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IPCG

INTERNATIONAL POLYMER COLLOIDS GROUP

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NEWSLETTER

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IPCG Meetings

- Macro 98 World Polymer Conference (13 - 17 July 1998, Gold Coast, Australia), co-chaired by Don Napper and Bob Gilbert, will have a major polymer colloids component; co-organizer is Mohamed ElAasser.
- Lyon Colloquium on ***Polymers in dispersed media***, in honour of Alain Guyot. From Sunday April 11 to Thursday April 15 1999. First circular in January '98. Organizer Christian Pichot.
- Gordon Research Conference, tentatively June 27-July 2 1999.
- Ted Provder (ICI, Cleveland OH) is organizing a symposium on latex film formation for the New Orleans ACS meeting in Sept 1999.
- Symposium on polymer colloids at ACS colloids meeting June 18-22 2000.
- European Gordon Research Conference 2002; organizer is Klaus Tauer.

Call for Papers

Fifth Meeting of the UK Polymer Colloids Forum

16-17 April 1998

Loughborough University, United Kingdom

Organiser: Professor Doug Hourston

If you wish to offer a paper then please send a 200-300 word abstract to Mrs. Jackie Baseley before 30 November 1997 via:

EITHER post: IPTME, Loughborough University, Loughborough, Leicestershire, LE11 3TU, United Kingdom

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October, 1997

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INTERNATIONAL POLYMER COLLOIDS GROUP NEWSLETTER

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

NONLINEAR CONTROL FOR MAXIMUM PRODUCTION RATE OF LATEXES OF WELL-DEFINED POLYMER COMPOSITION

Isabel Sáenz de Buruaga, Philip D. Armitage, José R. Leiza and José M. Asua

In this work, on-line strategies based on calorimetry were used to maximize the production of vinyl acetate/butyl acrylate latexes under safe conditions, maintaining simultaneously the copolymer composition of the polymer at predefined values. It was also shown that these strategies were able to avoid monomer accumulation in the reactor, and hence potentially dangerous thermal runaway situations, without any deleterious effect on the polymer composition, when a sudden inhibition was induced by deliberately adding a solution of hydroquinone. For this purpose, nonlinear model-based control strategies and conventional feedback controllers were used.

MOLECULAR WEIGHT DISTRIBUTION CONTROL IN EMULSION POLYMERIZATION

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

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

KINETICS OF THE PHOTOINITIATED INVERSE MICROEMULSION POLYMERIZATION OF 2-METHACRYLOYL OXYETHYL TRIMETHYL AMMONIUM CHLORIDE.

Alberto Sáenz de Buruaga, Ignac Capek, José C. de la Cal and José M. Asua

The polymerization of inverse microemulsions of 2-methacryloyl oxyethyl trimethyl ammonium chloride stabilized by a blend of nonionic emulsifiers (a sorbitan sesquioleate and a sorbitan monooleate) and initiated by UV light in the presence of Azobis (isobutyronitrile) (AIBN) was investigated. The effect of initiator concentration, light intensity, emulsifier concentration, and dispersed phase weight fraction on the polymerization rate (R_p), number of polymer particles (N_p) and polymer molecular weight (M_w) was studied. The application of this process to tubular reactors is discussed.

COLLOIDAL AND ELECTROKINETIC BEHAVIOUR OF POLY(METHYL METHACRYLATE-CO-BUTYL ACRYLATE) LATEX PARTICLES

Elias Unzueta, Jacqueline Forcada and Roque Hidalgo-Alvarez

Poly(methyl methacrylate-co-butyl acrylate) latex particles were synthesized by both seeded and unseeded semicontinuous emulsion copolymerization processes. Particle size and surface charge densities were characterized by TEM and potentiometric and conductimetric titrations, respectively. The electrophoretic mobilities of the latexes were studied at different ionic strength and constant pH and then at constant ionic strength and different pH. An investigation of the effect of surface density on z-potential is described. Conversion of mobility values into z potentials was accomplished according to the theory of Dukhin-Semenikhin in order to take anomalous surface conductance into account. The dimensionless relaxation factor (Rel) was calculated for the different surface charge density of the latexes obtained. The colloidal stability of the latex particles after addition of KBr at an appropiate concentration was followed monitoring the optical absorbance changes of the dispersion. The critical coagulation concentration (CCC) was obtained from the intersection points of the straight log W-log C line with the x-axis (stability factor versus concentration). The stability factors of the synthesized latexes were measured at pH 5, 7 and 9. The results indicate that these latexes are electrostatically stabilized.

ACETAL-FUNCTIONALIZED POLYMER PARTICLES USEFUL FOR IMMUNOASSAYS. II. SURFACE AND COLLOIDAL CHARACTERIZATION

Rosa María Santos and Jacqueline Forcada

The synthesis of core-shell type polystyrene monodisperse particles with surface acetal groups was carried out by a two-step emulsion polymerization process. In a first step, the core was synthesized by means of a batch emulsion polymerization of styrene (St), and in the second step, the shell was polymerized by batch emulsion terpolymerization of styrene, methacrylic acid (MAA) and methacrylamidoacetaldehyde dimethyl acetal (MAAMA), or methacrylamidoacetaldehyde diethyl acetal (MAADA), using the seed obtained previously.

With the aim of analyzing the stability of the surface groups during the storage time, the hydrophilic character of the latex surface and the colloidal stability of the latexes synthesized, new core-shell type acetal latex particles were synthesized by means of a two-step emulsion polymerization in a batch reactor.

The latexes were characterized by TEM and conductometric titration, in order to obtain the particle size distribution and the amount of carboxyl and acetal groups on the surface, respectively. The hydrophilic character of the surface of the polymer particles was determined by means of non-ionic emulsifier titration. The colloidal stability of the synthesized latexes was studied by measuring the critical coagulation concentration (CCC) against KBr electrolyte and the existence of a hairy layer on the surface of the latex particles was analyzed by measuring the hydrodynamic particle diameter at different electrolyte concentrations.

Contribution from the Department of Polymerization Reactions, Polymer Institute,Slovak Academy of Sciences, 842 36 Bratislava Slovak Republic

Reported by **Jaro Barton**

Following papers were prepared for publication :

INVERSE MICROEMULSION POLYMERIZATION OF ACRYLAMIDE IN THE PRESENCE OF N,N-DIMETHYLACRYLAMIDE

V. Juraničová [1], S. Kawamoto [2], K. Fujimoto [2], H. Kawaguchi [2], & J. Bartoň [1,*]
[1] Department of Polymerization Reactions, Polymer Institute of the Slovak Academy of Sciences, 84236 Bratislava, Slovak Republic
[2] Department of Applied Chemistry, Faculty of Science and Technology, Keio University,Yokohama 223,Japan

The presence of N,N-dimethylacrylamide (NDA) influences the stability of initial,clear,single-phase Winsor IV inverse microemulsion toluene/ AOT (sodium salt of bis-(2-ethyl hexyl) sulfosuccinate)/NDA/water/acrylamide (AAm). For molar fraction of n_{NDA} (= [NDA] / ([NDA] + [AAm]) = 0.200 a single-phase system turned to milky one during polymerization initiated by oil-soluble dibenzoyl peroxide or water-soluble ammonium peroxodisulfate and finally a two-phase system was formed. For n_{NDA} values greater than 0.200 also precipitation of polymeric product was observed during polymerization. The (co)polymerization rate of AAm and NDA exponentially decreases with the increasing value of n_{NDA}, while the reverse is true for (co)polymer particle diameter. The increase in size was ascribed to the enhanced swelling of (co)polymer particles with increasing concentration of NDA structural units during QELS measurement in toluene environment as well as by aggregation process of polymer particles documented by TEM measurements.

INVERSE MICROEMULSION POLYMERIZATION OF ACRYLAMIDE IN THE PRESENCE OF A MIXTURE OF OLEOPHILIC/HYDROPHILIC SURFACTANTS

Martin Lezovič[1], Kenji Ogino[2], Hisaya Sato[2], Ignác Capek[1], Jaroslav Bartoň [1]
[1] Department of Polymerization Reactions, Polymer Institute of the Slovak Academy of Sciences, 84236 Bratislava, Slovak Republic
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The effect of SDS (sodium dodecyl sulfate) on the formation of inverse microemulsion Toluene/AOT (sodium salt of bis(2-ethyl hexyl) sulfosuccinate) / Water / Acrylamide / SDS and on polymerization of acrylamide initiated by oil soluble dibenzoyl peroxide was studied. The presence of SDS shifts the value of the volume fraction, Φ_{aw}, at which forms a two-phase Winsor II system, to higher Φ_{aw} values. It was shown that an increase of the mass ratio of SDS/Water led to a decrease of acrylamide polymerization rate, of polyacrylamide particle size and of polyacrylamide molecular mass distribution. It was also found that in the presence of SDS in inverse microemulsion nearly constant value of acrylamide polymerization rate in the range of Φ_{aw} values between 5 and 50 % can be obtained.

Separation and molecular characterization of multicomponent polymer blends by means of full adsorption-desorption/SEC coupling

Son Hoai Nguyen, Dušan Berek and Raniero Mendichi*

Polymer Institute of the Slovak Academy of Sciences, Dúbravská cesta 9, 842 36 Bratislava, Slovakia
** Institute of Macromolecular Chemistry CNR, Via E. Bassini 15, 20 133 Milan, Italy*

Introduction

Binary, ternary and multicomponent blends of polymers find a wide application in many areas. For various reasons, it is often necessary to assess either actual values or changes of the mean molar masses (MMM) and molar mass distributions (MMD) of particular blend components, e.g. in the course of blend processing or application. Presently, the size exclusion chromatography (SEC) called also gel permeation chromatography in the case of lipophilic macromolecules, represents a method of choice for MMM and MMD measurements of single polymers. However, SEC that separates macromolecules according to their sizes, fails to discriminate blend components possessing similar molar masses. In the case of binary polymer blends, the hyphenated detection can partially overcome this problem. The selective detectors are often able to independently monitor the concentration of particular blend components and the chromatograms obtained are processed as in the case of the single homopolymers. Alternatively, the signals of two detectors with the fairly different response factors for the blends components are manipulated to obtain the separate SEC traces for each blend component. Unfortunately, the latter approach is not too precise and, in many cases, the coeluting, chemically different macromolecules mutually influence their retention volumes. Anyway, both above procedures are hardly applicable to ternary and multicomponent polymer blends.

Therefore, alternative methods are looked for: In this contribution we are reporting the novel liquid chromatographic method that combines two separation mechanisms, namely full adsorption and full desorption with size exclusion (FAD/SEC coupling).

Principle of method

The prerequisite of the successful FAD/SEC coupling is the appearance of a fast, complete and stable adsorption of macromolecules on the surface of appropriate adsorbent from an appropriate ADSORption promoting LIquid (ADSORLI) at appropriate temperature. In other words, macromolecules must be fully attached on the adsorbent when the diluted solution of macromolecules in an ADSORLI is brought into contact with the adsorbent. In the case of a polymer blend composed of n components, at least n-1 components must be fully adsorbed. The n-th, nonadsorbed blend component is directed into the SEC column where it is characterized in the usual way applying ADSORLI solvent as SEC eluent.

In the next step or in the next steps, the adsorbed macromolecules are (selectively) released from the adsorbent by (a stepwise) change of the temperature or eluent composition. The latter approach is experimentally more feasible: A displacer, that is a DESORption promoting LIquid (DESORLI) is added to eluent.

In this way, the second, third etc. blend component is successively desorbed and directed into the SEC column for characterization. The procedure and the corresponding set-up of the FAD/SEC procedure is visualized in the Fig. 1.

