the position of the peak maximum in the CHDF chromatogram) as a function of the amount of co-surfactant (cetyl alcohol) used in the recipe. These results show that an increased amount of co-surfactant leads to smaller droplets as expected. More importantly, they show what appears to be period of "instability" in the droplet size which increases to a plateau value. This phenomenon has not been observed before due to the unavailability of a rapid measuring technique. Further studies designed to expand and clarify these findings are currently underway.
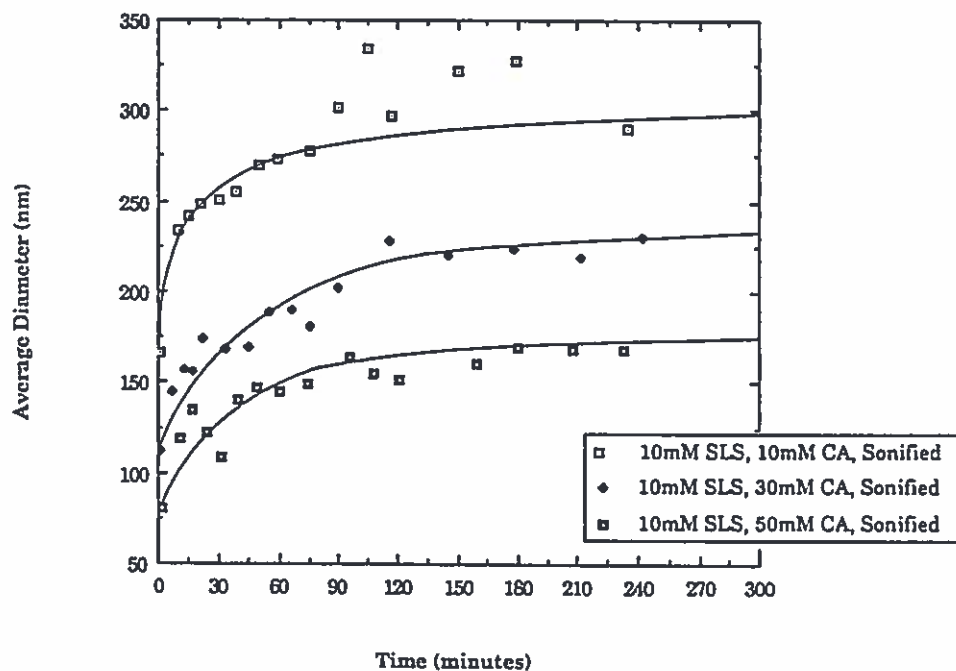
Figure 2. *Time evolution of the average droplet sizes of miniemulsions prepared with 10mM sodium dodecyl sulfate and 20% toluene as the oil phase as a function of the amount of added cetyl alcohol co-surfactant.*

3. Emulsion Polymerization of Vinyl Acetate Using a Polymerizable Surfactant
   (Belen Urquiola)

Reactive surfactants containing a polymerizable group can irreversibly bind to the surface of latex particles greatly increasing their colloidal stability. A reactive surfactant of the type sodium alkyl allyl sulfosuccinate (TREM LF-40, Henkel) containing a vinyl group is being used in the emulsion polymerization of vinyl acetate.

Kinetic studies were conducted varying the TREM LF-40 concentration using the recipe given in Table I. Figure 3 shows the effect of the reactive surfactant concentration on the conversion-time behavior in the emulsion polymerization of vinyl acetate. Surprisingly, the rate of polymerization was found to increase with decreasing surfactant concentration. This is the oppo-

site of the usual behavior found in conventional emulsion polymerization where the rate increases with increasing surfactant concentration.

Table I. Recipes for Copolymerization of TREM LF-40 with Vinyl Acetate at 60°C.

Recipe Component	Concentration[a]	Weight (g)
TREM LF-40[b]	16.7 -50.1 mM	0.5 - 2.25
Vinyl Acetate	5.0 mM	45.0
H_2O	-----	105.5
$NaHCO_3$	2.87 - 11.5 mM	0.025 - 0.1
$Na_2S_2O_8$	1.01 - 4.06 mM	0.025 - 0.1

[a] based on water
[b] based on solid active ingredients
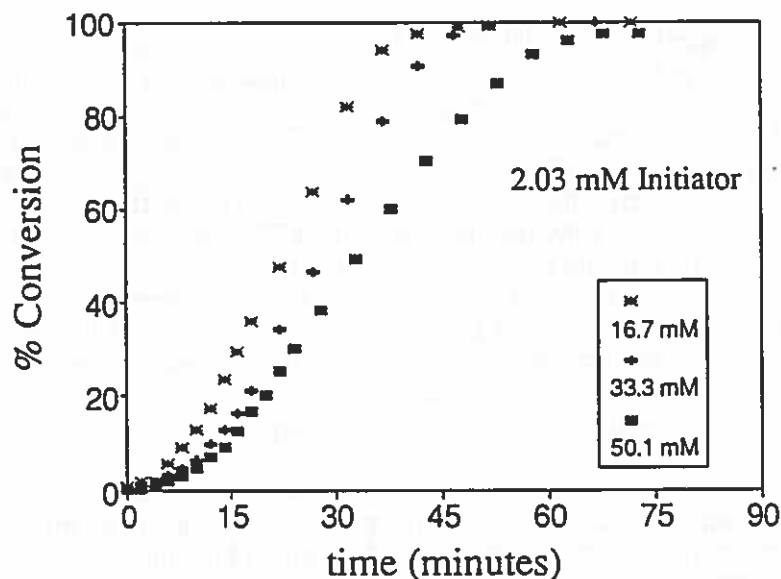
Figure 3. *Effect of TREM LF-40 concentration (based on water) on conversion-time behavior for the emulsion polymerization of vinyl acetate at 60°C.*

It is well known that there is a difference between allyl copolymerizations and ordinary vinyl copolymerizations. Chain transfer between an active growing chain and an allylic monomer can lead to the termination of the kinetic chain as well as the growing polymer chain. To test the possibility that chain transfer is the cause of the results shown in Figure 3, the efficiency of TREM LF-40 as a chain transfer agent was measured. The resulting value of C_s for TREM LF-40 and other chain tranfer agents are given in Table II. The chain transfer constant obtained for TREM LF-40 indicates that chain transfer may occur during the polymerization. However, this constant is much lower than the values found for typical chain transfer agents such as mercaptans. This might indicate that even though chain transfer may be one of the mechanisms affecting the polymerization kinetics, there can be other causes for the observed behavior as well.

Table II. Chain Transfer Constants for Various Chain Transfer Agents
with Vinyl Acetate at 60°C.

Transfer Agent	$C_s \times 10^4$	Reference
Monomer	1.75 - 2.8	1
Polymer	1.2 - 8	1
Isopropylbenzene	89.9	2
TREM LF-40	110	this work
Chloroform	150	2
Carbon Tetrachloride	10,700	2
n-Butyl Mercaptan	480,000	2

1. *Polymer Handbook*, Brandrup, J. and Immergut, E.H., Eds., Wiley-Interscience, New York, 1975.
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Due to the hydrophilicity of TREM LF-40, as well as the high water solubility of vinyl acetate, it is likely that the polymerization in the aqueous phase plays a significant role. Therefore, the composition of the aqueous phase was studied using Fourier Transform Infrared Spectroscopy (FTIR). For TREM LF-40, the characteristic peak is at 1052 cm^{-1} corresponding to the S=O stretch of the sulfonate salt. For PVAc, the C-C-C symmetric stretch at 1025 cm^{-1} was used as the characteristic peak. Samples taken during the polymerization, as well as the final latex, were centrifuged and the serum separated from the polymer particles. The FTIR absorbance spectrum of the serum was then measured. In this way the composition of the aqueous phase was obtained. Figure 4 shows the spectrum of the aqueous phase corresponding to a latex prepared with TREM LF-40. It is important to point out that both TREM LF-40 and PVAc are present in the aqueous phase as indicated by the presence of both characteristic peaks in the spectrum. The presence of PVAc in the aqueous phase may be due to copolymerization of VAc and TREM LF-40 in the aqueous phase together with the increased water solubility of the copolymer.

Another important result of the aqueous phase analysis is related to the concentration of TREM LF-40 in the serum. In order to separate the polymer particles from the aqueous phase, the latex samples were centrifuged for 7 hours at 30,000 rpm. Thus, not only the components dissolved in the aqueous phase but also the species that were adsorbed on the polymer particles were removed. Therefore, only the materials chemically bound in or on the particles remained with the particles. Only part of the initial amount of the added TREM LF-40 was detected in the aqueous phase at the end of the polymerization indicating that most of it reacted and was incorporated in or on the particles.

Further work is now being conducted with the analogue surfactant without the vinyl group (hydrogenated TREM) for comparison to these results.

4. Dispersion Polymerization of n-Butyl Acrylate for Impact Modifier Applications
   (Gilbert Garcia)

The incorporation of a rubber phase into a continuous plastic matrix increases its flexibility and provides significant inprovements in toughness. In a core/shell or multilayered impact modifier particle, the outer polymer layer will be in contact with the polymer matrix and thus these two

polymers should be compatible with each other. The polymer particles that we are interested in preparing as impact modifiers consist of a poly(n-butyl acrylate) core polymer covered by a shell of polystyrene.
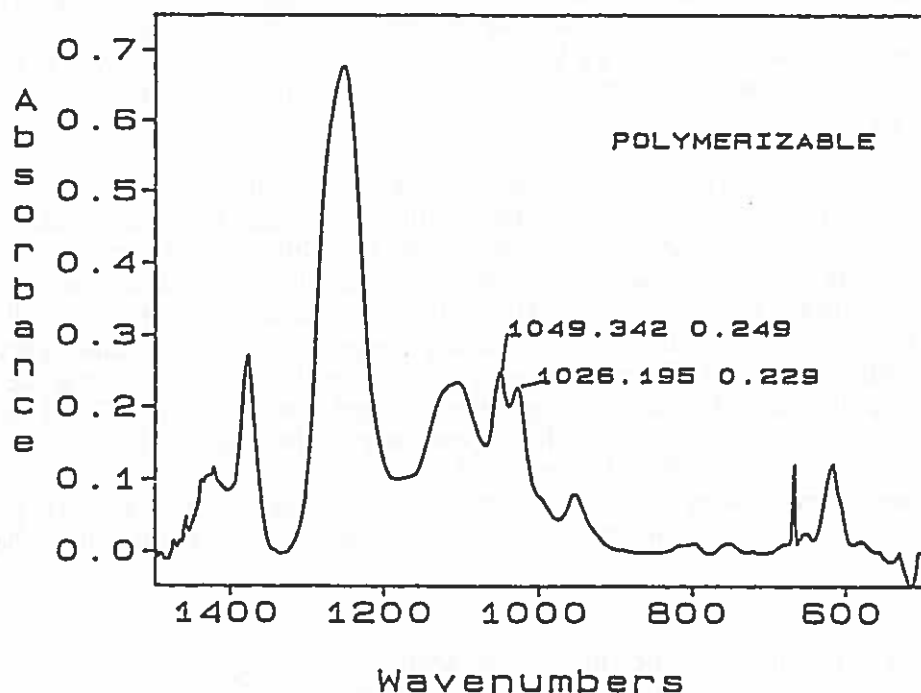

Figure 4. *FTIR spectrum of the aqueous phase of a latex prepared with TREM LF-40.*

The core particles were prepared by dispersion polymerization of n-butyl acrylate via batch reaction in bottle reactor at 70°C. Unlike polystyrene which precipitates from the continuous ethanol phase to form polymer particles, poly(n-butyl acrylate) was found to be completely soluble in ethanol. The solubility parameter of the dispersion medium was increased by the addition of water to the ethanol which subsequently produced micron sized poly(n-butyl acrylate) polymer particles by dispersion polymerization. The recipe used is presented in Table III.