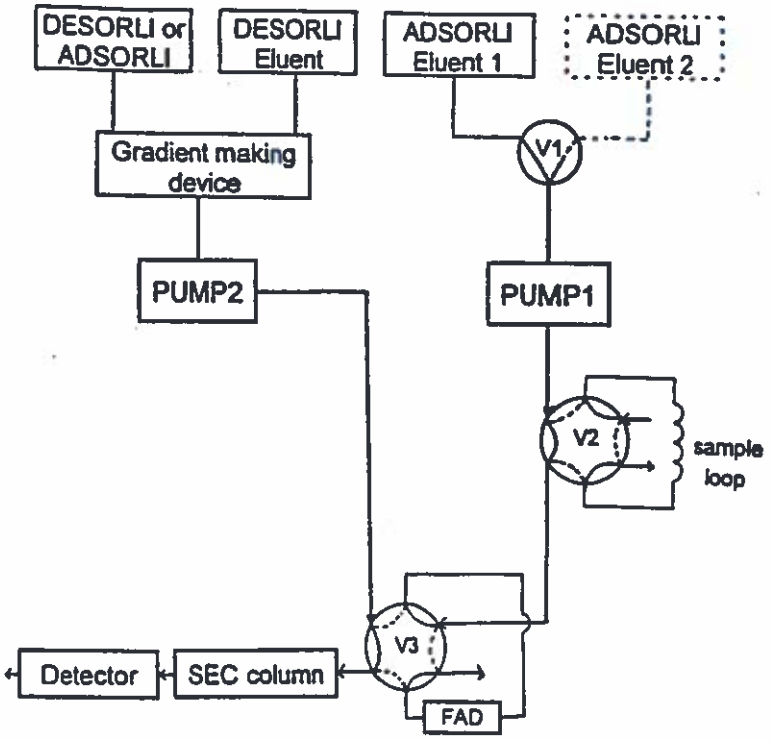

Fig. 1 Schematic representation of the FAD/SEC assembly

The common HPLC hardware was used in our studies: Waters 510 pumping system, Rheodyne injection a switching valves, PL linear SEC column, home-made FAD minicolumns with volumes from 140 to 250 µl and an evaporative light scattering detector DDL-21.

Polymers were polystyrenes (PS), poly(methyl methacrylate)s (PMMA), poly(n-butylmethacrylate)s (PBMA), poly(glycidylmethacrylate)s (PGMA), poly(vinyl acetate)s (PVAC), poly(ethylene oxide)s (PEO), poly(tetrahydrofurane)s (PTHF).

The method development

Adsorbent: Porous and nonporous silica gels as FAD column packings were compared. Nonporous adsorbents produced better results than porous ones. The latter gave multiple SEC peaks

[1]. The sample capacity of nonporous adsorbents is, however, large enough so that small FAD columns can accommodate sufficient amount of polymers [1]. Packings of the FAD columns must withstand sudden changes of eluents and exhibit stable and repeatable adsorption properties.

FAD column size: Large FAD columns may produce the problems if SEC column possesses strong adsorptive properties [2].

ADSORLI must reliably retain polymer(s) on the adsorbent. On the other hand, ADSORLI must not be too strong if the SEC column applied shows the ability to retain analysed macromolecules [2]. ADSORLI is identified in a following way: A small portion of the diluted solution of polymer studied is repeatedly injected into the FAD column. SEC column is removed so that the FAD column effluent flows directly into the HPLC detector. As far as polymer is fully adsorbed, the detector does not show any response. The first detector response indicates the FAD adsorbent saturation threshold. Further injections give increased detector response since increasing part of polymer passes FAD column non-retained. Eventually, entire amount of polymer flows through the FAD column (full saturation point). The adsorption curves obtained in this way allow to choose the appropriate adsorbent/ADSORLI system for given polymer. Moreover, the adsorbent capacity (FAD column size) and the adsorption velocity can be evaluated.

Adsorption-desorption kinetics was found surprisingly fast [3] so that the polymer residence time of six seconds was enough to allow macromolecules their quantitative attachment/detachment onto/from the adsorbent surface.

Temperature: It is known that the extent of polymer adsorption depends on temperature. The adsorption may either increase or decrease with temperature and therefore FAD column temperature control must be provided [3].

DESORLI identification is rather simple in the case of binary polymer blends with one component non-retained by the FAD column [1,2]. For more complex polymer blends, however, a tailored eluent desorption strength must be provided. We proposed to monitor the courses of the integral desorption isotherms for particular components: A small amount of polymer (below the saturation threshold) is deposited onto FAD column packing. Subsequently, the FAD column is flushed with various liquids to evaluate their displacing ability that is visualised by the detector response. Next the chosen displacer is mixed with ADSORLI at various compositions and the FAD column is successively flushed with this series of DESORLI eluents. The integral desorption isotherm is constructed as a function of desorbed polymer amount vs. the DESORLI composition (Fig. 2).

It is evident from the course of desorption isotherms in Fig. 2 that PBMA can be easily and efficiently separated from either PMMA, PTHF, PVAC or PGMA using silica as adsorbent and dichloroethane (DCE) as an ADSORLI and DCE/THF as ADSORLI/DESORLI mixtures. Moreover, THF

is still an ADSORLI for PEO on silica so that it can be separated from other polymers. In this way the mixture(s) containing PS + PBMA + PEO + PMMA or PTHF or PVAC or PGMA with both similar and different molar masses will be fully discriminated. On the other hand, PMMA, PTHF, PVAC and PGMA cannot be separated from each other in the above system. PS was not retained within FAD column and it was directly characterized in the first step by the SEC in all cases. The molar mass values determined by SEC either directly or after adsorption-desorption step for single polymers and for polymer blends are given in Table 1.

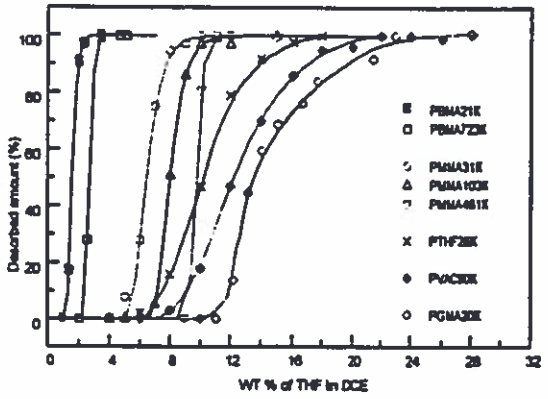

Fig. 2 Integral desorption isotherms for selected polymers

Table 1 Comparison of molar mass values for selected polymers

Procedure	Polymer	Eluent or DESORLI mixture	$M_w.10^{-3}$ (g/mol)	$M_n.10^{-3}$ (g/mol)	M_w/M_n
SEC for single polymers	PS15K	DCE	14.7	11.7	1.26
	PBMA21K	THF	23.7	19.6	1.21
	PMMA461K	THF	446	249	1.79
	PEO45K	DMF	43.4	35.9	1.21
FAD/SEC for quaternary blend	PS15K	DCE	14.0	11.0	1.27
	PBMA21K	3.7wt.% THF in DCE	24.9	20.2	1.23
	PMMA461K	THF	430	238	1.81
	PEO45K	DMF	42.3	34.4	1.23

One can conclude that the FAD/SEC coupling can be applied for efficient discrimination and consequent molecular characterization of ternary - and quaternary polymer blend components. The studies aimed at the further extension of the FAD/SEC method is in progress.

References

[1] Jančo, M., Prudskova, T., Berek, D. Polymer 1995, **36**, 3295
[2] Jančo, M., Prudskova, T., Berek, D. Int. J. Polym. Anal. Charact., in press
[3] Berek, D. and Nguyen H.S., Macromolecules, submitted

Model Nonionic Telechelic Associative Polymers in Superimposed Simple and Oscillatory Shear Flows

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Recently we have used the superposition of oscillation on steady shear flows to measure the state of network structure under different shear conditions [1,2]. The technique involves applying a steady shear deformation on the fluid, and once equilibrium is achieved, imposing a small amplitude oscillation on the sample to measure linear viscoelastic properties.

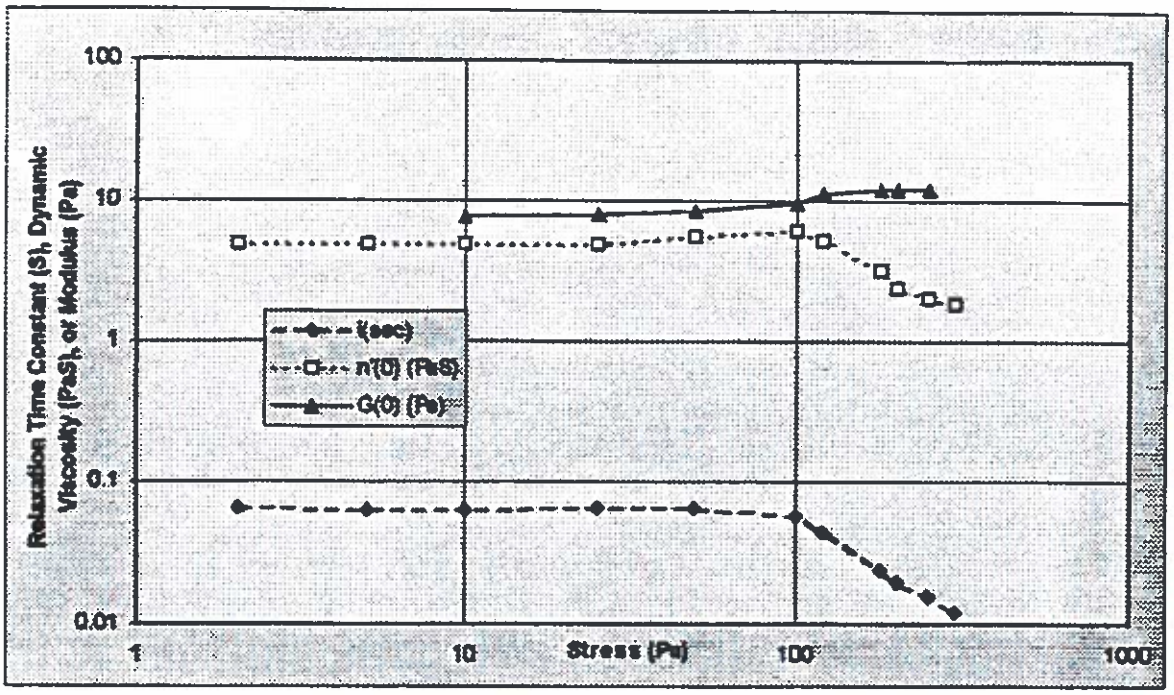
A 2% nonionic model associative polymer solution was studied using this technique to determine the nature of the network structure of "rosette" micelles under various shear conditions. The model polymer was AT 22-3 (described previously) with hexadecyl end-groups and number average molecular weight of 51,000 as calculated from reaction stoichiometry.

This polymer solution exhibits a steady shear viscosity profile with a Newtonian region at low shear rates, a shear-thickening region at moderate shear rates, and shear-thinning at high shear rates. Within the shear-thickening region the plateau modulus is larger than in the Newtonian region. This suggests that the shear-thickening region is caused by incorporation of free micelles into the network structure, thus increasing the network junction densities. In the shear-thinning region, the Maxwell relaxation time decreases with increasing shear stresses or rates (see Figure 1 below). The exit rate, which is the inverse of the relaxation time, increases with applied shear. This is probably the first experimental evidence where the relaxation time at various shear conditions are measured.

Combining superposition of oscillation data with thixotropic experiments, we are able to verify the reversibility of the network structure within different shear regimes. A modified structure model describing the network structure is proposed by refining the rosette model [3].

[1] Tirtaatmadja, V; Tam, K. C.; Jenkins, R. D.; and Bassett, D. R.; Contributions to the IPCG Newsletter, December 1995 and June 1996.
[2] Tirtaatmadja, V., Tam, K.C., and Jenkins, R.D., "Superposition of Oscillations On Steady Shear Flow as a Technique for Investigating the Structure of Associative Polymers", *Macromolecules* 30(5), p. 1426-1433 (1997)."
[3] Forthcoming paper currently under review.

Figure 1: Dependence Of The Longest Relaxation Time, Dynamic Viscosity, And Plateau Modulus On Applied Stress As Measured By The Superimposed Oscillatory And Simple Shear Technique.



POLYMER COLLOID GROUP NEWSLETTER

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

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

Associating Behavior of Polyacrylamides Hydrophobically Modified with Dihexylacrylamide (E. Volpert, J. Selb, F. Candau, Polymer, in press)

Polyacrylamides hydrophobically modified with a small amount of dihexylacrylamide (HMPAM) have been prepared by means of an aqueous micellar polymerization technique. This process leads to copolymers in which the hydrophobic molecules are randomly distributed as blocks in the acrylamide backbone. Keeping constant the hydrophobe level (1 mol%), the length of the blocks was adjusted by varying the surfactant content used in the synthesis, i.e. by varying the number of hydrophobes per micelles, N_H. The resulting copolymers are homogeneous in composition but have a different microstructure (blockiness). The rheological properties of the samples in aqueous solution have been investigated as a function of polymer concentration, polymer conversion, temperature and in the presence of surfactant, using steady flow and oscillatory experiments. The hydrophobic modification of the polyacrylamide backbone induces a slowing down of the reptation movement of the polymer chains. The results stress the major role of the hydrophobe distribution in the copolymer for a good control of the thickening efficiency of associating HMPAM.

The Influence of Salicylate Counterions on the Aggregation Behaviour of a Polymerizable Cationic Surfactant (G. Tuin, F. Candau, R. Zana, Colloids and Surfaces, in press)

The aggregation behaviour of the cationic polymerizable surfactant dimethylhexadecyl-(2-acrylamidoethyl)ammonium bromide (AM16) has been studied with time-resolved fluorescence quenching (TRFQ) and viscometry. The quencher-averaged aggregation number N_q was determined in the absence and presence of

strongly binding salicylate ions using TRFQ. In the absence of sodium salicylate (NaSal) AM16 behaves very much like other cationic surfactants with an aggregation number increasing with surfactant concentration and decreasing with increasing temperature. In the presence of NaSal at constant temperature, N_q, increases first slowly with NaSal concentration (C_{Sal}), until the critical concentration C_{Sal}^* above which N_q increases sharply. At constant C_{Sal}, N_q decreases more strongly at $C_{Sal} > C_{Sal}^*$ than at $C_{Sal} < C_{Sal}^*$, with increasing temperature. Viscosity measurements have confirmed the trends observed with TRFQ. The values of C_{Sal}^*, as determined with the two different techniques, agree well. The copolymerization of the surfactant with acrylamide leads to water-insoluble copolymers, because of the large compositional drift during copolymerization.

Aqueous Solution Properties of Polyampholytes : Effect of the Net Charge Distribution (A. Ohlemacher, F. Candau, J.P. Munch, S.J. Candau)

Viscometric and light scattering studies have been performed on aqueous solutions of polyampholyte terpolymers based on sodium-2-acrylamido-2-methylpropanesulfonate (NaAMPS), 2-(methacryloyloxy)-(ethyltrimethylammonium chloride (MADQUAT), and acrylamide (AM), prepared by an inverse microemulsion polymerization technique. The distribution of net charges among the chains was varied by adjusting the initial monomer composition and the degree of conversion. The effect of this distribution on the solubility of the samples and on the chain conformation was studied. It was found that samples with a narrow distribution of net charges were soluble in pure water even if the average net charge is small. Addition of salt induces a transition from an extended conformation to a more compact one, in qualitative agreement with theoretical predictions. A practically alternated NaAMPS-MADQUAT copolymer prepared by polymerization in homogeneous solution and with a small average net charge shows a behavior quite similar to that of the terpolymers.

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Sequential adsorption of polymers - displacement or trapping?

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Abstract

Sequential adsorption of carboxylated pullulan and pullulan on polystyrene-coated wafers was studied by reflectometry. The incoming pullulan partially displaced the preadsorbed carboxylated pullulan from the surface. Mixed adsorption layers were formed. By increasing the pH of the solution the carboxylated pullulan dissociated and desorbed, whereas the neutral pullulan was not influenced and remained adsorbed. A positively charged polyelectrolyte (quaternised polyvinylpyridine) was used as a probe for detecting the amount of trapped, negatively charged carboxylated pullulan remaining on the surface after the desorption step. By a mass balance calculation the fraction of displaced, desorbed and trapped carboxylated pullulan could be found for pullulans with different molecular weights.

International Polymer Colloids Group Newsletter

E.S. Daniels, V.L. Dimonie, M.S. El-Aasser, A. Klein,
O.L. Shaffer, C.A. Silebi, E.D. Sudol, and J.W. Vanderhoff

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The titles of our current research projects are given in the Contents of our *Graduate Research Progress Reports*, No. 48, July, 1997, which can be found at the end of this report. Abstracts of several presentations made at the Annual Review Meeting of the Emulsion Polymers Institute's Industrial Liaison Program are given below.

Miniemulsion Copolymerization of Styrene with Poly(Methyl Methacrylate) Macromonomers

Katharina Landfester

Heterogeneous polymers such as polymer blends and block copolymers consist of a combination of different polymer components. Due to the incompatibility of most polymers, phase separation of the components occurs. A disadvantage of incompatible polymers is often the weak bonding of one phase to another. This can lead to poor stress transfer across the interface resulting in inferior mechanical properties of the material. To increase the mechanical compatibility between the polymer phases, an improvement in the interfacial adhesion is required. This can be achieved by the addition of compatibilizing agents such as block or graft copolymers possessing segments that are miscible with those of the polymers being blended. The macromonomer technique allows the preparation of copolymers with uniform graft length. Macromonomers are linear oligomeric or polymeric chains with one polymerizable end-group, such as a vinyl, acrylic, or a heterocyclic group. These reactive end-groups can be copolymerized with other monomer species. Copolymer latex particles containing the compatibilizing agent can be prepared and used as seed for the synthesis of composite particles.

The miniemulsion polymerization kinetics and the copolymer composition of styrene/PMMA macromonomer latexes were studied using gravimetry and nuclear magnetic resonance (NMR) measurements. Capillary hydrodynamic fractionation (CHDF) was used for particle size and size distribution measurements. ^{1}H NMR spectroscopy has proven to be a convenient technique for monitoring copolymerizations, even with a macromonomer present as one component. Latexes were first prepared by the miniemulsion copolymerization of styrene with PMMA macromonomer. Based on previous experimental evidence [C.M. Miller, E.D. Sudol, C.A. Silebi, and M.S. El-Aasser, *Macromol.*, 28(8), 2754 (1995] showing that the presence of 1-2 % polymer in monomer droplets enhances droplet nucleation, 2 % polystyrene based on the styrene monomer was added to the oil phase in order to limit homogeneous nucleation. This was expected to reduce or eliminate the formation of styrene homopolymer particles.

The conversion of styrene was determined by gravimetric measurements of samples taken during the reaction of styrene and macromonomer. The results suggest that the reaction of styrene in the presence of macromonomer *or* polystyrene as the second component leads to comparable kinetics; however, the combination of macromonomer *and* polystyrene dramatically changes the kinetics of the polymerization.

Gravimetry allows one to determine the conversion of the styrene, while CHDF measurements give detailed information about the particle size evolution during the polymerization. However, these methods do not give any information about the degree of macromonomer incorporation during the reactions. For this purpose, ^{1}H solution NMR was used. ^{1}H NMR spectroscopy allows one to measure the conversion of the styrene as well as the conversion of the macromonomer. One goal of the NMR analysis is the determination of the conversion of the macromonomer. Additionally, it is possible to

detect unreacted styrene units during the reaction. These units can not be removed under vacuum and represent shorter oligomer chains with double bonds in the systems. These double bonds are consumed in later stages of the reaction.

Miniemulsion and Conventional Emulsion Copolymerization and Homopolymerization of Vinyl Acetate and Vinyl 2-Ethylhexanoate Monomers Using Reactive Surfactant TREM LF-40

Ervin L. Kitzmiller

The application of poly(vinyl acetate) (PVAc), e.g., in latex coatings, is limited by the environmental conditions in which the pure homopolymer can be used. PVAc possesses a relatively high glass transition temperature (T_g = 30° C) and suffers from poor resistance toward aqueous alkaline and acidic conditions, readily undergoing hydrolysis. These problems prevent PVAc from seeing significant application in exterior use. Copolymerization of VAc with monomers, whose homopolymers have desired characteristics, may impart to the copolymer properties, which are better suited toward the end-use application.

It has been proposed that copolymerization with certain vinyl esters may aid in the film formation, yield greater film flexibility, and improve PVAc's resistance to hydrolysis. Requirements of the comonomer would include itself being more resistant to hydrolysis, that it be able to adequately interrupt the vinyl acetate sequences in the copolymer chain, and that it should have a lower T_g, thus giving the copolymer a glass transition temperature within the desired temperature range. For this project, vinyl 2-ethylhexanoate (V2EH) was chosen.

This study is currently examining the VAc/V2EH miniemulsion and conventional emulsion polymerization systems. Miniemulsions are stable oil-in-water emulsions with droplet diameters in the 50-500 nm range. A mixed emulsifier combination is used consisting of an ionic surfactant along with a cosurfactant, such as a long chain alkane. Emphasis has been placed upon the miniemulsion system as opposed to the conventional emulsion system due to the differences that exist between them. These differences include the locus of nucleation which influences the polymerization kinetics and perhaps the evolution of the copolymer composition.

In the current work, kinetics of the conventional and miniemulsion polymerizations are followed via calorimetry (Mettler RC1 calorimeter). The ionic surfactant used is itself a reactive emulsifier, sodium dodecyl allyl sulfosuccinate (TREM LF-40, HENKEL). TREM LF-40 was selected because of its successful previous application in conventional emulsion homopolymerizations of VAc. In addition to TREM LF-40, the polymeric form, poly(TREM), will also be shown to perform well as an emulsifier and be compared to the TREM LF-40. Lastly, characterization of the copolymer produced and how the emulsion system used affects the final properties will be presented.

The Role of Mixed Anionic-Nonionic Systems of Surfactants in Emulsion Polymerization

Damien Colombié

Mixed anionic-nonionic systems of surfactants are frequently used in the synthesis of polymer latexes. This technique often results in better stability and increased monodispersity of the resulting latexes. In this work, a model system was chosen. The monomer is styrene and the two surfactants are sodium lauryl sulfate (anionic) and Triton X-405 (octyl phenoxy polyethoxy ethanol with an average of 40 ethylene oxide units per molecule, nonionic surfactant from Union Carbide).

The interaction between the surfactants and the newly formed polymer particles is being studied. The area occupied by each molecule of surfactant on the surface of the particles can be determined by constructing an adsorption isotherm of the surfactant using the "serum replacement" technique. The objective is to determine the adsorption behavior as a function of the ratio of the two surfactants. The area occupied by one molecule of SLS on polystyrene particles was determined to be

44(2, and the area occupied by one molecule of Triton X-405 was determined to be 230(2. However, the results for the nonionic surfactant need to be confirmed.

The second part of this work is focused on the study of particle growth kinetics using seeded emulsion polymerizations. The objective is to determine if the kinetics of seeded emulsion polymerization is affected by the use of different ratios of the two surfactants. A recipe using a monodisperse polystyrene seed latex with SLS as surfactant was developed in the Mettler RC1 reaction calorimeter. This tool provides extensive data on the rate of polymerization as a function of time and conversion especially in the early moments of a seeded emulsion polymerization. The average number of free radicals per particle was determined as a function of time and conversion and the results were analyzed using the "slope-intercept" method [Gilbert, R. G. in "Emulsion Polymerization, A Mechanistic Approach", Academic Press, London (1995)] to determine the entry (() and exit (k) rate coefficients.

The Effect of Crosslinking on Latex Film Formation

Hafsah Mohd Ghazaly

Incorporation of crosslinking agents in latex polymer films generally results in better physical and chemical properties of the films. The ultimate strength of the films is also dependent on the ability of the polymer chains to interdiffuse during the formation of the film. Increased rigidity of the polymer chains due to chemical crosslinking can retard the interdiffusion of the polymer chains. It is envisaged that the molecular weight of the crosslinking agent may give rise to different kinetics of interdiffusion and hence, the physical, chemical, and mechanical properties of the films.

A crosslinkable macromonomer with a molecular weight of ~2600 g/mol (^{1}H NMR) was synthesized from a hydroxy terminated, saturated ethylene-butylene polymer by reaction with acrylic acid. To prevent loss of the double bonds in the acrylic acid, 1400 ppm of either methyl hydroquinone or t-butylcatechol was found to provide effective inhibition of their loss during the synthesis. Several methods of purifying the macromonomer were investigated. Placing the macromonomer and residual reactants after the synthesis over solid sodium bicarbonate gave a similar product to that produced by a purification employing an extensive washing with aqueous sodium hydroxide. ^{1}H NMR analysis showed that the crosslinkable macromonomer has long ethylene type units which typically form a crystalline material. Crystalline structures were observed in the neat and dissolved (in toluene) macromonomer under the optical microscope.

The crosslinking ability of the synthesized macromonomer was verified by the formation of a gel when a solution polymerization in toluene was carried out for five hours at 70°C in the presence of AIBN initiator; the gel was insoluble in toluene, THF, acetone, and chloroform.

Encapsulation of Inorganic Particles via Miniemulsion Polymerization

Bedri Erdem

Polymer-encapsulated pigment and filler particles which exhibit higher gloss, better scrub resistance, weather resistance, adhesion, hiding power, flexural strength, and durability have become the main focus of various applications, such as in pharmaceuticals, agriculture, paint production, and construction. The encapsulation of inorganic particles in an organic polymer shell via emulsion polymerization will prevent their agglomeration during film formation and provide better film appearance after application. Another possible method to obtain encapsulated particles is through miniemulsion polymerization in which polymer particles between 50 and 500 nm in diameter can be obtained and where particle nucleation occurs primarily in the miniemulsion droplets.