Table IIL Dispersion Polymerization of n-Butyl Acrylate at 70°C.

Components	Amount (g)
n-Butyl Acrylate	5.0
AIBN[a]	0.05
Ethanol	35.0
Distilled-deionized water	15.0
Aerosol OTS[b]	0.3
PVP[c]	0.5 - 0.15

[a] azobisisobutryonitrile (VAZO 64, DuPont)

[b] sodium dioctyl sulfosuccinate (Cyanamid)

[c] poly(vinyl pyrrolidone): PVP K-15 (M_w=10,000), K-30 (M_w=40,000), K-90 (M_w=360,000) (GAF)

Table IV shows the influence of the molecular weight of the polymeric stabilizer on the particle size and dispersity as determined by optical microscopy and light scattering (Coulter N4M). The amount of stabilizer was arbitrarily fixed at 2 wt% based on the continuous phase. The stabilization efficiency increased with increasing molecular weight of the PVP; the particle size decreased and narrowed with increasing PVP molecular weight. The T_g of poly(n-butyl acrylate) is -54°C, and at room temperature is very soft. Thus the particles require a high degree of stabilization as provided by the PVP K-90.

In order to use the poly(n-butyl acrylate) particles as the core in the impact modifier, it is necessary to crosslink the particles to prevent deformation. The crosslinking agent can be incorporated prior to or following the dispersion polymerization. Two difunctional monomers were tested as crosslinking agents: divinylbenzene (DVB) and ethylene glycol dimethacrylate (EGDM). A series of polymerizations was carried out using different amounts of each crosslinker and the degree of crosslinking was measured by determining the proportion of insoluble polymer in n-butanol (a good solvent for poly(n-butyl acrylate)) to the total polymer. Plotting the degree of crosslinking versus the molar fraction of crosslinker showed that DVB and EGDM have similar crosslinking efficiencies in this system. The dependence of the degree of crosslinking on the amount of crosslinking agent was found to follow the relationship, $D_{cl} = 1.5[M_{cl}]^{0.73}$ where $[M_{cl}]$ is the mole fraction of crosslinker in the monomer mixture. The particle size analysis showed that in order to preserve a narrow distribution, the amount of crosslinker in the monomer phase should be lower than 3 wt%.

Table IV. Results of Dispersion Polymerizations of n-Butyl Acrylate at 70°C
Using Different Grades of Polymeric Stabilizer

poly(vinyl pyrrolidone)[a]	PVP K-15	PVP K-30	PVP K-90
size or size range (μm)	3.0 - 7.0	1.75 - 2.5	1.61
standard deviation	broad	broad	12%
final solids content	10.2	10.4	10.8

solvent: EtOH/H$_2$O = 70/30, [AIBN] = 1 wt% based on monomer,
[n-butyl acrylate] = 10 wt%, [Aerosol OTS] = 0.6 wt% based on solvent
[a] concentration of stabilizer (PVP)=2 wt% based on solvent

With the seed particles prepared, experiments with the addition of the shell polymer (polystyrene) are currently underway.

Recent Presentations

The following were presented at the Gordon Research Conference on Polymer Colloids, Tilton, New Hampshire, July 1-5, 1991:

"Rheology of Associative Thickened Latexes", a paper by C.A. Silebi.

"Latex Film Formation and Chain Diffusion Across Particle Interfaces", a paper by A. Klein.

"Use of Compatibilizing Agents in Controlling Particle Morphology in Composite Latexes", a poster presented by V.L. Dimonie.

"Kinetics and Phase Transition of Polymer Adsorption on Colloidal Surfaces" a poster by D.H. Oy Yang.

"An Evanescent Wave Probe of Interfacial Phenomena in Polymer Systems" a poster by M.M. Santore.

The following were presented at the 7th International Conference on Surface and Colloid Science, Compiègne, France, July 7-13, 1991:

"Theoretical Aspects of Developing Latex Particle Morphology", a paper by Y.C. Chen, V.L. Dimonie, and M.S. El-Aasser.

"Polymerization of Reactive Surfactants", a paper by M.B. Urquiola, V.L. Dimonie, and M.S. El-Aasser.

"Adsorption, Stability, and Rheological Behavior of Latexes that Contain Model Associative Polymer", a paper by R.D. Jenkins, M. Durali, M.S. El-Aasser, and C.A. Silebi.

"Role of Surfactants in Emulsion Copolymerization of Acrylic Monomers with Vinyl Acetate", a poster by V.L. Dimonie, M.S. El-Aasser, and J.W. Vanderhoff.

"Effect of Electrostatic and van der Waals Forces on the Capillary Hydrodynamic Fractionation of Colloidal Particles", a paper by M. Durali and C.A. Silebi.

"Particle Size Distributions of Colloids by Capillary Hydrodynamic Fractionation Using a Photo-diode Array Detector", a poster by J. Venkatesan and C.A. Silebi.

Recent Publications

"A Biaxial Lytropic Nematic Phase in Dilute Solutions of Sodium Lauryl Sulfate-1-Hexadecanol-Water", C.C. Ho, R.J. Goetz, and M.S. El-Aasser, *Langmuir*, **7**, 630-635 (1991).

"Seeded Emulsion Polymerization of n-Butyl Acrylate Utilizing Miniemulsions", P.L. Tang, E.D. Sudol, M.E. Adams, M.S. El-Aasser, and J.M. Asua, *J. Appl. Polym Sci.*, **42**, 2019-2028 (1991).

"Preparation and Morphological Characterization of Microscopic Composite Particles", S. Shen, M.S. El-Aasser, V.L. Dimonie, J.W. Vanderhoff, and E.D. Sudol, *J. Polym. Sci., Polym. Chem.*, **20**, 857-867 (1991).

"Semicontinuous Seeded Emulsion Copolymerization of Vinyl Acetate and Methyl Acrylate", B. Urquiola, G. Arzamendi, J.R. Leiza, A. Zamora, J.M. Asua, J. Delgado, M.S. El-Aasser, and J.W. Vanderhoff, *J. Polym Sci., Polym. Chem.*, 29, 169-186 (1991).

"Steady-Shear and Linear-Viscoelastic Material Properties of Model Associative Polymer Solutions", R.D. Jenkins, C.A. Silebi, and M.S. El-Aasser, *ACS Symposium Series 462*, 222-233 (1991).

"Emulsion Copolymerization of Vinylidene Chloride and Butyl Methacrylate, 83:17 in Mol%", K.C. Lee, M.S. El-Aasser, and J.W. Vanderhoff, *J. Appl. Polym. Sci.*, 42, 3133-3145 (1991).

"Effect of Interfacial Phenonena on the Development of Particle Morphology in a Polymer Latex System", Y.C. Chen, V.L. Dimonie, and M.S. El-Aasser, *Macromolecules*, 24, 2779-2787 (1991).

"Effects of Electrolyte on Stability of Concentrated Toluene in Water Miniemulsions", R.J. Goetz and M.S. El-Aasser, *ACS Symposium Series 448*, 247-259 (1991).

Recent Ph.D. Dissertations

"Coagulation Studies of Polystyrene Latexes" by John Wydila.

"Preparation and Characterization of Water Absorbent Poly(Acrylamide-Co-Acrylic Acid Salt)'s" by Yin-Shen Chang.

"Kinetic Factors in Miniemulsion Polymerization" by Phan L. Tang.

"The Morphology of Microscopic Composite Particles Prepared by Two-Stage Polymerization" by Shiji Shen.

EMULSION POLYMERS INSTITUTE
Lehigh University

Graduate Research Progress Reports
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CONTENTS

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TIME-DEPENDENT SIZE DISTRIBUTIONS OF AGGREGATING COLLOIDAL SILICA

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Abstract

We develop a new scheme to monitor structures formed during the aggregation of colloidal particles. This approach, based on numerical inversion of the autocorrelation function measured in a dynamic light scattering experiment, provides a means to monitor both diffusion-limited (DLA) and reaction-limited (RLA) cluster aggregation processes. We combine the theory of light scattering with the Smoluchowski rate equation to model the intensity distribution of light scattered by colloidal aggregates. We use a constrained inverse Laplace Transform routine, CONTIN, to track the cluster intensity distribution of Ludox HS and SM silica colloids as a function of time. A fit of the model prediction to the output from CONTIN provides fractal dimensions, d_f, agreeing with those from static light scattering measurements for both DLA and RLA. We observe an increase of d_f with aggregation time in DLA, indicating a possible reorganization of clusters after they aggregate; this phenomenon does not appear in RLA. The polydispersity exponent τ for the power-law mass distribution for RLA clusters is 1.5. A consistent decrease of τ with aggregation time is attributed to the presence of rotational diffusion associated with large clusters. We are currently investigating the aggregation behavior of silica colloids in the presence of adsorbing polymers.