In order to encapsulate titanium dioxide (TiO_2) particles via miniemulsion polymerization, a minimum particle size and good dispersion stability of these particles in the monomer phase must be obtained prior to the formation of the miniemulsion droplets. Dispersion of TiO_2 particles in the oil

phase can be achieved by using different types of stabilizers such as steric stabilizers, block copolymers, and linear polymers with a reactive group at one end, which can interact with the surface of the TiO_2 in the presence of a strong shear force such as provided by a sonifier. In this study, OLOA370 (polybutene-succinimide diethyltriamine; Chevron) and PEG600 dioleate (Henkel) are being successfully employed as oil phase stabilizers for inorganic particles.

The characterization of the encapsulated particles, unencapsulated inorganic particles, and polymer particles is being carried out using the density gradient column (DGC) method in which particles separate in the column depending on their density or, in other words, their inorganic particle/polystyrene content. DGC has provided both quantitative and qualitative results describing the degree of encapsulation. On the other hand, transmission electron microscopy (TEM) is being employed to characterize the particles collected from each density level.

The focus of this presentation will be on the dispersion and stability of inorganic titanium dioxide particles in the oil phase using different stabilizers and applied shear. The quantification and characterization of the encapsulation are determined using the density gradient column method and transmission electron microscopy.

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Emulsion Copolymerizations of Styrene and n-Butyl Acrylate in an Automated Reaction Calorimeter (E. (zde(er)

Towards an Understanding of the Role of Water-Soluble Oligomers in the Emulsion Polymerization of the Styrene/Butadiene/Acrylic Acid Termonomer System (X. Yuan)

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

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

Miniemulsion Copolymerization of Styrene with Poly(Methyl Methacrylate) Macromonomers (K. Landfester)

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

Miniemulsion Copolymerization of Styrene and n-Butyl Acrylate
(C.D. Anderson)

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

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

The Role of the Polymerizable Surfactant Sodium Dodecyl Allyl Sulfosuccinate in the Emulsion Polymerization of Styrene
(J. Chu)

Influence of the Homopolymer of Sodium Dodecyl Allyl Sulfosuccinate (Trem LF-40) on the Kinetics of the Emulsion Polymerization of Styrene
(X. Wang)

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

Effect of Agitation on Scale-Up of Reactors for Emulsion Polymerization (M.N. Dave)

Micron-Size Structured Particles via Dispersion Polymerization
(D. Wang)

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

Telechelic Polybutadiene: Synthesis, Characterization, and Crosslinking in Latex Films (J. Xu)

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

Film Formation from Latex Blends (J. Tang)

Hybrid Composite Latexes (P. Jeong)

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

Particle Morphology of Poly(n-Butyl Acrylate)/Poly(Methyl Methacrylate) Composite Latex Particles (S. Kirsch)

BROWNIAN DEPOSITION KINETICS of LATEX PARTICLES onto PLANAR SURFACES

by
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ABSTRACT

There has been a large body of work on the depostion of colloidal particles on to many different kinds and shapes of surfaces [2]. Nearly all work in the past has involved flowing systems in which a well-defined hydrodynamic layer exists at the collector surface. Such methods have advantages and disadvantages: incidental convection is avoided at the expense of having shear forces at the interface which can force particles to desorb, and which can enhance blocking by preadsorbed particles because of flow parallel to the collector surface. We have chosen a still system in which transport of particles to the collector surface occurs solely by diffusion. Both particles and surfaces were negatively charged, so that deposition was driven by dispersion forces.

A photomicroscopic technique has been used to visualize deposition and to determine absolute values of intial rates of deposition. Three monodisperse polystyrene colloids of various particle sizes and surface charge densities were synthesized. Their zeta potentials were determined by microelectrophoresis in $Ba(NO_3)_2$ solutions of various concentrations. Collector surfaces were cleaned glass microscope coverslips and glass coated with polystyrene and nylon. Their zeta potentials were determined from their streaming potentials in various concentrations of electrolyte. Direct determination of diffusion coefficients indicate that the particles behave normally.

Within the range of $Ba(NO_3)_2$ solution concentrations where the polymer colloids are stable, the initial deposition rates exhibit strong dependence on ionic strength, indicating that a large double layer barrier exists between particle and collector. The most regular behavior occurred in deposition on polystyrene-coated glass, presumably because roughness and highly reactive sites on the glass surface were largely eliminated. Plots of log (initial rate constant) *vs* log (ionic strength) were linear and in the order anticipated by Reerink-Overbeek theory [3].

Like the work of others, rates of deposition fell off with time, but probably for different reasons. Surface coverage when this occurred was less than 0.1%, so that we were far from the jamming limit. If the decrease in rates with time is due to the presence of "hot spots," i.e. highly localized areas of greater reactivity, the must have high potentials compared to the average on the collector surface, because the curvature is very dependent upon ionic strength.

Correlation of the initial rate constants with the maximum in DLVO plots of sphere/plate interaction potential gave linear ln (k) *vs* V_{max} graphs in accordance with Ruckenstein-Prieve theory [4]. Although qualitatively in agreement with theory, like so many others, quantitative discrepancies were beyond experimental error. Reasons for these differences are discussed.

[1‡] Work done at the University of Connecticut, Storrs

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Contribution to the International Polymer Colloids Group Newsletter

Alice P. Gast

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The Gast research group is made up of six Ph.D. students. Eric Furst, Dean Wang, and Albert Lee are advised by Alice P. Gast, Szu Wang and Mike Yatcilla are jointly advised by Alice P. Gast and Channing R. Robertson, and Joe Hur is jointly advised by Alice P. Gast and Eric S. G. Shaqfeh. We are interested in studying the physical and chemical processes governing the behavior of macromolecular liquids. In our research we aim to understand these processes and their influence on bulk properties through a combination of colloid science, polymer physics, and statistical mechanics. The following are abstracts from research projects of members of the group.

Investigation of Two-Dimensional Streptavidin Crystallization

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

Abstract:

Many applications motivate the study of the fundamental physical factors that govern ordered protein assembly on surfaces. These include two-dimensional (2D) protein crystallization for complex structural analyses, biosensors, and medical diagnostic devices. Growth of 2D streptavidin crystals at various pH values has been used to study protein molecular interactions. A mixture of streptavidin and avidin molecules bound to biotinylated lipids form a monolayer on a Langmuir trough. Lateral diffusion allows streptavidin to arrange in an ordered array, creating 2D crystals with distinct macroscopic morphologies. These morphologies are observed with fluorescence microscopy, while the lattice arrangement is seen using transmission electron microscopy.

Under conditions of pH > 6.0, dendritic X-shaped morphologies are formed and show C222 symmetry. Needle-like crystals observed at acidic conditions (pH < 4) correspond to reported P1 symmetry. Between pH 4.5-6, several unique domain shapes exist, including inverse S-shaped chiral morphologies. These domains are composed of coexisting crystal types. One of these phases is a new crystal type with P2 symmetry, and is characterized by relatively weak and anisotropic molecular interactions. Interestingly, the packing arrangement for the new P2 crystal at intermediate pH exhibits characteristics of the pH 4 crystal and of a different crystal obtained at pH 7.

Light Scattering in Magnetorheological Fluids

Eric M. Furst and Alice P. Gast

Abstract:

Magnetorheological fluids are suspensions of colloidal particles which acquire dipole moments when subjected to an external magnetic field. At sufficient field strengths, suspensions of these dipolar particles rapidly aggregate to form long chains. We seek to investigate the particle dynamics with respect to changes in structure and interactions. Additionally, the ability to experimentally probe colloidal suspensions interacting through tunable anisotropic potentials is of fundamental interest. Due to the concentrated nature of the suspensions, the relatively new technique of diffusing wave spectroscopy is ideal for probing the particle and aggregate dynamics. The absorption of light by the particles was independently measured and incorporated into our analysis. We have also taken into account changes in the optical properties of the system during aggregation. By measuring the static transmittance through the sample we separate variations due to optical changes from changes in the dynamics. Finally, we compare our experimental results to brownian dynamic simulations.

Density Functional Theory of Freezing:
Application of the Modified Weighted Density Approximation to Soft Spheres

Dean C. Wang and Alice P. Gast

Abstract:

First-order phase transitions, such as freezing, are important processes which occur in many widely-varying systems, from the basic elements to colloidal suspensions to plasmas. A theory of freezing would help elucidate such phenomenon as the order-disorder transition found in colloidal systems, as well as facilitate such technological processes as fabrication of large crystals from the melt. One such theory that has been the subject of much research is density functional theory, which utilizes information about the liquid state to locate an equilibrium fluid-solid transition. We investigate the modified weighted density approximation (MWDA) formalism of density functional theory as proposed by Denton and Ashcroft for the inverse nth power potentials. For the liquid input data, we have chosen the perturbative hypernetted chain (PHNC) integral equation of Kang and Ree due to its small computational time, as well as its high degree of accuracy. In agreement with previous investigators, we find that the quality of the MWDA results decreases as the potential becomes softer and longer-ranged. To improve upon the prediction of MWDA, we attempt to incorporate imformation about the static lattice in the theory. We find that a single parameter, independent of the potential and thermodynamic properties, can drastically improve results for the coexisting densities. Other properties, such as the Lindemann parameter, are also improved.

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PHASE BEHAVIOR AND VISCOELASTICITY OF AOT MICROEMULSIONS CONTAINING TRIBLOCK COPOLYMERS U. Batra and W.B. Russel, Department of Chemical Engineering, Princeton University, Princeton NJ 08544-5263; M. Pitsikalis, S. Sioula, and J.W. Mays, Department of Chemistry, University of Alabama at Birmington, Birmingham AL 35294, J.S. Huang, Exxon Research and Engineering Co., Annandale NJ 08801

Abstract

Mixtures of AOT(sodium 2-diethyl hexyl sulfosuccinate)/water/decane microemulsions with polyethylene oxide/polyisoprene/polyethylene oxide (PEO/PI/PEO) triblock copolymers form highly associated solutions with unusual phase behavior and concentration dependence of the viscoelastic moduli. A gas-liquid phase transition, reported here for the first time in these mixtures, is attributed to the entropic gain accompanying the conversion of loops to bridges, in accord with theories for polymer brushes. The homogeneous condensed phase is highly viscous and elastic. The volume fraction dependence of the high frequency modulus conforms to expectations from theories for either reversible networks or solutions of flowerlike micelles. The apparent low shear, or plateau, viscosity, on the other hand, exhibits a maximum at a volume fraction roughly twice that at the phase boundary. This unusual behavior is predicted qualitatively for solutions of flowerlike micelles, but the quantitative aspects of the response are more difficult to rationalize.

HIGH FREQUENCY SHEAR MODULUS OF POLYMERICALLY STABILIZED COLLOIDS S. L. Elliott and W. B. Russel, Department of Chemical Engineering, Princeton University, Princeton, NJ 08544

Synopsis

Rheological measurements on concentrated colloidal dispersions at high frequencies probe interactions at small separations and provide the most direct link between the shear modulus and the pair potential. For colloids stabilized with a grafted polymer layer, others have extracted the pair potential from measurements of the high frequency shear modulus via a molecular theory, which does not account for hydrodynamic interactions. Here we apply a nonequilibrium theory that includes the repulsion between polymer layers and its effect on the equilibrium structure, while accounting for flow of the suspending fluid within the layer in evaluation of the hydrodynamics. Predictions with a simple approximation for the

hydrodynamic interactions, which interpolates between the lubrication and far field limits, are compared with the molecular theory. We also demonstrate qualitative agreement with experimental data and assess over what range of effective volume fractions neglect of hydrodynamic interactions permits data to be inverted to obtain an interaction potential.

THE EFFECTS OF ADSORBED LAYERS AND SOLUTION POLYMER ON THE VISCOSITY OF DISPERSIONS CONTAINING ASSOCIATIVE POLYMERS

Q. T. Pham, W. B. Russel, Department of Chemical Engineering, Princeton University, Princeton, New Jersey 08544, U.S.A.; W. Lau, Research Laboratories, Rohm and Haas Company, Spring House, Pennsylvania 19477, U.S.A.

SYNOPSIS

Associative polymers adsorb on particle surfaces via hydrophobic interactions to generate dense layers that reduce the polymer concentration in solution, thereby decreasing the continuum viscosity. The telechelic polymer adsorbs with one hydrophobe on the particle surface, allowing the other hydrophobe to couple both the associative network and adsorbed layers on other particles. Detailed measurements of adsorption and steady shear viscosity provide consistent quantitative support for this scenario. Measured adsorbed amounts and layer thicknesses of hydrophobically-modified poly(ethylene oxides) on PMMA particles suggests a dense layer of moderately stretched chains in dilute solution. In concentrated dispersions, the effect of adsorption on the particles can be quantified by the Huggins coefficient and intrinsic viscosity which indicate strong couplings among particles with adsorbed layers and with the associated solution. Enhancement of the dispersion viscosity arises from both the high viscosity of the polymer solution, in which the particles are incorporated via their adsorbed layers, and direct interactions between adsorbed layers. Existing theory for terminally anchored polymers helps us to describe the adsorbed layer and Martin's equation correlated the polymer concentration and volume fraction dependence of the dispersion viscosity.

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

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

Termination rate coefficients from molecular weight distributions. P.A. Clay, D.I. Christie, R.G. Gilbert. *ACS Symposium Series: Advances in Free-Radical Polymerization*, ed. K. Matyjaszewski. American Chemical Society, Washington DC, 1997.

An extended Mayo method is deduced to obtain rate coefficients and mechanistic information from molecular weight distributions (MWDs), using the high molecular weight part of the full instantaneous number MWD, $P(M)$, together with rate data. $P(M)$ is readily obtained from the GPC MWD. The method can yield the following rate coefficients (a) termination, $\langle k_t \rangle$ (the average of chain-length dependent termination rate coefficients over the chain lengths of the radical population) (b) transfer, and, for emulsion polymerizations, (c) entry; all of these can be obtained over a wide range of conversion. The technique is applied in an extensive series of experiments on styrene seeded emulsion polymerizations (persulfate initiator, stabilized by anionic surfactant), wherein MWDs are obtained at successive conversions, from which instantaneous MWDs are obtained by successive subtraction. Values for $\langle k_t \rangle$ as a function of conversion are in moderate but imperfect accord with those obtained from data on relaxation kinetics; the difference, which is within experimental uncertainty but seems real, may arise from chain-length dependent termination, since the different radical fluxes in the two means of measuring $\langle k_t \rangle$ sample different radical populations over which the average is taken. Either set of $\langle k_t \rangle$ values can be represented by theory based on diffusion control, with minor adjustment of parameters. Results for entry coefficients had large uncertainty but were consistent with the literature. An exceptionally low molecular weight species seen at high conversion is ascribed to surface-anchoring effects causing increased termination as entering radicals are confined to a shell.

Chain transfer to monomer in the free-radical polymerizations of [illegible], styrene and α-methyl styrene. D. Kukulj, T.P. Davis, R.G. Gilbert.

Chain transfer constants to monomer (C_M) are measured for these monomers in bulk polymerization using the number molecular weight distribution method [e.g., P.A. Clay, R.G. Gilbert, G.T. Russell, Macromolecules, 30, 1935-46 (1997)] and compared to values from the Mayo method. Values at 50°C are $C_M = 5.2\times10^{-5}$, 5.3×10^{-5} and 1.5×10^{-2}, for MMA, styrene and α-methyl styrene, respectively. The extremely high value for α-methyl styreneoriginates from its low propagation rate coefficient; all three monomers had similar values for the transfer rate coefficient. The stromng influence of transfer to monmer as a chain-stopping mechanism for α-methyl styrene was confirmed by end-group analysis using MALDI.

Catalytic chain transfer in miniemulsion polymerization. D. Kukulj, T.P. Davis, R.G. Gilbert.

The influence of cobalt catalytic chain transfer agent to control molecular weight in the miniemulsion polymerization of MMA was studied. The solubility of the cobalt catalyst was found to have a large influence on the mechanism of the reaction. Two catalysts were selected for study: cobaloxime boron fluoride (COBF), which partitions approximately equally in the water and oil phases, and tetra-phenyl cobaloxime boron fluoride, which resides exclusively in the oil phase. The COBF-mediated reaction was found to be extremely sensitive to the selection of initiator, displaying poor catalytic activity in the presence of oxygen-centered radicals (derived from potassium persulfate). In contrast, the COPhBF catalytic activity proved to be independent of initiator type as the catalyst does not come into direct contact with the initiator-derived radicals. The results are consistent with a mechanism whereby the cobalt catalyst is poisoned or degraded in the presence of oxygen-centered radicals. In miniemulsion polymerization, the catalyst can effectively be isolated from the initiator radicals, thereby allowing a batch system to proceed without significant loss of catalytic activity. The conclusions are supported by comparison of chain transfer constants obtained in miniemulsion and bulk polymerizations.

Transition-state theory model for the diffusion coefficients of small penetrants in glassy polymers. A. Gray-Weale, R.H. Henchman, R.G. Gilbert, M.L. Greenfield and D.N. Theodorou. Macromolecules, in press (MA970349F).

Previous molecular dynamics simulations have shown that the diffusion of a penetrant in a glassy polymer involves occasional jumps between cavities through the opening of a "neck", and thus, because this is a rare event, that the diffusion coefficient can be estimated using transition-state theory. We treat this process as a unimolecular rearrangement, and develop semi-empirical means of estimating the activation energy, frequency factor and jump length. The activation energy is obtained by treating the polymer as a continuous solid, and calculating the energy required to expand a neck in that continuum. The model for the frequency factor uses the result from simulations that the distribution of frequencies of the modes in the transition is very similar to that distribution for the reactant state. The frequency factor is estimated by considering only the motion of the penetrant. These motions are treated as harmonic oscillators. The jump length is obtained from simple geometric considerations of the polymer chain. The parameters are readily evaluated from bulk properties of the polymer such as the isothermal compressibility. The model reproduces experimental trends semi-quantitatively, and could be used to interpolate and extrapolate experimental diffusion data.

Emulsion Polymerization in a Hybrid Carbon Dioxide/Aqueous Medium. M.A. Quadir, R. Snook, R.G. Gilbert and J.M. DeSimone. Macromolecules, in press.

The development of a new reaction medium is reported, based on a bi-phasic mixture of carbon dioxide and water for emulsion polymerizations: a surfactant-free aqueous emulsion polymerization of methyl methacrylate using potassium persulfate under a varying head pressure of CO_2 (0 - 350 bar) at 75 °C. The resulting polymer is a stable latex with particles of submicron size. The effect of CO_2 on polymerization is relatively small, until there is a significant change at high CO_2 pressure. This is seen by examining the molecular weight distribution in the form of the log(number distribution), $P(M)$ (readily obtained by GPC). At pressures of 140 bar and below, the $P(M)$ show the form expected for chain-stopping events dominated by transfer and by diffusion-controlled termination. At 280 bar, $\ln P(M)$ is significantly steeper than its lower-pressure counterpart at relatively low conversion (45%). This is attributed to swelling by supercritical CO_2 reducing the viscosity of the particles, allowing more rapid termination.

* The following publications have appeared since the previous Newsletter:

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

Propagation rate coefficient of vinyl neo-decanoate by pulsed laser polymerization. R. Balic, R.G. Gilbert, M.D. Zammit, T.P. Davis and C.M. Miller, Macromolecules, **30**, 3775 - 3780 (1997).

Exit in the emulsion polymerization of vinyl acetate. H. De Bruyn, R.G.Gilbert and M.J. Ballard. Macromolecules, 29, 8666-8669 (1996).

Mechanisms for radical entry and exit: – Aqueous-phase influences on polymerization. R.G. Gilbert. Chapter in *Polymeric Dispersions. Principles and Applications*, ed. J.M. Asua, Kluwer Academic, 1997, 1-15.

Particle size distributions. E.M. Coen and R.G. Gilbert. Chapter in *Polymeric Dispersions. Principles and Applications*, ed. J.M. Asua, Kluwer Academic, Dordrecht, 1997, 67-78.

Polymerization at high conversion. D. Kukulj and R.G. Gilbert. Chapter in*Polymeric Dispersions. Principles and Applications*, ed. J.M. Asua, Kluwer Academic, Dordrecht, 1997, 97-107.

Determination of kinetic parameters for propagation in free-radical polymerizations: an assessment of ab initio procedures. J.P.A. Heuts, R.G. Gilbert and L. Radom. J. Phys. Chem.100, 18997 - 19006 (1996).

The penultimate unit effect in free-radical copolymerizations. J.P.A. Heuts, R.G. Gilbert and I.A. Maxwell. Macromolecules, 30, 726-736, 1997.

First-principles prediction and interpretation of propagation and transfer rate coefficients. J.P.A. Heuts, Sudarko and R.G. Gilbert. Macromol. Symp.111, 147-57 (1996).

Catalytic chain transfer for molecular weight control in the emulsion homo- and co-polymerization of methyl methacrylate and butyl methacrylate. D. Kukulj, T.P. Davis, K.G. Suddaby, D.M. Haddleton, R.G. Gilbert. J. Polym. Sci. Polym. Chem. Ed., 35, 859-878, 1997.

An experimental investigation on the evolution of the molecular weight distribution in styrene emulsion polymerization. C.M. Miller, P.A. Clay, R.G. Gilbert and M.S. El-Aasser. J. Polym. Sci., Polym. Chem. Edn., 35, 989-1006 (1997).

Molecular weight distributions in free-radical polymerizations. 2. Low-conversion bulk polymerizations. P.A. Clay, R.G. Gilbert, G.T. Russell, Macromolecules, 30, 1935-46 (1997).

Contribution to the International Polymer Colloid Group Newsletter
August 1997

from

Finn Knut Hansen

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Applications and developments of the DROP Instrument.

As described earlier in this newsletter, we have developed an instrument for Axisymmetric Drop Shape Analysis, the DROP instrument. The instrument can measure interfacial tensions of pendant or sessile drops and bubbles in addition to contact angles. The use of the instrument is made easy through a user-friendly computer program, and one advantage of this program is that it is very fast, up to 25 p/sec (PAL) with a Pentium PC. The instrument is also described in our Web pages: **http://www.kjemi.uio.no/~fhansen/dropinst.html**.

Below I will describe 2 applications of the instrument.

1. The Influence of Oil Phase on the Adsorption of Non-ionic Surfactants Investigated by the Automatic Sessile Drop Method.

Finn Knut Hansen and Hege Fagerheim

Interfacial tension between five different organic liquids and water have been measured, using nonylphenol-poly(oxyethylene) surfactants with 10, 16, 20 and 40 OE-groups. In these systems the interfacial tension of a freshly formed oil/water interface always drops in well-known manner (in milliseconds) from the value of pure oil/water systems to a low initial value. From here a further decrease is often observed, dependent on the nature of the organic phase and the surfactant system. In the dodecanol system, interfacial tension is almost constant, and increases with the water solubility of the surfactant as expected. In systems with more polar oils, such as trichloroethylene and chlorobenzene, the interfacial tension decreases with time, mostly dependent of the hydrophilicity of the surfactant. The equilibrium values, when plotted against the number of OE-groups (n) often show a minimum that shifts towards higher n as the oil's polarity increases. By using the initial "extrapolated zero-time" (EZT) value of the interfacial tension and the equilibrium values a mathematical model has been formulated, based on nonsteady-state diffusion in the oil phase based on Danckwerts' solution of Fick's second law.
The degree of surfactant coverage can then be expressed as

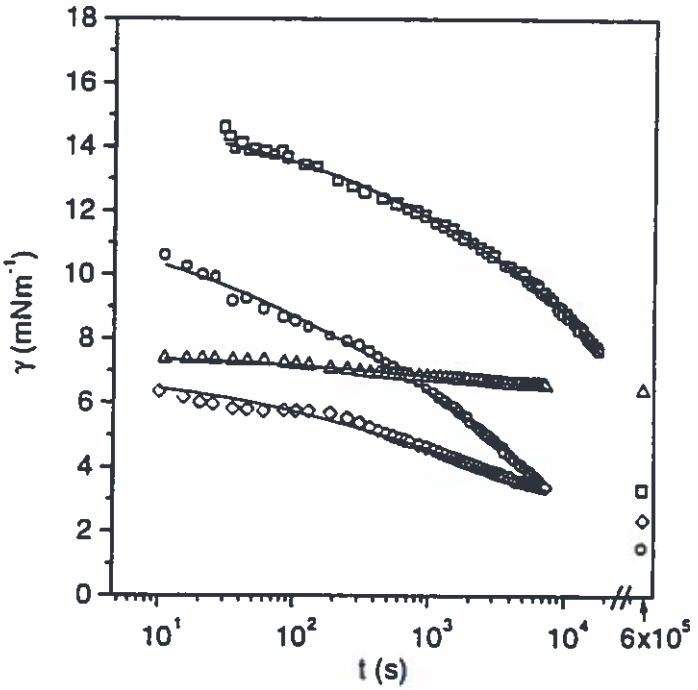
$$\theta = \frac{\Gamma}{\Gamma_{max}} = \frac{1}{2}\left\{\frac{\theta^{\infty}}{\theta^{EZT}}F(t) + \theta^{\infty} + 1 - \left[\left(\frac{\theta^{\infty}}{\theta^{EZT}}F(t) + \theta^{\infty} + 1\right)^2 - 4\theta^{\infty}(1 + F(t))\right]^{\frac{1}{2}}\right\}$$

where $$F(t)=\frac{8\pi r D_B}{k_{1B}A}f(t)=\frac{2D_B}{k_{1B}r}f(t) \quad \text{with} \quad f(t)=\sum_{i=1}^{\infty}\exp\left(-tD_B i^2\pi^2/r^2\right)$$