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Visualization of magnetizable particle aggregation

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We investigate the magnetic field-induced aggregation of micron-size superparamagnetic polystyrene latex particles suspended in an aqueous solution. As a result of field-induced dipole-dipole interactions, the particles aggregate into long chains and crosslinked networks. We have used video-enhanced optical microscopy to characterize this aggregation process. We collect images from a video camera on a frame grabber installed in a personal computer. Then, we process images on a Silicon Graphics Personal Iris workstation. At low solid volume fractions, aggregates are linear chains of particles aligned parallel to the external field. We identify each cluster in a given picture and determine the cluster size distribution and the moments of this distribution. This statistical anlysis is repeated at each recorded time step. The mean chain length increases as the square root of time while the total number of particle clusters decreases as the inverse square root of time. This result is consistent with experimental results on other systems with dipolar interactions and with numerical simulations of diffusion-limited aggregation. There is a characteristic time scale for aggregation which is inversely proportional to the square of the applied magnetic field. At higher volume fractions, aggregation results in thick fibers of particles as thin chains coalesce side by side. A further increase in solid content leads to a crosslinking of the fibers. We believe this crosslinking step has an important influence on the rheological properties of the suspension and of related systems such as the electro-rheological fluids.
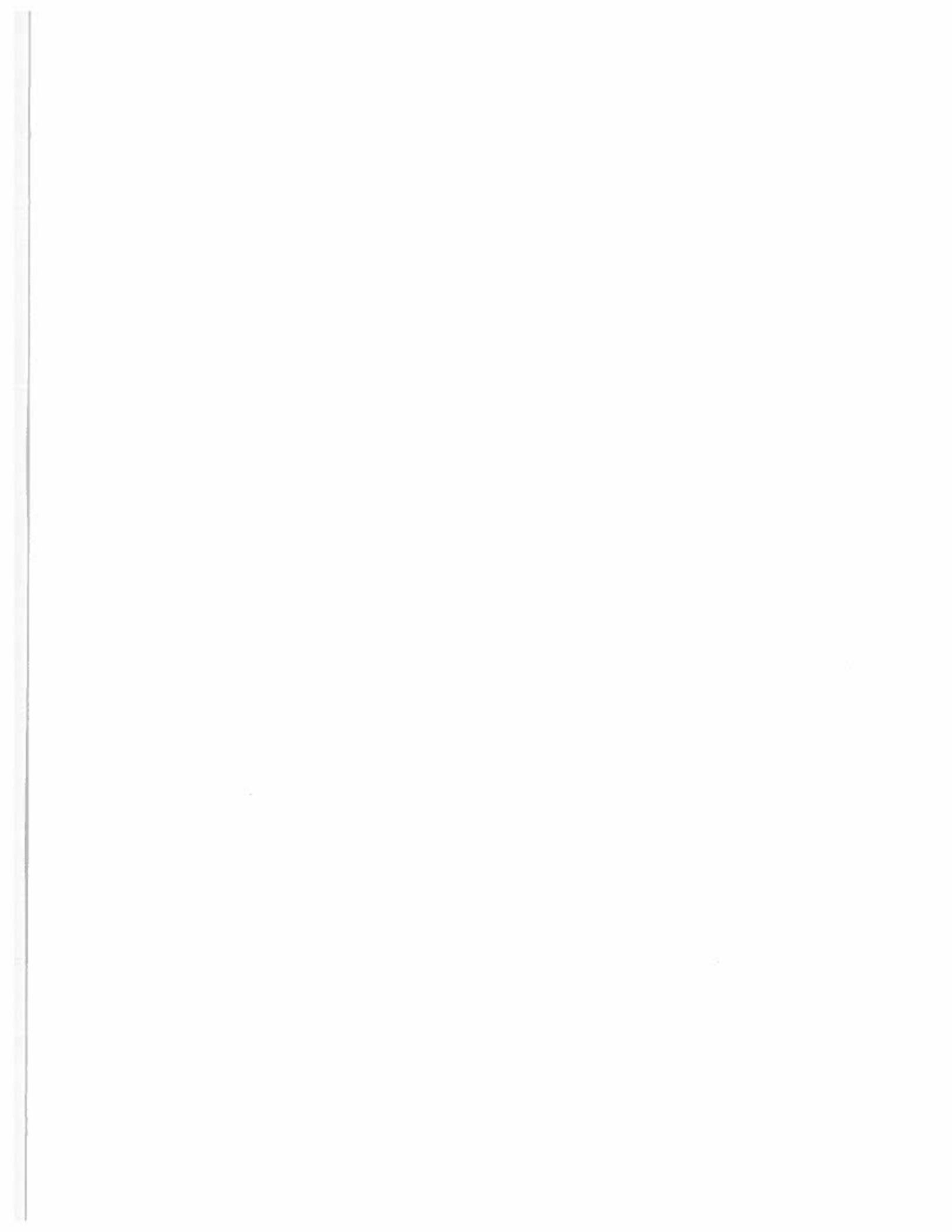
Dynamics of Polymer Induced Colloidal Aggregation

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The structure and dynamics of aggregation processes are dictated by the forces between the aggregating particles. Colloidal dispersions are well-suited to the study of this process because of our ability to manipulate these interactions. Ions in solution, for example, will screen repulsions between colloidal particles leading to irreversible aggregation due to London van der Waal forces. One can also induce an attraction between particles through the addition of non-adsorbing polymer. This interaction, normally smaller in magnitude than those due to either charge repulsions or van der Waals forces, occurs at separations less than two times the polymer radius. The addition of polymer thus allows us to fine tune both the magnitude and range of the interparticle potential, and thereby vary aggregate structure and dynamics with somewhat dramatic results. We can alter a suspension to produce a variety of structures from low density, irreversibly grown aggregates to dense, equilibrium clusters. In addition, the dynamics vary from catastrophic growth at high polymer concentrations, and a correspondingly high interaction strength, all the way to a slow nucleation and growth process at polymer concentrations approaching the equilibrium phase boundary. We study the aggregation experimentally; dynamic light scattering provides us with a means to observe, *in situ*, the aggregation process. Information such as average cluster size and aggregate nucleation time can be monitored for comparison to theoretical predictions. To make these predictions, we require free energies of both colloidal solid and liquid phases and calculate them using a new approach combining density functional and perturbation theories. Phase diagrams are then generated along with interfacial energies for inclusion into a classical nucleation theory for a prediction of cluster evolution.

September 1991

Study of surface active initiator ("inisurf")
in a seeded
emulsion polymerization of styrene.

Kusters, J.; German, A.; Napper, D.; and Gilbert, R.

A study has been carried out of the seeded kinetics of particle growth in an emulsion polymerization of styrene, where initiation is by a surface active initiator ("inisurf"). The inisurf is synthesized by an esterification of 4,4'-azobis(4-cyanopentanoic acid) and a poly(ethylene oxide) nonylphenol.

The aim was to study the behaviour of surface active radicals at the surface of the particles; hence requiring a seed which had exceptional stability, that could, after thorough cleaning with ion-exchange resin, be swollen with monomer in the complete absence of added surfactant. This was accomplished by using sodium p-styrenesulphonate as comonomer in a surfactant free emulsion polymerization of styrene.

It is shown that the emulsion polymerization of these clean seeds with inisurf is characterised by a low ñ (average number of radicals per particle).

The rate coefficient (k) for exit was obtained using gamma-radiolysis relaxation experiments, using the non-initiating equivalent of the inisurf. The resulting value for k is then used to determine ρ (entry rate coefficient) of the inisurf system and subsequently to determine the initiator efficiency in seeded studies initiated by inisurf, with varying surface coverages of the inisurf.

It is found that initiator efficiency is very low (ca. 0.04%) and is independent of surface coverage of inisurf. This result is readily explained qualitatively and quantitatively by comparison of the time for geminate recombination of the two free radicals formed by inisurf decomposition with the time for escape by diffusion of one of those free radicals from the surface of the particle.

Partial Swelling of Latex Particles with Monomers

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SUMMARY:

Two methods are described for experimentally determining the concentrations of monomer in both the aqueous phase and latex particle phase during partial swelling of latex particles, and therefore also during Interval III of an emulsion polymerization. The ratio of the monomer aqueous phase concentrations, both below and at saturation, can be related to the volume fraction polymer in the latex particles via the Vanzo equation[1,2]. Experiments for the methyl acrylate and poly(methyl acrylate-co-styrene) system show that monomer partitioning is very insensitive to temperature, latex particle radius, polymer composition, polymer molecular weight and polymer cross-linking. Thermodynamic treatment of these new results and previously published partitioning results (styrene in polystyrene[3], methyl methacrylate in poly(methyl methacrylate)[4], and vinyl acetate in poly(vinyl acetate)[5]) show, at higher volume fractions of polymer, that the conformational entropy of mixing of monomer and polymer is the significant term in determining the degree of partial latex particle swelling by monomer (Fig.1). Theoretical predictions of experimental results are quite insensitive to values of the Flory-Huggins interaction parameter and to the latex particle-water interfacial tension. A simple model is developed for the estimation of monomer partitioning which requires only the saturation monomer concentrations in the particle and aqueous phases.

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Theory of Partial Swelling of Latex Particles by Monomers: Vanzo et al.[1] were the first to derive an analogue for the Morton equation that dealt with partial swelling of latex particles. Gardon later derived the same expression.[2] If the latex particles are not saturated by monomer then there is no pure monomer phase present (i.e. no monomer droplets). The partial molar free energy of the monomer in the latex particle phase is then given by:[1]

$$\Delta F = R \, T \, \ln (a) \tag{1}$$

where a is the activity of the monomer. Vanzo et al. pointed out that the monomer activity can be approximated by p/p_0 – the ratio of the vapor pressure of the monomer at a given volume fraction of polymer (p) to the vapor pressure at saturation swelling (p_0). Gardon[2] showed that, since Henry's Law holds for latex free water, the ratio p/p_0 can be approximated by the ratio of the aqueous phase solubilities of monomer below and at saturation:

$$\frac{p}{p_0} = \frac{[M]_{aq}}{[M]_{aq,sat}} \tag{2}$$

where $[M]_{aq}$ is the concentration of monomer in the aqueous phase and $[M]_{aq,sat}$ is the saturation concentration of monomer in the aqueous phase.

The final result for partial swelling of latex particles by monomer and solvents, hereafter called the Vanzo equation, is:[1,2]

$$\ln (1 - v_p) + v_p \left(1 - \frac{1}{M_n}\right) + \chi \, v_p^2 + \frac{2 \, V_m \, \gamma \, v_p^{1/3}}{R_0 \, R \, T}$$
$$= \ln \left(\frac{[M]_{aq}}{[M]_{aq,sat}}\right) \tag{3}$$

where v_p is the volume fraction of polymer in the particle, M_n the average polymer degree of polymerization, χ the Flory-Huggins interaction parameter, V_m the molar volume of monomer, γ the latex particle-water interfacial tension, R_0 the latex particle unswollen radius, R the gas constant and T the temperature.

Estimation of monomer partitioning: First, estimate the value of the sum of the residual free energy and the particle-water interfacial free energy terms in the Vanzo equation from the

2

saturation swelling volume fraction of polymer. This can be done by utilizing the Morton equation:[6] we calculate a correction term:

$$\text{corr.} = -\left[\ln\left(1 - v_{p,sat}\right) + v_{p,sat}\right] \tag{4}$$

where $v_{p,sat}$ is the volume fraction of polymer in the latex particles at saturation swelling by monomer. Then we can utilize this correction term in the Vanzo equation:

$$\ln\left(1 - v_p\right) + v_p + \text{corr.} = \ln\left(\frac{[M]_{aq}}{[M]_{aq,sat}}\right) \tag{5}$$

Note that, for simplicity, we have ignored the contribution of polymer molecular weight upon the partial molar free energy of mixing of monomer and polymer in eq.4-5 (i.e. $M_n \gg 1$). The approach used to derive eq. 5 incorrectly assumes that the both the interfacial free energy and the residual free energy term are independent of the volume fraction of polymer. However, since the absolute values of these terms are small compared to the conformational entropy term, this approach, as a first estimate, gives quite good results for the MA-poly(methyl acryate-co-styrene) system (Fig.2). Comparison of the predictions of eq.5 with more experimental results are needed before complete confidence can be expressed in this approach. It is important to note that the only parameters needed to predict the partial monomer partitioning between the latex particle and aqueous phases by this approach are the saturation concentrations of monomer in the particle and aqueous phases.