Here θ^{∞} is the equilibrium degree of coverage and θ^{EZT} is the initial value. D_B is the diffusion coefficient in the internal (drop) phase, k_{1B} is the adsorption constant (Langmuir) from the internal phase to the interface, r is the drop's radius (assumed spherical). Interfacial tensions are calculated from the degrees of coverage by means of the Szyskowski-Langmuir equation

$$\gamma=\gamma_0+RT\Gamma_{max}\ln(1-\theta)$$

Here Γ_{max} is the maximum surface excess. The model gives D_B ca 2×10^{-10} m^2s^{-1} which is quite realistic, in addition the surfactants' interfacial area, $a_S=1/\Gamma_{max}$, and k_{1B} have been calculated. The values of a_S vary between 53 and 145 $Å^2$ per molecule, the highest values are obtained with the strongest hydrogen bonding oil. The values of k_{1B} are unreliable when calculated by this model. The figure below illustrates some of the results.



Correspondence between experiment and theory. Experimental values for toluene plotted with theoretical curves. NP-OE_{10} (□), NP-OE_{16}, (○), NP-OE_{20} (◇), and NP-OE_{40}(△). (The points to the far right are equilibrium values, measured after 7 days.)

This paper has been submitted for publication *in Colloids and Interfaces.*

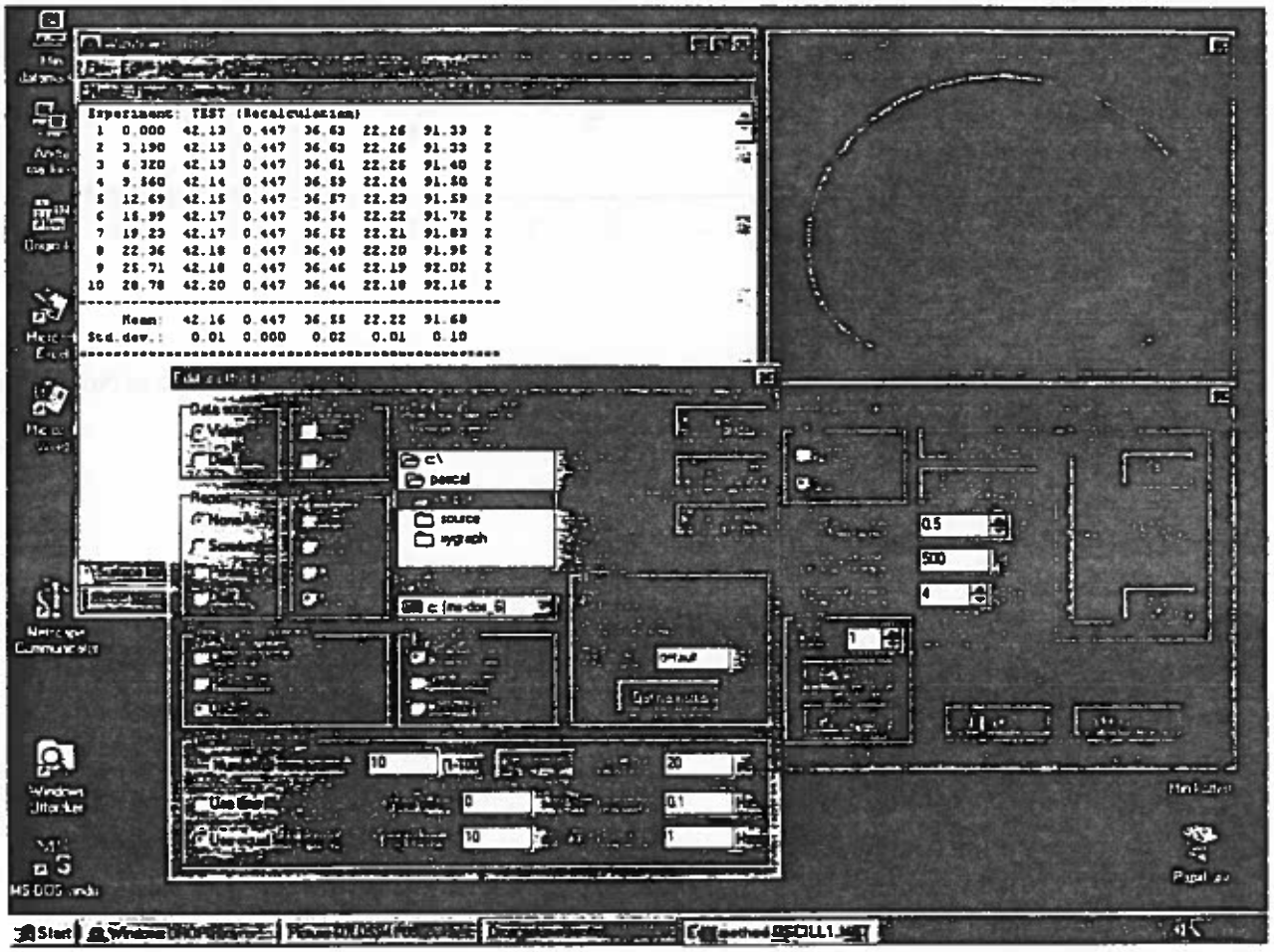
2. The Adsorption and Surface Rheological Properties of Hydrophobically Modified Polymers on the Air/Water Interface Measured by Means of Automatic Axisymmetric Drop Shape Analysis.

Finn Knut Hansen and Rolf Myrvold

The most commonly observed film property of hydrophobically modified polymers on fluid interfaces is the surface pressure, or surface tension lowering. The reliability of such data as often obtained from surface tension measurements by for instance the ring or Wilhelmy plate methods is quite low, due to the often slow adsorption kinetics and long equilibration time necessary. A convenient method for measuring time dependent surface tensions is the pendant or sessile drop

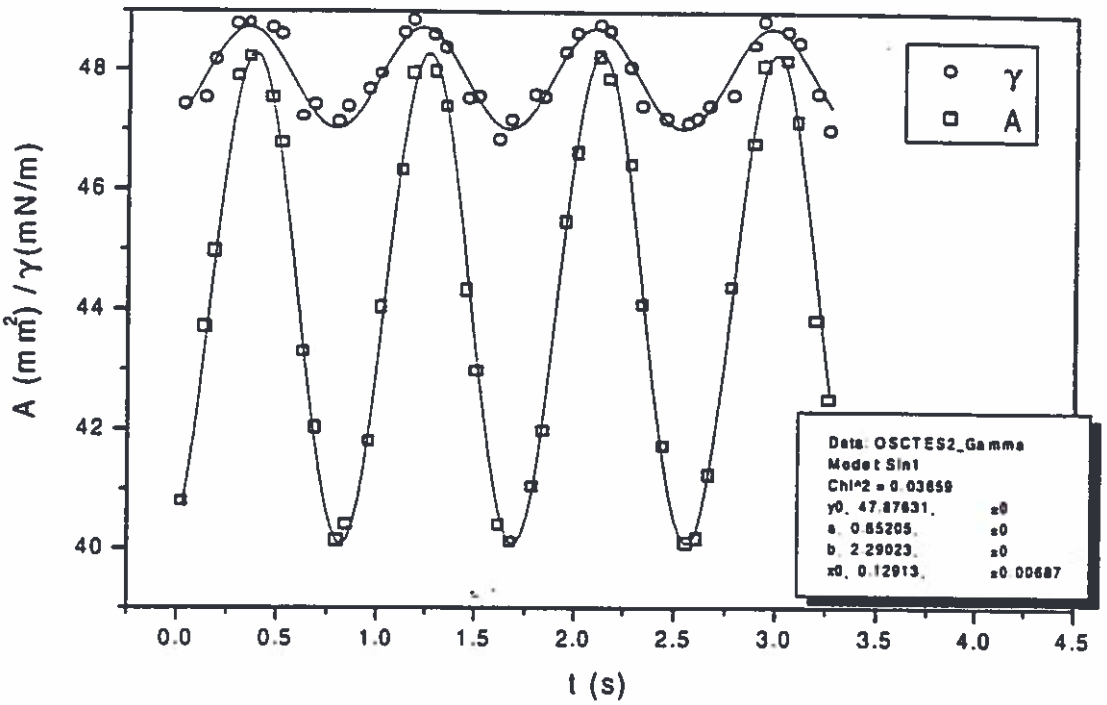
method. In this laboratory we have developed an instrument for axisymmetric drop shape analysis based on a goniometer equipped with a macro lens and a video camera connected to a PC frame grabber. The in-house developed software is based on image analysis and can calculate the surface tension of sessile or pendant drops or bubbles in a very short time. The method of sessile bubble have been used to measure the time dependence of the surface pressure of unmodified and hydrophobically modified associating polymers. The surface pressure increase is concentration dependent with an initial high rate due to absorption and a subsequent slow process due to conformation changes of possibly redistribution of adsorbed molecules.

Recently, the DROP instrument has been improved by new hardware and software modifications in order to further increase speed and usefulness. A drop control unit has been added consisting of a dispenser and a motor driven oscillating syringe in series. By this unit, both relaxation and oscillation experiments may be performed. The computer side also has been improved and now makes it possible to measure video pictures in real-time, i.e. 25 frames/sec. By this system sinusoidal oscillating bubbles have been produced and analysed by means of a non-linear curve fitting method. This method makes it possible to calculate simultaneously the viscous and elastic parts of the complex surface dilation module, in the same way as an oscillating viscometer.



The picture above shows a screen snapshot of the DROP program with the Method editor, drop volume device control and a drop bitmap.

Below is shown a result form an oscillation experiment at 1 Hz. The curves are fitted sinusoidal functions. These preliminary result show that the surface films of associating polymers are predominantly elastic (the surface area and tension are almost in phase). The elastic surface dilatational modulus also seems to increase with increasing frequency. Work is presently being done with polymer-surfactant systems.



This work will be presented at the Associating Polymers 1997 meeting in France in November.

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

Reporter: D. Sunil Jayasuriya

Full Paper Published in Thermochimica Acta 289 (1996) 243 – 265

Developing Feed Policies to Maximize Productivity in Emulsion Polymerization Processes

Paul E. Gloor and Robert J. Warner

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Abstract

This work deals with maximizing the productivity of our emulsion polymer reactors. Increasing productivity means manufacturing latexes with adequate monomer conversion and final properties, safely, in the shortest possible time. This translates to reduced costs and added capacity. We set out to answer the following questions:

- Are we getting the most productivity from our manufacturing reactors?
- Can we better optimize new and existing products to increase productivity?

The most efficient use of our reactor time requires that we operate at the limit of our heat removal capability (with safety margins). The first step is to quantify what this capability is. One could perform many time consuming studies on each of our manufacturing reactors to identify heat transfer coefficients and rates for each product. Our alternative approach was to use an existing product as a benchmark. Experience had demonstrated that this product was at the limit of our capabilities. This benchmark product was then characterized using reaction calorimetry (Mettler Toledo RC1) and other methods. In this manner, we quickly identified an empirical maximum heat flow "ruler" against which we could evaluate existing and new products. We could now test different feed policies and be assured that we could scale them up economically. These feed policies were identified from calorimetry and pilot plant experiments and by using computer simulation models.

Keywords: process development, reaction calorimetry, emulsion polymerization, computer modeling, safety analysis

INTERNATIONAL POLYMER COLLOIDS GROUP NEWSLETTER

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

Reported by Jung-Hyun(Jay) Kim

Effects of Carboxyl Groups Dissociation and Dielectric Constant on Particle Size of Polyurethane Dispersions1 - SH Son, IH Kim, HJ Lee, JH Kim, and JI Kim*

**Polymers Division, Plastics, Bayer Corporation, 730 Worcester Street Springfield, MA 01151-1089*

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

- Accepted in Colloids and Surfaces A: Physicochemical and Engineering Aspects (1997.6)

-1 Part of this paper was presented at the 4th Pacific Polymer Conference (1995. 12, Hawaii)

Effects of Surface Functional Groups on Film Formation and Tensile Strength Development in Reactive Latex Systems - YJ Park and JH Kim

The effects of surface functional groups have been investigated into the chain interdiffusion movement at the interfacial zone of reactive latexes. For that, a series of latexes having different surface functionality were prepared using batch or shot growth emulsion polymerization method. The particle surface properties were varied by changing the number density of functional groups. The rate of tensile strength development was decreased with increasing number density of surface functional groups. This indicated that the interpaticular crosslinking reaction restricted the interdiffusion of polymer chains during film formation and annealing process. The average diffusion coefficient D of polymer chains across particle interfaces was obtained from dynamic mechanical analysis to compare the results of the rate of tensile strength development. The magnitude of D of reactive latex film was lower than that of homopolymer film. The lower chain mobility of reactive latexes prevented mechanical strength development.

- Accepted in Polym. Eng. & Sci., (1997.5)

Simulation of Secondary Particle Formation in Seeded Emulsion Polymerization : Effect of the Surface Charge Density of Seed Particle - IW Cheong and JH Kim

Mathematical modeling and simulation were carried out to investigate the effects of the surface charge density of the seed particle on secondary particle formation and the rate of polymerization in early stage of the emulsifier-free seeded emulsion polymerization of methyl methacrylate. The limited coagulation theory was applied to simulate the new particle nucleation. The main factor influencing the capture rate of oligomeric radicals in the growing seed particle was assumed to be the electrostatic repulsion of seed particles. DLVO theory was also introduced to estimate the electrical repulsions between the seed particles and the oligomeric radicals in the aqueous phase. In the case of highly charged seed particle, the adsorption rate of oligomeric radicals in the aqueous phase showed a strong effect on the polymerization rate. The low adsorption of oligomeric radicals results in the low value of average number of radicals per particle. The surface charge density of seed particle was found to play an important role in limiting the polymerization rate at the beginning of the reaction and even in affecting the formation of secondary particle at a certain condition.

- Accepted in Macromolecular Theory and Simulation (1997.7.)

Current Research Projects

1. Dynamic Mechanical Properties of Composite Latexes
2. Film Properties of Reactive Latex Systems
3. Kinetic Study on Alkali-Soluble Random Copolymer in Emulsion Polymerization of Styrene
4. Synthesis and Characterization of R/F Emulsion Gel Using Supercritical Fluid
5. Kinetics Study on Modification of Polyurethane Dispersion
6. Kinetics Study on Highly Sulfonated Seeded Emulsion Polymerization Using RC Method

LEIDEN COLLOID AND INTERFACE SCIENCE GROUP

The staff members of the Leiden Colloid and Interface Science Group are
Prof. dr. D. Bedeaux
Dr. ing. G.J.M. Koper
Dr. E.M. Blokhuis

Furthermore, there is a varying number of post-docs, graduate (PhD) students and undergraduate students.

Research topics:

- *Microemulsions and Dispersions*
- **Aggregation and phase behaviour of droplet phase microemulsions,** Smeets, Sager (Technical University Twente), Koper, Bedeaux
- **Dielectric and elecro-optical properties of "living polymers",** Cirkel, Koper, Schurtenberger (ETH Zürich)
- **Electro-optical light scattering and rheology of electro-rheological fluids,** Cavaco, Koper, Bedeaux
- **Thermodynamics of small systems,** Koper, Reiss (UCLA)

- *Statistical Mechanics of Surfaces*
- **Phase behaviour of the water/AOT/oil system,** Sager (Technical University Twente), Blokhuis, Koper
- **Optical properties of particles at surfaces,** van Duijvenbode, Koper, Bedeaux
- **Statistical thermodynamics of interfaces,** Groenewold, Blokhuis, Bedeaux
- **Irreversible thermodynamics of surfaces,** Kjelstrup (NTNU Trondheim), Bedeaux
- **Wetting phenomena of simple and complex fluid interfaces,** van Duijvenbode, Blokhuis, Bedeaux

- *Polymers and Polyelectrolytes*
- **Proton binding to complex materials,** Koper, Borkovec (ETH Zürich)

fax transmission

From: Irvin M. Krieger Date: September 23, 1997
To: Bob Gilbert
FAX number: 61 2 9351 3329

Number of pages (including this one) 1

Although I am no longer active in research, I would still like to remain a member of the ICPG, if the IPCG is willing!

Here is a contribution in abstract form of a manuscript submitted to the *Journal of Rheology*. I will send the full ms to anyone requesting it.

Best regards!

Synopsis of manuscript submitted to the Journal of Rheology.

THIXOTROPIC-LOOP TESTS ON VISCOELASTIC MATERIALS

Irvin M. Krieger
Department of Chemistry, Case Western Reserve University
Cleveland. Ohio 44106-7078

Synopsis

The thixotropic-loop test is used to estimate the structural relaxation time λ of a colloidal dispersion. Starting from rest, this test subjects the sample to a linear increase of the shear rate for a period t_1, followed by a linear decrease of the shear rate back to zero at time $2t_1$. When the results are graphed with shear rate as the ordinate and shear stress as the abscissa, non-Newtonian fluids whose viscosity depends on previous shear history will give counter-clockwise loops. The area of the clockwise loop depends on the ratio λ/t_1.

This paper demonstrates that, for samples which possess significant elasticity, clockwise loops may be encountered.

Full reprint available upon request.

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Contribution to IPCG Newsletter
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UK Polymer Colloids Forum

I am in the final stages of preparing a booklet of profiles of all UK academics who are active in the field of Polymer Colloids. Each profile has full contact information and comprises a one-page overview of the research interests, expertise and facilities available to the academic in the form of a bulleted list for ease of reading. The individual profiles have been brought into a single style of presentation in the booklet, which also includes a contents list and index to assist people when using the booklet to identify UK academics with interests and/or facilities appropriate to their needs. Please let me know by e-mail or fax if you would like to receive a copy of the booklet. I expect that it will ready for mailing some time in September 1997.

Professor Doug Hourston is organising the fifth meeting of the Forum which will take place from 16-17 April 1998 at Loughborough University. If you wish to offer a paper, you should send a 200-300 word abstract to Mrs. Jackie Baseley (by post: IPTME, Loughborough University, Loughborough, Leicestershire, LE11 3TU, United Kingdom; by fax: +44 (0)1509 223949; by e-mail: j.a.baseley@lboro.ac.uk). You should also find details about the meeting near the front of this issue of IPCG Newsletter.

Chain Transfer to Polymer in Free-Radical Polymerisations of n-Butyl Acrylate

Research Student: Mr. Nasir Ahmad
Collaborator (NMR): Dr. Frank Heatley, Chemistry Department, University of Manchester
Sponsor: ICI Acrylics, Pakistan Government

We have made important new observations concerning how the extent of chain transfer to polymer varies with initial monomer concentration, $[M]_o$, and % conversion in free-radical solution polymerization of n-butyl acrylate. The polymerizations were carried out in cyclohexane at 70 °C using 0.1 % (w/w) 2,2'-azobis-(2-cyanopropane) as initiator. The mol% branched repeat units (mol% branches) in the poly(n-butyl acrylate) was determined from unique resonances of branch-point carbons in the ^{13}C NMR spectra [1-3]. For rapid pulse spectra, the mol% branches data determined from the branch C_q resonance were significantly lower than those determined from the branch $CH+CH_2$ resonances because the total backbone carbon integral was used in the denominator for the calculations and comes predominantly from CH and CH_2 carbons, which relax more rapidly and have a greater NOE than carbons with no attached hydrogens. When spectra were recorded under conditions which suppressed the NOE and allowed complete relaxation of all carbon nuclei between pulses, the mol% branches obtained from the branch C_q and $CH+CH_2$ resonances were identical within experimental error. The mol% branches obtained from branch

$CH+CH_2$ resonances increased only slightly under these conditions, showing that by comparing the intensities of like carbons in fast pulse spectra, the relative intensities reflect reasonably accurately the relative abundance of the corresponding type of carbon. The mol% bracnhes data given below are from rapid pulse spectra and were calculated using integrals for the branch $CH+CH_2$ resonances.

At $[M]_o$ > 10 % (w/w) the mol% branches is independent of $[M]_o$ and increases from 0.8 to ~2.2 % as conversion increases from 35 to ~95 %. However, for more dilute solutions, with $[M]_o \leq 10$ % (w/w), the mol% branches increases as $[M]_o$ decreases and is higher than at equivalent conversions for the more concentrated solution polymerizations, *e.g.* at ~25 % conversion the mol% branches increases from 2.7 % for $[M]_o$ = 10 % (w/w) to 5.9 % for $[M]_o$ = 3 % (w/w). These observations can be explained in terms of the ratio of the concentrations of polymer repeat units and monomer in the vicinity of the propagating chain end. In more concentrated solutions, intermolecular chain transfer to polymer dominates because, at all except the lowest % conversions, the overall polymer repeat unit concentration is sufficient for overlap of individual polymer coils. However, in the dilute solutions the overall polymer repeat unit concentration is too low for overlap of individual polymer coils and intramolecular chain transfer to polymer dominates. Under these conditons, the local polymer repeat unit concentration within the isolated propagating chains is defined by the chain statistics and is approximately constant, whereas the monomer is distributed uniformly throughout the solution. Thus, for dilute solutions, as $[M]_o$ decreases, the probability of chain transfer to polymer (and hence the mol% branches) increases. The results, therefore, highlight the significance of intramolecular chain transfer to polymer and emphasise the need to consider local concentrations in the vicinity of the propagating chain.

Similar studies of free-radical solution polymerization methyl acrylate and ethyl acrylate are underway and we are now beginning studies of the extent of chain transfer to polymer in emulsion homopolymerizations of methyl acrylate, ethyl acrylate and n-butyl acrylate.

1. P.A. Lovell, T.H. Shah and F. Heatley, *Polym. Commun.*, **32**, 98 (1991)
2. P.A. Lovell, T.H. Shah and F. Heatley, *Polym. Mat. Sci. Eng.*, **64**, 278 (1991)
3. P.A. Lovell, T.H. Shah and F. Heatley in *Polymer Latexes: Preparation, Characterisation and Applications*, E.S. Daniels, E.D. Sudol and M.S. El-Aasser, Editors. 1992, American Chemical Society: Washington, DC. p. 188.

Chain Transfer to Polymer in Emulsion Polymerisations of Vinyl Acetate

Research Assistant: Dr. David Britton
Collaborator (NMR): Dr. Frank Heatley, Chemistry Department, University of Manchester
Sponsor: Engineering and Physical Sciences Research Council, United Kingdom

This new project started at the beginning of this year and concerns the use of ^{13}C NMR spectroscopy to study chain transfer to polymer and grafting of protective colloids in emulsion polymerizations of vinyl acetate. We began by looking at simple bulk polymerizations with a view to assigning all resonances in the ^{13}C NMR spectrum of poly(vinyl acetate) before attempting emulsion polymerizations. Work on simple semi-

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

batch emulsion polymerizations of vinyl acetate (carried out in the absence of protective colloids) has been underway over the past few months.

The poly(vinyl acetate) spectra have been fully interpreted in terms of structural features arising from (i) normal and inverted repeat unit placements, (ii) partial hydrolysis of the poly(vinyl acetate), and (iii) chain transfer to polymer. Although evidence was obtained for chain transfer to polymer via H-abstraction from both backbone tertiary C–H bonds and methyl side-groups, the latter make the dominant contribution. The spectral assignments facilitated calculation of the mol% branches and the mol% of inverted repeat units in the poly(vinyl acetate) samples produced. By a process of elimination, we were able to show that the mol% of branched repeat units in poly(vinyl acetate), could be reliably calculated using the ratio of the integral of the end-goup CH_2O peak (δ_C 61) (from the $-CH_2CH_2OAc$ end-groups that result from chain transfer to polymer) to half the total backbone carbon integral ($24 < \delta_C < 74$). Compared to data from spectra that were run under quantitative conditions, the values of mol% branches from the corresponding fast pulse spectra were about 24% higher due to the greater NOE of the end-group CH_2O carbons compared to the backbone carbons. Thus the fast pulse spectra give mol% branches data that are somewhat high but of the correct magnitude. All mol% branches data presented below were calculated from fast pulse spectra and, being self-consistent, are suitable for use in establishing effects of polymerization variables on the extent of chain transfer to polymer.