Experimental Part: A number of seed latices were prepared, composed of polystyrene, poly(methyl acrylate), and copolymers of these two polymers. The monomer utilised in these experiments, methyl acrylate (MA), was added to a sample of the latex and allowed to come to thermodynamic equilibrium between the two phases, after which the latex and water phases were separated by two separate means, ultracentrifuge and dialysis. The concentration of monomer in each phase was determined by GC.
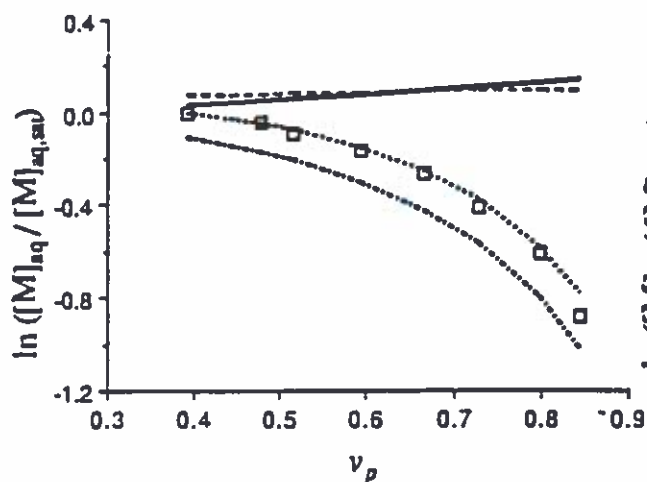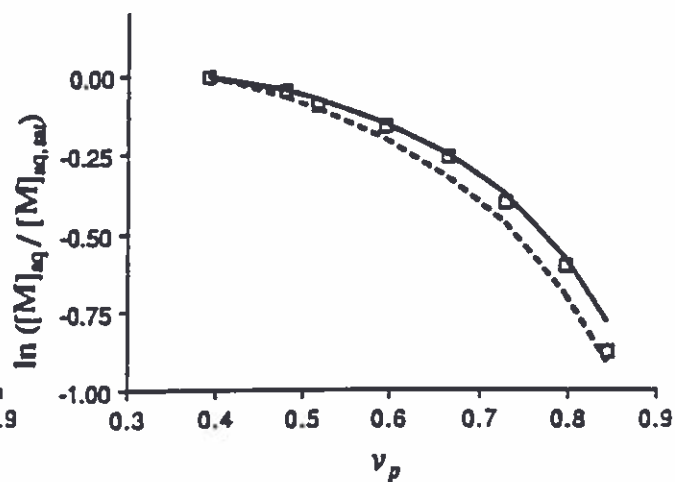
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FIG. 1. FIG.2

Fig. 1. Comparison of theoretical predictions and experimental measurements of MA partitioning at 45°C for seed latex SMA6 (R_0=32 nm, 25:75 copolymer of styrene and methyl acrylate). Theoretical predictions: conformational entropy term given by $\ln([M]_{aq}/[M]_{aq,sat})=\ln(1-v_p)+v_p$ (—·—·—); residual free energy term given by $\ln([M]_{aq}/[M]_{aq,sat})=\chi v_p^2$, with χ=0.2 (———); interfacial free energy term given by $\ln([M]_{aq}/[M]_{aq,sat})=2V_m\gamma v_p^{1/3}/R_0RT$, with γ=45 dyne.cm^{-1} (-----); and Vanzo equation (eq. 3) with χ=0.2 and γ=45 dyne.cm^{-1} (··········).

Fig. 2. Comparison of theoretical predictions and experimental measurements of MA partitioning at 45°C for latex SMA6. Theoretical predictions with Vanzo equation (eq.3) (χ=0.2 and γ=45 dyne.cm^{-1}) (———) and eq.5 (corr.=0.1) (-----).

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Dr. Hans Kast

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Dispersionen

Contribution to Polymer Colloid Group Newsletter

Crystals made of close packed polymeric spheres

- a neutron scattering study on latex films

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The dense packing of polymeric spheres in latex films has been investigated by means of small angle neutron scattering. The films were prepared by complete evaporation of the water out of a dispersion consisting of monodisperse charged spherical polymeric particles with a diameter in the submicron range. Analysis of the Bragg peaks which were found in the intensity versus scattering vector curves reveals that the close packed particles are arranged in a face centered cubic lattice structure. An interesting suppression of some Bragg peaks due to the influence of the particle scattering form factor is observed. Taking into account the smearing of the peaks by apparatus effects it can be seen that a well developed order with extended crystalline domains is realized in the latex films. The process of structure formation is a very robust one which hardly can be suppressed in the present system by varying the rate at which the water is evaporated during the film formation. Furthermore, it is found that the system still owns memory about its initial structure upon prolonged annealing at temperatures far above its glass temperature.

THE UNDERESTIMATION OF ZETA POTENTIALS OF POLYSTYRENE LATICES AT LOW IONIC STRENGTH

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Zeta potentials of latices are usually inferred from electro-phoretic mobilities. For the required conversion it has become customary to use the O'Brien-White theory, which duly accounts for relaxation phenomena but does not consider any contribution of surface conductance that takes place between the particle surface and the slipping plane, the so called anomalous surface conductance. Midmore and Hunter (1) have shown already that this anomalous conductance can be substantial and dramatically influences the calculated value of the zeta potential at low ionic strengths. Among other things, correcting for this effect eliminates the maximum in the zeta potential as a function of ionic strength, despite the obvious maximum in the mobility vs. concentration.

Also in our electrokinetic investigations on positive and negative latices have we encountered the substantial effect of anomalous conductance on the zeta potential, both in electrophoresis and in streaming potential measurements. Fig.1 (R.Hidalgo Alvarez et al. (2)) illustrates the large differences in zeta potentials of a positive latex as a function of ionic strength as obtained with the classical Smoluchowski equation (lower line) or the O'Brien-White theory (middle line), respectively when correcting for anomalous conductance according to Dukhin-Seminikhin (upper line). A most important consequence of these observations is that serious errors can be made if these differences are ignored in the interpretation of stability measurements.

In experiments with plugs of the same samples of which the electrophoretic mobilities had been measured, the values of the surface conductance could be experimentally established. They proved to be much higher than calculated from the Bikerman theory . When these high conductance values are not properly accounted for, once more at low electrolyte concentrations far too low values of the zeta potential are obtained (van der Linde and Bijsterbosch (3)).

Fig.2 shows that when all corrections are taken into account, the results reasonably match, although at low concentrations those for electrophoresis (squares) are yet higher than those for streaming potentials(circles). These differences might well be caused by the underlying assumption that the liquid pathways in

the plug have a cylindrical geometry, which definitely is a simplification of reality.

When the latices are given a heat treatment (Chow and Takamura (4)) the anomalous contribution to the surface conductance can be almost eliminated (Bijsterbosch and van der Linde (5)). As a result the maximum in the mobility vs. the ionic strength disappears and the calculated zeta potentials cause a highly improved correspondence between theoretical and experimental dielectric spectroscopy data (Rosen and Saville (6)).

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ζ-Potential (mV)

κ·a
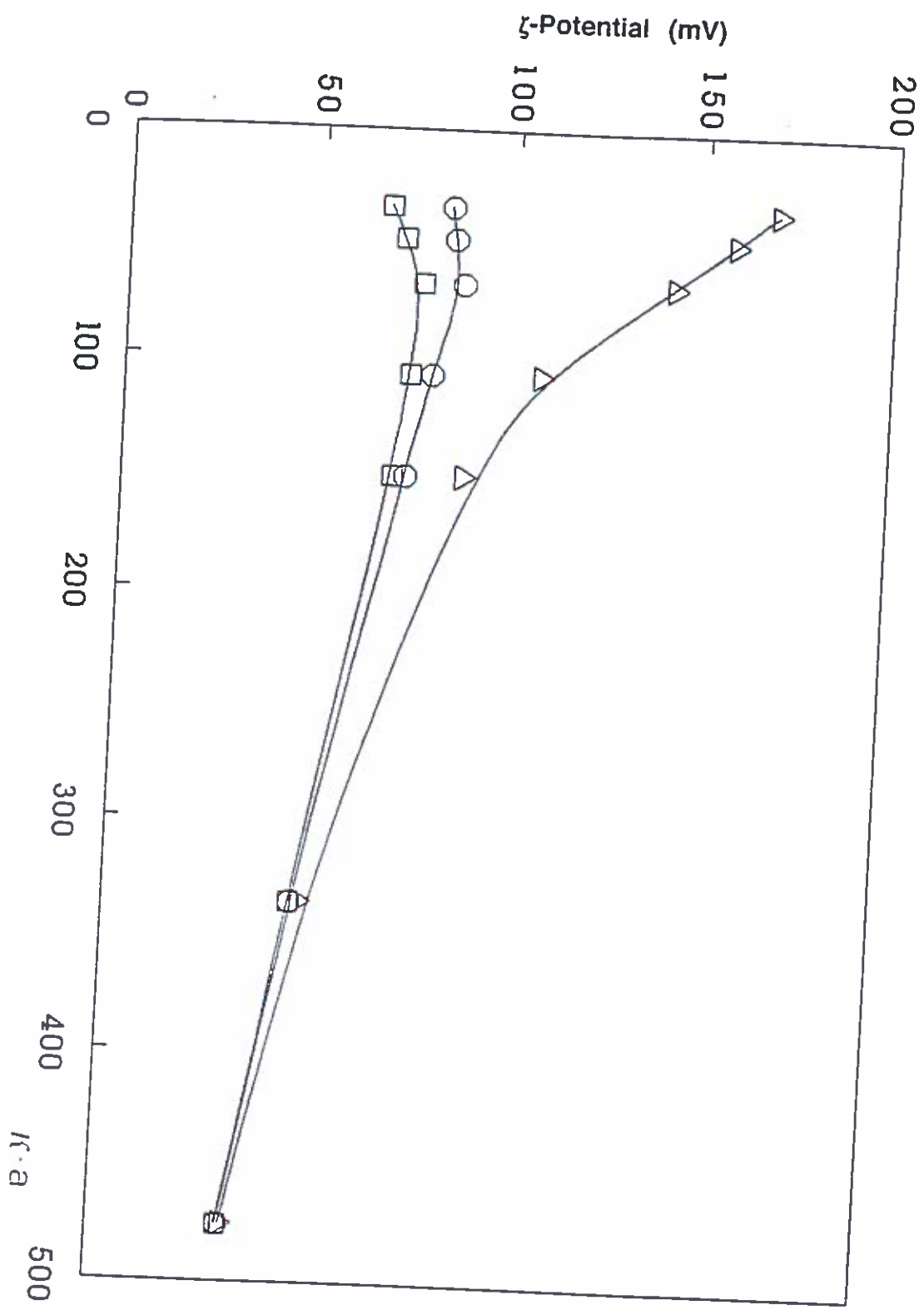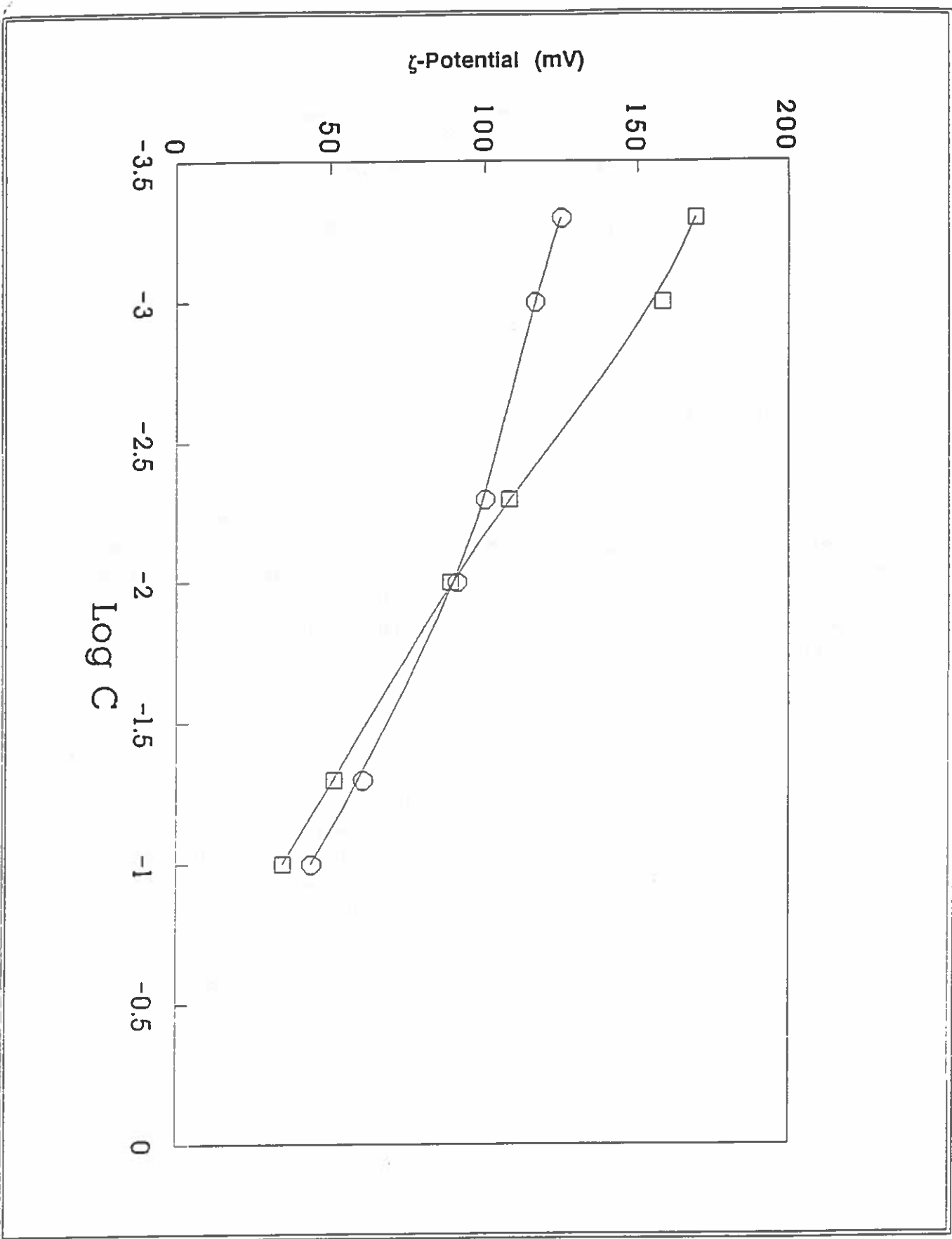
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The interaction of poly(N-isopropylacrylamide) with SDS

Background:

For the last few years we have been interested in the preparation of polymer latexes based on poly(N-isopropylacrylamide). More recently we have found that the preparations were improved by the addition of low concentrations of SDS. This led to two questions: does the surfactant raise the cloud point of poly(N-isopropylacrylamide) above the polymerization temperature; and, can SDS be removed by dialysis at room temperature.

Results:

Figure 1 shows the differential conductivity (i.e. the slope of the conductivity vs concentration curve) for the addition of SDS to various concentrations of aqueous poly(N-isopropylacrylamide). Two transitions were observed and are labeled CAC and CMC. The CAC corresponds to the formation of SDS-poly(N-isopropylacrylamide) complex whereas we believe the CMC corresponds to the formation of free SDS micelles. The CMC increased with polymer concentration whereas the CAC was independent of poly(N-isopropylacrylamide) concentration.

The surfactant raised the cloud point of poly(N-isopropylacrylamide), however, the conditions corresponding to our latex preparations were above the cloud points.
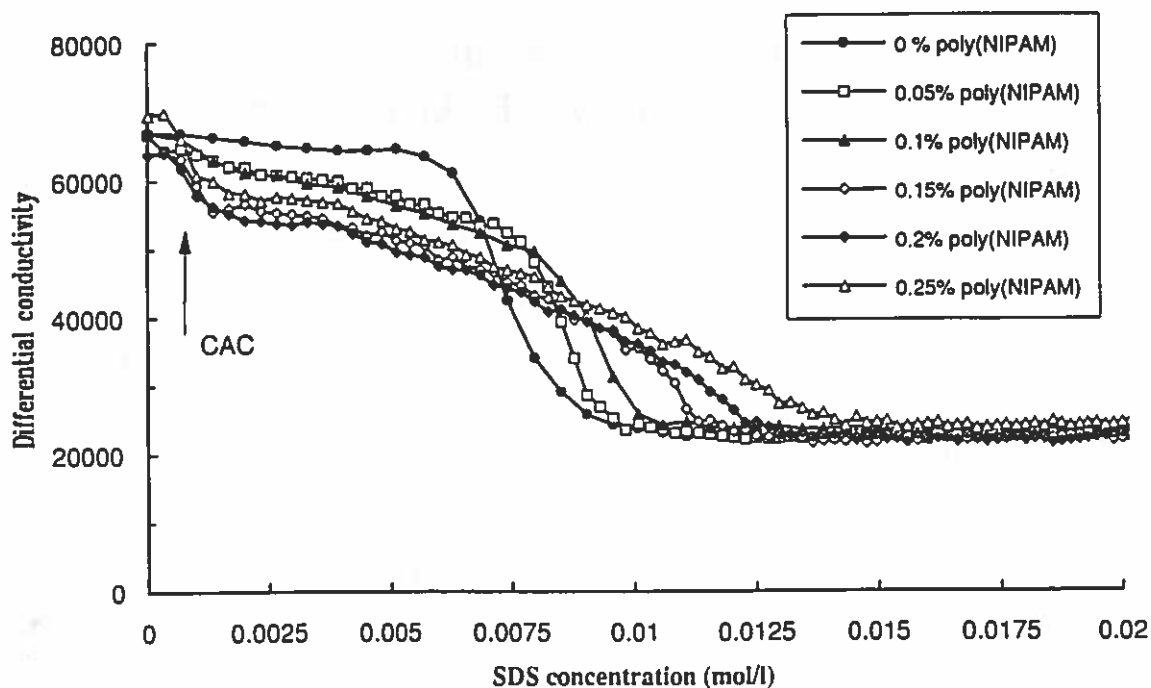
Figure 1

First derivative of conductometric titration curve of pNIPAM with SDS.

Rheological Properties of pNIPAM

K.C. Tam and R.H. Pelton

Viscosity measurements as a function of temperature were used to characterize the phase transition when aqueous poly(N-isopropylacrylamide), poly(NIPAM), was heated past the lower critical solution temperature, LCST, at 32 $^{\circ}$C. Upon heating the viscosity showed a large increase as the LCST was approached; this was attributed to intermolecular aggregation increasing the effective molecular weight of the polymer in solution. Beyond the LCST, reduction of viscosity was observed which is consistent with the viscometric properties of a diluted dispersion of colloidal particles.

Viscosity-Temperature curve of 1.5 wt% Poly(NIPAM) solution
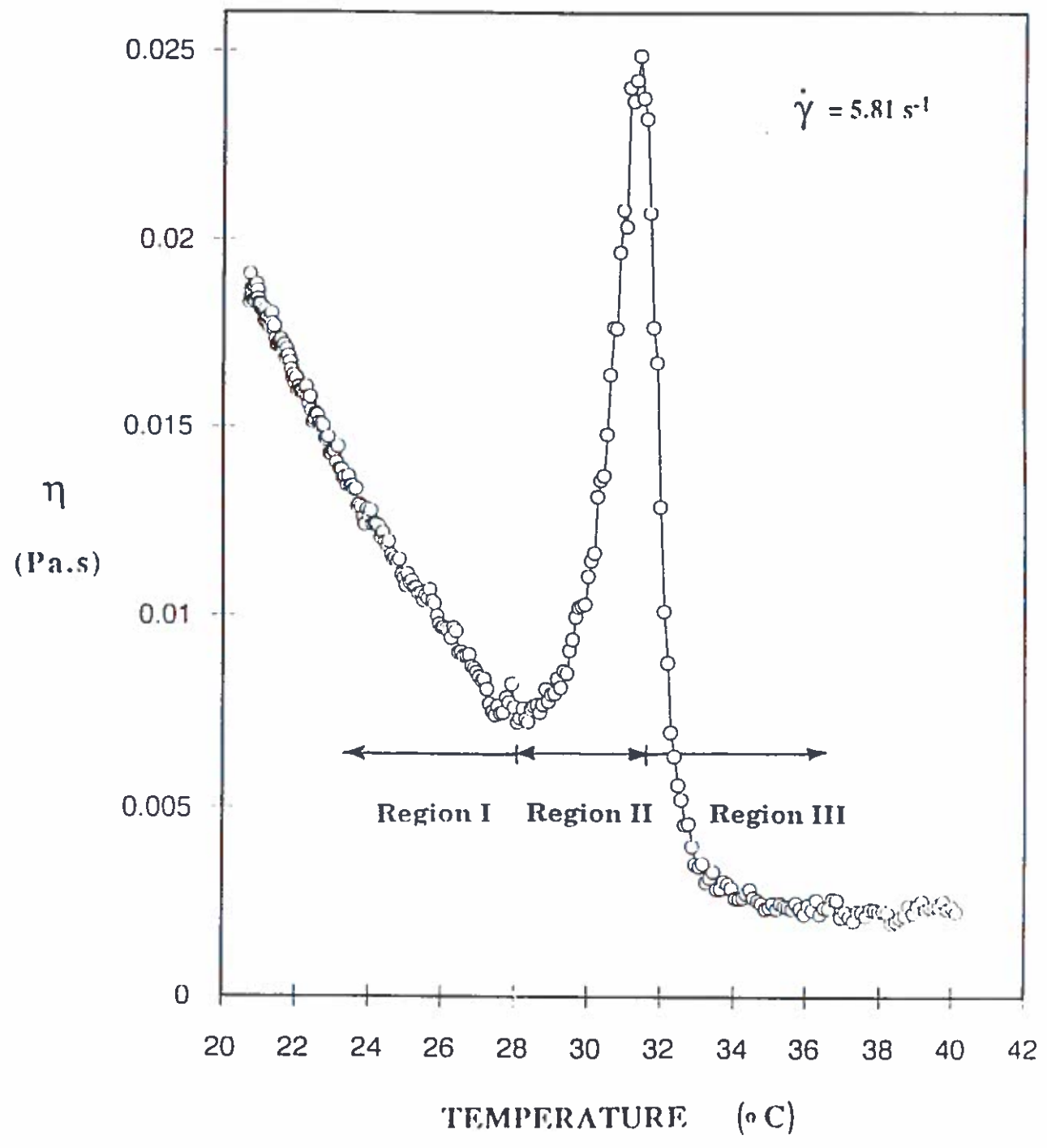
Contribution to Polymer Colloids Group Newsletter

from CNRS/Lyon

submitted by C. Pichot
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Some theoretical aspects on morphology development in seeded composite latexes.
I. Batch conditions below monomer saturation.
(Yvon G.J. Durant and Jean Guillot, LMO -Solaize)

In seeded emulsion polymerization, during the second stage, new interfaces appear and the surfaces size change. A thermodynamic equilibrium approach is presented to predict particles morphology of a whole range of non spherical particles upon polymer conversion.

The following graph represent a reduced Gibbs free energy as a function of the polymer conversion x, where several composites latex structures are plotted : core-shell, inverted core-shell, individual particles, bispherical particles, five exotic structures named "intermediate" as they are bispheric-like structure and a curve showing the most stable structure (named "minimal").

Simulation takes into account swelling ratio, molar volumes, and interfacial tension. As the particles geometry is complex, a new mathematical procedure is detailed.

The computed data are useful to discuss either the stability or the instability of the particles morphology. These results must be compared with the actual experimental structures.
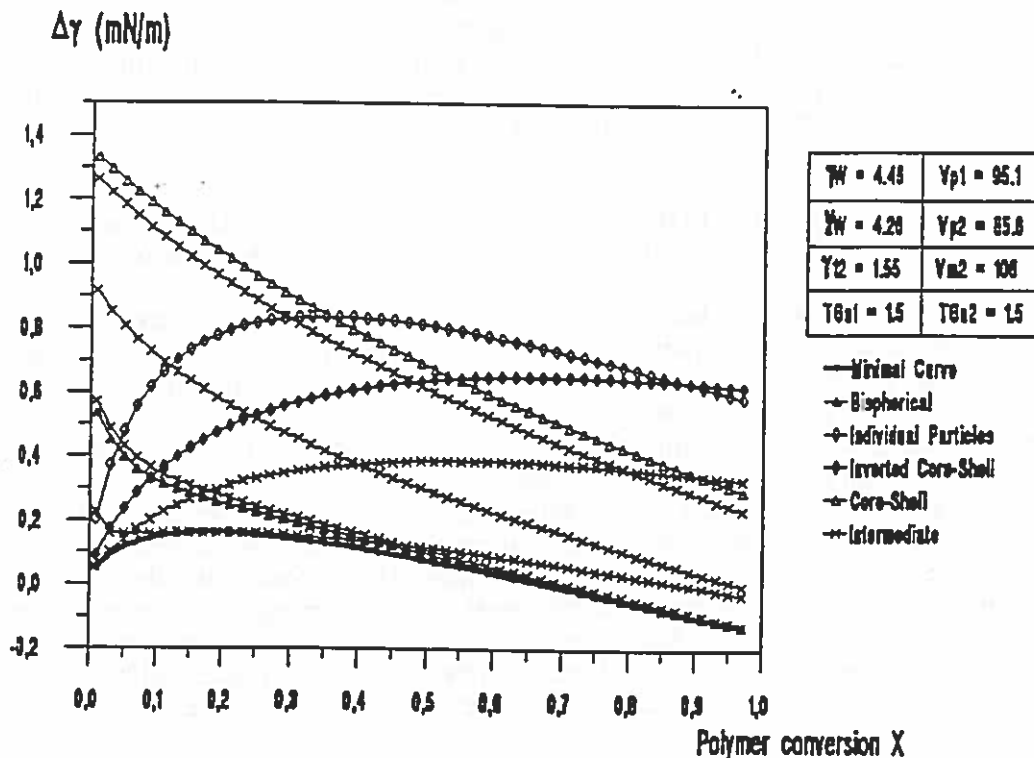

Fig. 1. Reduced Gibbs free energy DG/S for different geometries

Dynamic Mechanical Behaviour of Films From Polystyrene(1) - Poly(Butyl Acrylate-Crosslinkable Monomer) (2) Core-Shell Latexes

M. Hidalgo, J. Y.Cavaillé, J. Guillot (LMO- Solaize)

Several semicontinuous emulsion polymerizations of mixtures of Butyl Acrylate (BA) {90%} and a crosslinkable monomer {10%} were carried out upon a polystyrene (PS) seed (core to shell ratio =2/3). Three crosslinkable monomers were employed: N-Methylol Acrylamide (NMA), N-Methylol Methacrylamide (NMMA), and N-(iso-Butoxymethyl) Acrylamide (IBMA). Films cast from these latexes at 40° C constitute composite systems in which the PS cores remain as spherical inclusions in a soft and continuous P(BA-crosslinkable monomer) matrix. When heating such a composite film at a temperature higher than the glass transition temperature (Tg) of PS, the PS inclusions should coalesce, and the mechanical behaviour of the film should evolve towards that of a bicontinuous phase system. While this certainly occurs for films containing no crosslinkable monomers, coalescence of PS inclusions upon annealing is blocked in those films containing these monomers. In general, the observed mechanical properties of as-dried and annealed films were found to be dependent upon the crosslinkable monomer distribution between the phases of the original latex.

Emulsion polymerization in the presence of various zwitterionic carboxy-betaine type emulsifiers

(H.Essaddam, C.Graillat, Y.Chevalier, A.Guyot, LMO-Solaize).
C.Pichot, UM CNRS-bioMérieux)

Recent work has been developed on the properties of three different carboxybetaines of general formula $C_{12}H_{25}N+(CH_3)_2(CH_2)_nCOO-$ (with n =1,3,7, respectively named NC112, NC312, NC712, corresponding to the number of carbon atoms between the N atom and the carboxy group.They have been first characterized in terms of surface activity showing a strong effect of the intercharge distance on the CMC and adsorption energy at water- air and water-styrene interfaces.Then, a systematic study was investigated on the use of such carboxybetaines in emulsion polymerization of styrene based on a conventional recipe upon varying emulsifier concentration. Particular attention was paid to the particle size and particle size distributions vs conversion, as measured by QELS and TE microscopy. First results indicate that monodisperse and small particles can be obtained in a large range of pH but with using a large amount of NC112 (x 25 CMC) as already reported by Kato et al. More work is also currently carried out in order to examine the stabilizing efficiency of those carboxybetaines in comparaison of that of sulfobetaines.

Functionalization of latex particles with hydrophilic macromonomers

(B.Charleux, M.T Charreyre, C.Pichot,UMR CNRS bioMérieux)

New macromonomers have been designed with the objective to prepare functionalized latex particles with a well defined hydrophilic layer.Two main types of hydrophilic macromonomers have been synthetized. The first one, a styrene-terminated polyvinylalcohol (with n = 10)was prepared by aldol group transfer polymerization and the second one, a hexyl methacrylate terminated oligosaccharide using a five-step synthesis starting from cellobiose.They have been characterized with respect to some physiochemical properties as well as in radical homo and copolymerization with styrene. After selecting optimal experimental conditions, emulsion polymerization of these macromonomers was carried out onto polystyrene seed particles using various addition procedures of the macromonomer. It was found that the hexyl methacrylate terminated monomer was indeed more efficiently copolymerized at the water-polymer interface mainly due its surface activity. Additional study was investigated in order to analyse the surface composition and morphology of the final particles using ESCA and NMR technnniques. More work is curently developed to characterize various colloidal properties of these functionalized model particles.

CONTRIBUTION TO POLYMER COLLOID GROUP NEWSLETTER

from

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Copolymerization of Chlorotrifluoroethylene (CTFE) with Vinyl Acetate and Vinyl Propionate

David Murray and Dr. Irja Piirma

A study was performed to investigate the copolymerization of CTFE with vinyl acetate and vinyl propionate. The polymerizations were carried out in water with ammonium perfluorooctanoate as the surfactant. All polymerizations were carried out with persulfate/bisulfite redox initiators at 25 °C to conversions of less than 20 wt%.

The copolymer compositions were determined by elemental analysis. The r_1 and r_2 values were then determined using the method outlined by Kelen and Tudos [1]. Refinement of the reactivity ratios was done using the method of Mortimer and Tidwell [2].
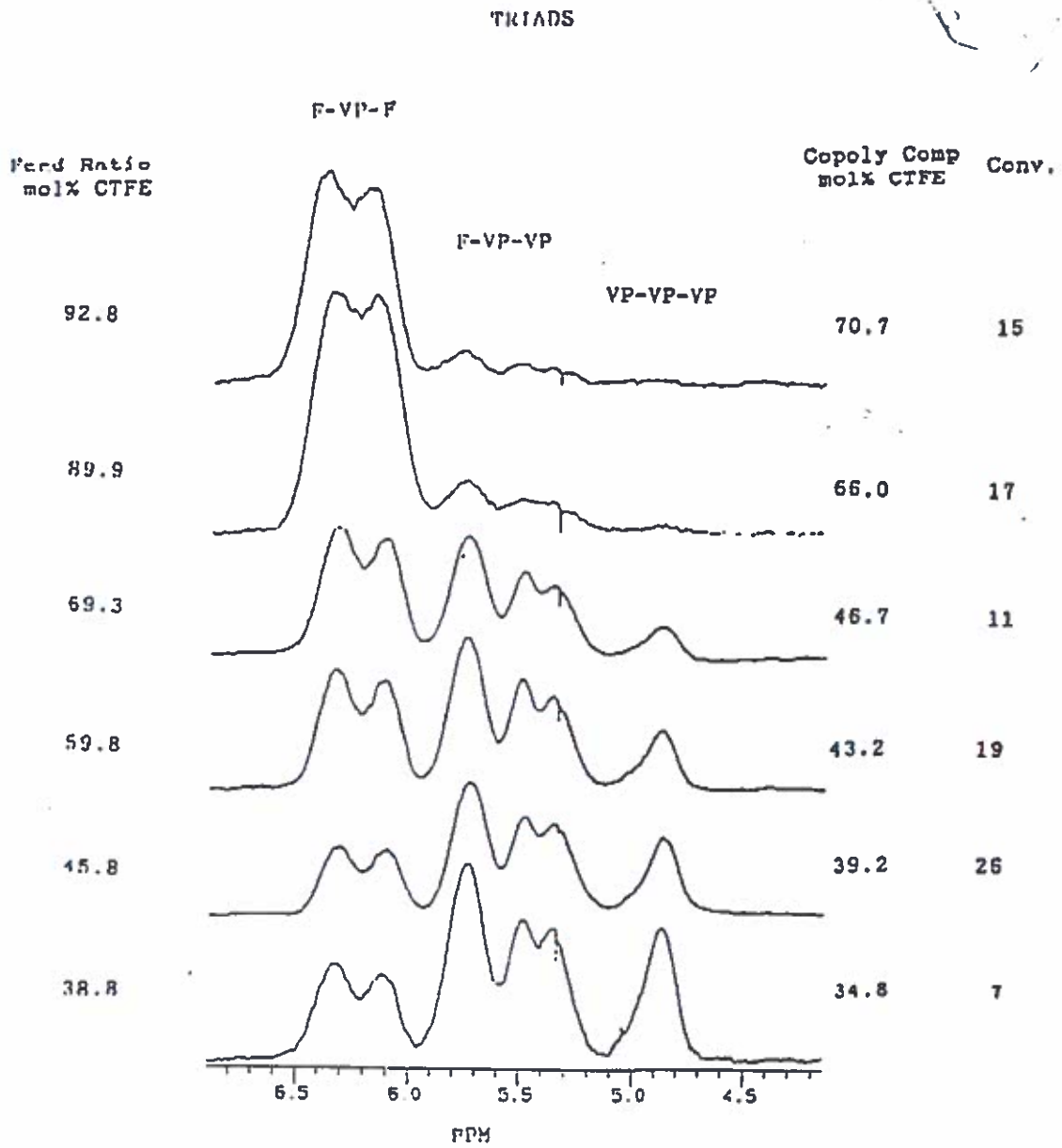
The H^1 NMR spectra of the copolymers were obtained using a Varian 200 MHz NMR. The methine region of the vinyl esters was found to contain information of the vinyl ester centered triads. Peak assignment was made by comparing the integrated regions of the methine peaks to the statistical terminal model predictions for the copolymerization. Figures 1 and 2 show the stacked methine regions for a series of CTFE/vinyl acetate and CTFE/vinyl propionate copolymers, respectively.

A comparison of the experimental and observed triad fractions shows that it is not possible to describe the copolymerization with one set of r_1 and r_2 values over the entire feed ratios. This is more likely due to monomer concentration effects (ie. partitioning of the monomer between water and particle phases) than to a penultimate effect.

We are now looking into the possibility of determining the apparent monomer concentration form the triad function.

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FIGURE 2

METHINE REGION OF POLY(CTFE-CO-VINYLPROPIONATE)

TRIADS

Feed Ratio
mol% CTFE

Copoly Comp
mol% CTFE Conv.

F-VP-F

F-VP-VP

VP-VP-VP

Feed Ratio mol% CTFE	Copoly Comp mol% CTFE	Conv.
92.8	70.7	15
89.9	66.0	17
69.3	46.7	11
59.8	43.2	19
45.8	39.2	26
38.8	34.8	7

PPM

(axis: 6.5 6.0 5.5 5.0 4.5)

^{1}H NMR of Poly(chlorotrifluoroethylene-co-vinylpropionate)

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CHARACTERIZATION OF STYRENE - CARBOXYLIC ACID MONOMER EMULSION COPOLYMERIZATION

Abstract

A kinetic analysis of styrene emulsion copolymerization with acid monomers is presented. The effects of acid monomer addition on styrene emulsion polymerization kinetics were examined under two conditions. First, the system was analyzed under conditions in which radical desorption from particles is significant and aqueous - phase termination effects are negligible. Second, reaction conditions were adjusted to provide significant aqueous - phase termination effects with negligible radical desorption. Comparison of the results for these two situations provides insight into the influence of acid monomer on the mechanisms of styrene emulsion polymerization and also yields estimates of related kinetic parameters. Radical desorption from particles appears to be a mechanism that is considerably enhanced by acid monomer addition.

MODELING OF STYRENE - CARBOXYLIC ACID MONOMER EMULSION COPOLYMERIZATION IN A SERIES OF SEED - FED CONTINUOUS STIRRED TANK REACTORS

Abstract

A steady - state model has been developed to account for the copolymerization of styrene with small amounts of carboxylic acid monomers (acrylic acid and methacrylic acid) in a seed - fed continuous stirred tank reactor (CSTR). This model was also applied to a series of CSTR's with the intention of studying the copolymerization when reactor conditions are altered with intermediate feed streams. The model is based on an age distribution analysis of a seed - fed CSTR. Simulation results provide estimates of individual polymerization rates of each monomer and the resulting particle size distribution.

COPIES OF MANUSCRIPTS AVAILABLE BY REQUEST

Contribution to the Polymer Colloid Group Newsletter

Block-Copolymers as Surfactants in Emulsion Polymerization :
Preparation of "Hairy Latexes"

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The PhD thesis of J.L. MURA, submitted on October 17, 1991, reports on the emulsion polymerization of styrene and butyl acrylate, using polystyrene-poly (ethylene oxide) di- and triblock copolymers as polymeric surfactants, in order to prepare "hairy latexes", e.g. latex particles having on their surface a fringe of PEO with a thickness being a function of the PEO block molecular weight.

In a first step a series of PS-PEO and PEO-PS-PEO block copolymers have been prepared by anionic polymerization, with molecular weight from 7,000 to 70,000 and PEO contents in the range of 45 to 80 wt %.

The micellar behavior of these block copolymers has been studied in collaboration with Prof. WINNIK and the results have been reported elsewhere. The characteristic feature to be mentioned here is that the CMC is very low (in the order of 10^{-7} mole/l), and that the aggregation number of the micelles varies in between 20 and 200, depending on the molecular weight and the composition of the copolymer.

From the reaction kinetics of the styrene emulsion polymerization it appeared that :

- in contrast to classical low molecular weight surfactants, block copolymers lead to a number of latex particles in the same order of magnitude as the number of starting micelles (about 50 % of the starting micelles generate latex particles (see Fig. 1)

- the reaction scheme corresponds essentially to the HARKINS model, with exception of the nucleation step (stade I)

- the PEO fringe on the particle surface has a tendency to chain transfer with primary free radicals leading to latex instability ; this secondary reaction could however be avoided by addition of thiols

- the rate of polymerization (in stade II) as a function of the copolymer concentration can be written as

$$Rp_2 = K \; [\; Cop \;]^{\; 1.3}$$

Fig. 1 : Styrene emulsion polymerization in the presence of PEO–PS–PEO block copolymers. Variation of particle size $\emptyset_w$ (weight average in nm) and relative number of particles N/N_o as a function of conversion
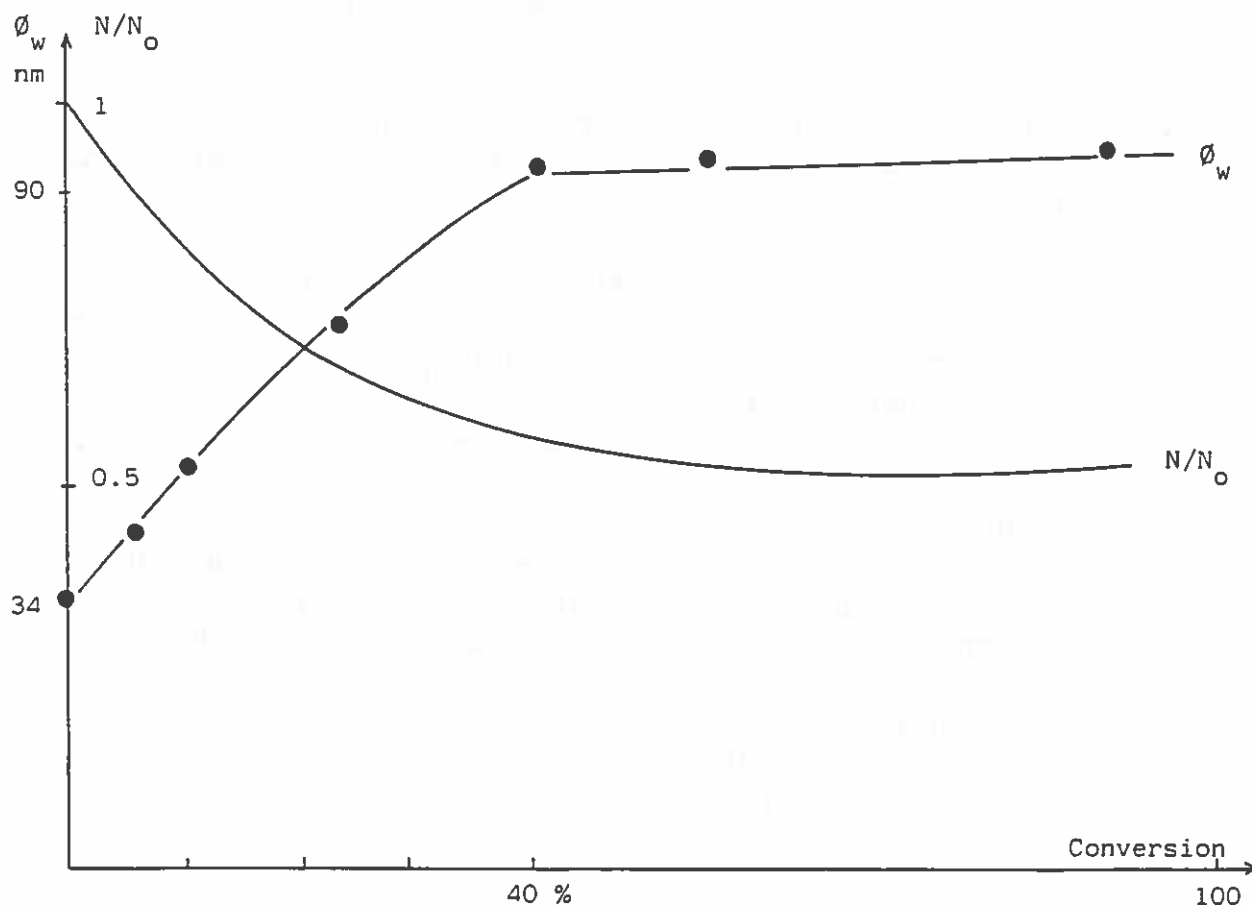
Run (M 105) : 30 g styrene in 300 g water

           0.5 g $K_2S_2O_8$

           1 g dodecylmercaptan

           3 g triblock Copolymer   PEO (2900) – PS (1600) – PEO (2900)

           70°C

           $N_o \cong 5.10^{14}$ micelles/cm^3

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Abstracts of papers which have recently been submitted for publication are as follows:

1.   "Conversion Dependent Morphology Predictions for Composite Emulsion Polymers.   I.   Synthetic Latices", with C. L. Winzor

Phase structure develops within composite latex particles during the polymerization process and is potentially dependent upon both the latex recipe and the polymerization process characteristics. An equilibrium thermodynamic approach is presented to predict the particle morphology as a function of the extent of conversion of a seed latex polymerization reaction.   The discussion highlights the role of the monomer as it influences the phase compositions and interfacial tensions throughout the polymerization.   It is found that a number of different particle morphologies possess nearly the same total interfacial energy throughout a significant portion of the polymerization reaction and that is is quite likely that occluded structures will form in addition to the more fully phase separated structures, such as core-shell and hemispheres.   Detailed methods to predict the probabilities of forming a variety of different morphologies are presented.

2.   "Conversion Dependent Morphology Predictions for Composite Emulsion Polymers.   II.   Artificial Latices", with C. L. Winzor.

An equilibrium thermodynamic analysis of composite particle morphology development within artificial latices is presented.   The analysis emphasizes the role of the solvent upon phase compositions and interfacial tensions, and predictions of the favored morphology

are made as a function of the extent of solvent removal.
Experimental observations of the morphology of PMM/PSTY
composite particles agree well with the predictions and demonstrate
the significant role that the surfactant can have upon the preferred
particle structure. Consideration is given to the choice of solvent
used to produce the artificial latex and it is predicted that the
preferred particle morphology is unlikely to be dependent upon the
type of solvent used in the process.

3. "Morphology Development for Three Component
Emulsion Polymers—Theory and Experiments", with
E. J. Sundberg

   Three component emulsion polymer systems constitute an
overall four component system from a morphological viewpoint. The
aqueous phase is always the continuous phase within which twenty-
two distinct and thermodynamically stable particle morphologies
may exist. Six uniquely different categories of particles comprise
this morphological menu and may be identified as core-shell-shell,
hemi-core, hemi-shell, tri-sectional, "snowman", and cored-
hemisphere. Extension of previously published free energy
thermodynamic analyses of two component emulsion polymers has
resulted in the ability to predict the most likely equilibrium
morphology to be found for three component particles. Predictions
have been carried out for each possible three component
combination of polystyrene, poly(methyl methacrylate),
polycarbonate and poly(dimethyl siloxane). The results show that in
nearly every instance, two or three different morphologies are
computed to possess nearly equivalent free energies, while all other
possibilities would result in much higher free energies. This
indicates that more precise knowledge of all interfacial tensions is
required when considering three component systems than was found
to be generally needed for two component systems. Experiments
were carried out for each polymer combination using a very surface
active emulsifier (sodium lauryl sulfate) and separately, a weakly
surface active emulsifier (natural pectin). For this choice of polymers
and emulsifiers, only three of the six unique morphological categories
were found experimentally. In all cases the thermodynamic analysis
predicted the experimentally determined morphology to possess the
lowest or next to lowest free energy.

4.   "Emulsion Polymerization Kinetic Models for Composite Latex Particles.   I.   Core-Shell Morphology", with D. C. Nelson

A preliminary model for the kinetics of two phase emulsion polymerization in core-shell particles has been developed. Polymerization is accounted for in both phases and the total (i.e. measurable) reaction rate is expressed as the sum of the rates in each phase.   Free radical populations within each phase were computed from considerations of radical entry, exit and termination for each phase.   This included radical transport between the polymer phases.   The model computations also require an assessment of monomer partitioning between the phases and a calculation of the conversion dependent rate coefficients (k_t and k_p) in each phase. Results of the computations show the dependency of the reaction in the core phase upon that in the shell phase.   In particular it is found that shell phase is the reaction rate controlling phase, that being particularly striking when the shell phase is composed of high T_g polymer and the core phase being a low T_g polymer.   In such cases it is readily apparent that the morphological arrangement of the two polymers within the core-shell particle has a significant influence on the predicted overall reaction rate.

AN ATOMIC FORCE MICROSCOPIC VIEW
OF LATEX FILM FORMATION

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The study of the coalescence process of polymer latex films is of a great interest.[1] During the past few years, we have been able to show evidence as a result of coalescence, of polymer diffusion across particle boundaries above the MFT in latex films, using the fluorescent technique of direct energy transfer (DET). Our results [2] are in good agreement with studies carried out by Hahn et al.[3] on similar latex particles, using the SANS technique. More recently, we examined TEM images of our films obtained from freeze-fracture replicas. These exhibited perfect rhombic dodecahedra corresponding to a fcc structure.[4,5]

Now we would like to report our latest investigations by the new technique of Atomic Force Microscopy (AFM).[6] This technique enables us to get high resolution three-dimensional images of film surfaces in a non-destructive way. The substantial advantage of this technique is that we are now able to prepare a film from a latex

above its glass transition temperature, and re-examine it as often as we wish. It is not necessary in this experiment that the latex be labeled, as for SANS and DET experiments, or that the film surface be treated, as for SEM and TEM measurements.

Here we want to show the effect of annealing on latex film surfaces. Films were obtained from a poly(butyl methacrylate) [T_g=27°C] surfactant-free latex dispersion of a M_w of 220,000.[4] The diameter of particles is 337 nm. Films were prepared by casting a few drops of latex dispersion onto a freshly cleaved mica plate, and allowing to dry in air for four hours at 36°C. Figure 1 shows a typical surface of one of these films. The long range order is quite remarkable, although some dislocations can be noticed. The roughness of the surface can be estimated by looking at a section of the film along a row of particles. The z-variation parameter describes the average peak-to-valley distance for the surface oscillations in the film. It is probably one of the most meaningful parameters that can be used to appreciate the annealing effect. In this non-annealed film, the z-variation was measured to be equal to 40 nm, which is about one fourth of the radius of one particle. Figure 2 shows the same film annealed for 12 hours at 70°C. The z-variation has decreased to 10 nm. Finally, Figure 3 shows the same film annealed at 70°C, but for 55 hours. Here, the z-variation has decreased to 3 nm. The film has become quite smooth.
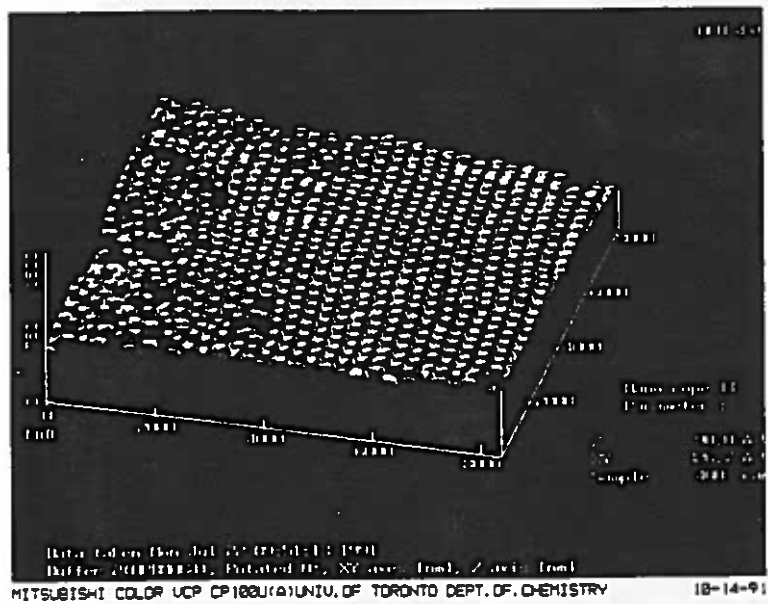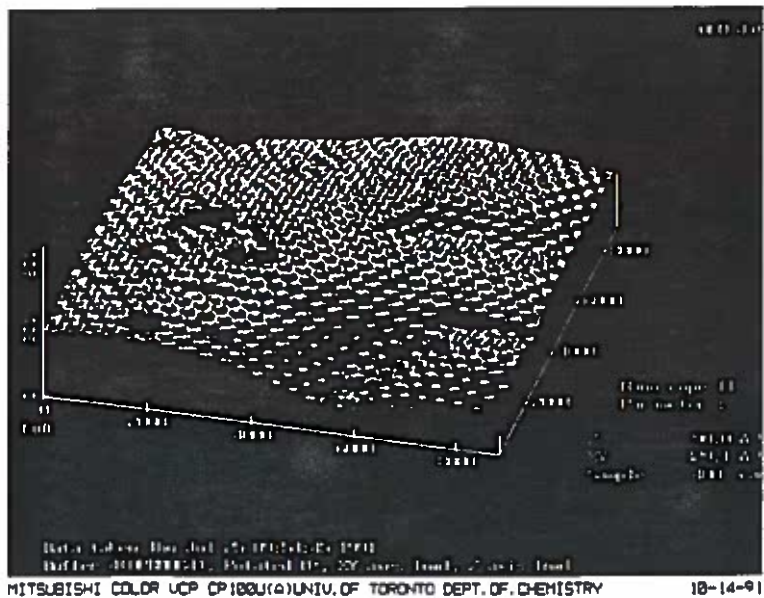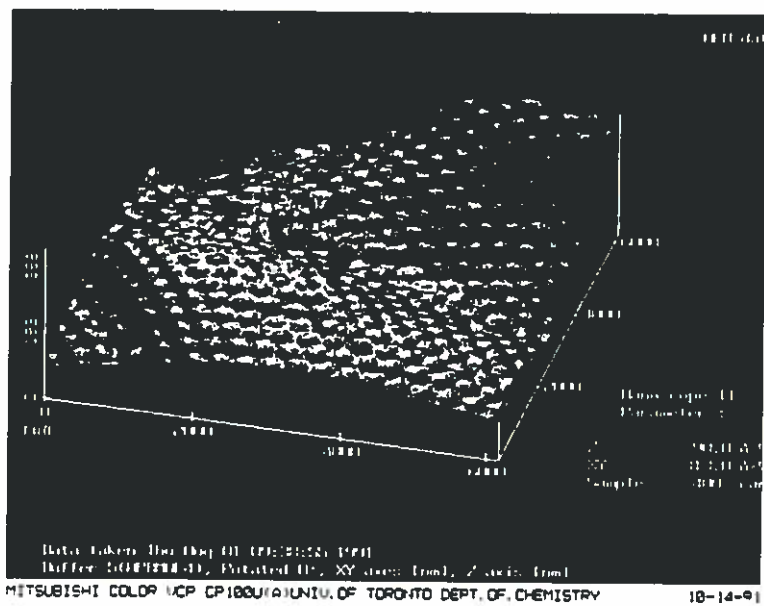
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Figure 1

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Figure 2

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Figure 3