Changing the initiator from 2,2'-azobis-(2-cyanopropane) to benzoyl peroxide had no effect on the mol% branches in the bulk polymerizations showing that the propagating poly(vinyl acetate) chain radicals are the principal hydrogen atom abstractors. This is consistent with previous observations by Don Sundberg [4]. In both bulk and emulsion polymerization, the mol% branches increased steadily with overall conversion. However, because the emulsion polymerizations proceed almost exclusively within the latex particles and at high instantaneous conversions, the levels of branching in the poly(vinyl acetate) produced (final levels = 0.76-0.90 mol%) were much higher than in the poly(vinyl acetate) from bulk polymerization (final levels = 0.16-0.31 mol%). Increasing the temperature of emulsion polymerization from 60 to 70 °C led to an increase in the mol% branches but had no measurable effect on the mol% of inverted repeat units (which took values of 1.38±0.22 mol% independent of conversion and temperature for the emulsion polymerizations).

4. N.-J. Huang and D.C. Sundberg, *J. Polym. Sci., Polym. Chem.*, **33**, 2551, 2571 (1995)

Contribution to the IPCG Newsletter September, 1997

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Main activity of our group is on colloidal crystals, their morphology, crystal structure, crystal growth kinetics and effect of external fields such as an gravitational field, electric field, and centrifugal field. This January and August microgravity experiments on the colloidal crystallization and colloidal polymerization were made using jet aircraft. Absorption and/or adsorption pnemomena of colloidal spheres, viscosity of colloidal gases, liquids and crystals, surface tension of synthetic and biological polyelectrolytes, and other physico-chemical properties of macroions have been studied.

Publications(1996-)

(1)"**Electrically Induced Shear Waves in Colloidal Crystals** ", M. Stoimenova, Vassil Dimitrov and T. Okubo, *J. Colloid Interface Sci.*, **184**, 1065-111(1996).

The static light scattering method is used for the detection of acoustic waves induced in colloidal crystals and liquids by low frequency electric pulses. The method is sensitive to both density and shear modes and can be applied for the study of the liquid-crystalline phase transitions. At low fields the variations of light scattering intensity follow both amplitude and the phase variations of the wave motion and enable the determination of resonance parameters, hence of viscoelastic parameters of the colloidal system.

(2)"**Static and Dynamic Light-scattering of Colloidal Gases, Liquids and Crystals**", T. Okubo, K. Kiriyama, N. Nemoto and H. Hashimoto *Coll.Polymer Sci.*, **274**, 93-104(1996).

Static and dynamic light-scattering measurements are made for colloidal-crystals, -liquids and -gases of silica spheres, 103 nm in diameter, in the exhaustively deionized suspension and in the presence of sodium chloride. Sharp peaks in the scattering curve are observed, for the first time, for the colloidal crystals in very diluted aqueous suspension. The product of the effective diffusion coefficient and the scattered light intensity is found constant over the whole range of the scattering angle measured for the colloidal crystals and liquids. Three and two dynamic processes have been extracted separately from time profiles of autocorrelation function of colloidal crystals and liquids, respectively from Marquadt histogram analysis. Decay curves of colloidal gases are characterized by a single translational diffusion coefficient, D_0. D_0 of the gases is always lower than the calculation from the Stokes-Einstein equation with the true diameter of spheres, and increases as ionic concentration increases. These experimental results emphasize the important role of the expanded electrical double layers on the diffusive properties in the colloidal crystals, liquids and gases.

(3)"**Colloidal Single Crystals of Silica Spheres in the Presence of Simple- and Poly-electrolytes, and Ionic Detergents**", T. Okubo, H. Fujita, K. Kiriyama and H. Yamaoka, *Coll.Polymer Sci.*, **274**, 73-80(1996).

Colloidal single crystals of silica spheres(103 nm in diameter) are formed in the presence of various kinds of salts, (1)simple electrolytes,i.e., sodium chloride, calcium chloride and lanthanum chloride, (2)polyelectrolytes such as 3-6 type ionen polymer(polybrene^{R}), poly-N-ethylpyridinium bromide, a copolymer of N-benzyl pyridinium chloride and N-hexadecyl pyridinium bromide, and sodium polyethylene sulfonate, and (3)cationic and anionic detergents, hexadecyltrimethylammonium bromide and sodium dodecylsulfate. Shape and size of their single crystals, phase diagram, and the relationship between the two parameters among the critical concentration of melting, conductance and pH of the crystal-like suspensions have been studied. Colloidal single crystals of *positively charged spheres* have been formed in this study by the method of the charge reversal of spheres through the strong adsorption of cationic polyelectrolytes onto the anionic silica spheres.

(4)"**Phase Diagram of Alloy Crystal in the Exhaustively Deionized Suspensions of Binary Mixtures of Colloidal Spheres**", T.Okubo and H.Fujita, *Colloid Polymer Sci.*, **274**, 368-374(1996).

Phase diagrams of liquid-like, alloy crystal-like and amorphous solid-like(AS) structures have been obtained for the exhaustively deionized aqueous suspensions of the binary mixtures of polystyrene or silica spheres. Diameter, polydipersity index(standard deviation of diameter divided by the mean diameter) and size ratio of the binary spheres(diameter of small sphere divided by that of large one) range from 85 to 136 nm, 0.07 to 0.26 and 0.76 to 0.93, respectively. Close-up color photographs of the alloy crystals are taken and the crystal structure has been analysed from reflection spectroscopy. Most of the alloy crystals are *substitutional solid-solution*(sss) type and body-centered cubic lattice structure. Formation of the alloy crystals is attributed to the important role of the expanded electrical double layers in the deionized condition and increase toward unity in the effective size ratio, which is the effective diameter of small sphere including double layer divided by that of large sphere. AS structure is formed at the rather high concentrations of two spheres, where the thickness of the electrical double layer is thin and the effective size ratio is comparatively small.

(5)"**Importance of the Electrical Double Layers in Structural and Diffusional Properties of Deionized Colloidal Suspension**", T. Okubo, *Colloids Surfaces*, **109**, 77-88(1996).

An important role of the electrical double layers in the structural, rheological, and diffusional properties of colloidal suspensions especially in the deionized state has been discussed. Formation of the giant colloidal single crystals, which are colored brilliantly and most beautiful, is due to the electrostatic intersphere *repulsion* and to the highly expanded electrical double layers surrounding colloidal spheres. Phase diagram, rigidity and viscosity of the colloidal crystals are nicely explained with the contribution of the electrical double layers. The translational and rotational diffusion coefficients of colloidal particles are quite sensitive to the ionic concentration of the suspension, which is also beautifully explained with the thinning of the electrical double layers with increasing ionic concentration. Furthermore, diffusive modes in the colloidal crystals and liquids analyzed by dynamic light scattering measurements are consistent with the important contribution of the electrical double layers.

(6)"**Static and Dynamic Light-scattering of Colloidal Crystals of Monodispersed Polystyrene Spheres**", T. Okubo and K. Kiriyama, *Ber.Bunsenges.Phys.Chem.* , **100**, 849-856(1996).

Static and dynamic light-scattering measurements are made for colloidal-crystals, -liquids and -gases of monodispersed polystyrene spheres, 109 nm in diameter, in the exhaustively deionized suspension and in the presence of sodium chloride. Sharp peaks in the scattering curve are observed for the colloidal crystals in very diluted aqueous suspension. The product of the effective diffusion coefficient and the scattered light intensity is found constant over the whole range of the scattering angle measured for the colloidal crystals. Three and two dynamic processes have been extracted separately from time profiles of autocorrelation functions of colloidal crystals and liquids, respectively from the non-negative least square analysis. Decay curves of colloidal gases are characterized by a single translational diffusion coefficient, D_0. D_0 of the gases at low ionic concentrations is lower than the calculation(D_c) from the Stokes-Einstein equation with the true diameter of spheres, and increases and reaches D_c as ionic concentration increases. These experimental results emphasize the important role of the expanded electrical double layers on the diffusive properties in the colloidal crystals, liquids and gases.

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

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

(8)"**Structural and Dynamic Properties in the Complex Fluids of Colloidal Crystals, Liquids and Gases**", T. Okubo and K.Kiriyama, J.Mol.Liquids, in press.

Static(SLS) and dynamic light-scattering(DLS) measurements are made for colloidal-crystals, -liquids and -gases of silica spheres, 110 nm in diameter, which are typical examples of the complex fluids. Very sharp peaks are observed in the light-scattering curves. At the peak scattering vectors in the scattering intensity(I), very small values of the effective diffusion coefficient(D_{eff}) are evaluated. Product of I and D_{eff} is roughly constant for the colloidal crystals, liquids and gases over the scattering angles measured. The structure factor, $S(q)$ are evaluated from the $I(q)$ observed and

the particle structure factor, $P(q)$. The nearest-neighboured interparticle distances of colloidal crystals and liquids estimated from the peaks in the $S(q)$ curves, l_{obs} agree excellently with the effective diameters of spheres(d_{eff}) including the electrical double layers in the effective hard-sphere model and also with the mean intersphere distances, l_0 calculated from the sphere concentration(l_{obs} ª d_{eff} ª l_0). Three and two dynamic processes have been extracted separately from time profiles of autocorrelation function of colloidal crystals and liquids, respectively from the non-negative least square analysis. Hydrodynamic diameters of spheres in the crystal-like and liquid-like suspensions can not be evaluated from DLS measurements. Decay curves of colloidal gases are characterized by a single translational diffusion coefficient. The latter is always lower than the calculation from the Stokes-Einstein equation using true diameter of spheres and increases as ionic concentration increases. These experimental results emphasize the importance of the expanded electrical double layers and the electrostatic intersphere repulsion on the structural and dynamic properties of the colloidal crystals, liquids and gases.

(9)"**Growth of Colloidal Crystals under Low-Gravity**(Japanese)", M.Ishikawa, H.Nakamura, S.Kamei, T.Okubo, T.Morita, K.Kawasaki and Y.Kono, *J.Microgravity Appl.Soc.Japan*, **13**, 149-157(1996).

Colloidal crystals are known as a particle system which forms ordered arrays in deionized water. Colloidal crystals offer an important oppotunity to study the dynamics of crystallization. In atomic or molecular fluids, the rate of attachment of particles to a growing interface is the order of picoseconds, whereas in a colloidal system it corresponds to the rate of diffusion of particles in the order of several ten milliseconds. This slows growth rates significantly and allows detailed mechanism of nucleation and growth of crystals to be studied on a convenient timescale. We aimed to clarify the effects of microgravity on nucleation and growth processes using colloidal crystals as a model material. Using reflection spectrum method, lattice constants Do were determined based on the Bragg reflection. The intensity measurements of Bragg reflections were executed to evaluate the appearance of small nuclie during the crystal growth under low-gravity. Light scattering methods were also applied to low-gravity experiments. Low-angle light scattering method and dynamic light scattering method were used to measure the size of grown crystallites and to evaluate diffusion coefficients of latex particles during the formation of colloidal crystals, respectively. Low-gravity experiments were executed during parabolic flights of MU-300 rear-jet airplane.

(10)"**Colloidal Crystals, Polymeric**", T.Okubo, *Polymeric Materials Encyclopedia*, J.C.Salamone(ed), CRC Press, Boca Raton, 2C, 1290-1298(1996).

Preparation, crystal structure, single crystls and crystal growth, phase equilibria, viscometric, elastic & dynamic properties, external field effect and applications are reviewed on the polymeric colloidal crystals.

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

Static(SLS)- and dynamic light scattering(DLS) measurements and the reflection spectroscopy are made for the kinetic analyses of the growing processes of colloidal crystals of silica spheres(103 nm and 110 nm in diameter) in the highly diluted and

exhaustively deionized aqueous suspensions. Changes in the SLS curves demonstrate that there exists an induction period in the nucleation process, which is prolonged with decreasing sphere concentration. Induction periods observed from DLS measurements are from 1 min to 21 min, and also increase as sphere concentration decreases. The diffusion coefficients of colloidal spheres in the super-saturated liquids and crystal-like structures are estimated to be $1x10^{-12}$ m^2/s and 5Å`$10x10^{-12}$ m^2/s, respectively, which are smaller and larger than the diffusion coefficient of the independent sphere evaluated using Stokes-Einstein equation, $4.36x10^{-12}$ m^2/s. Nucleation rates are $3.5x10^5$ s^{-1} to $8.1x10^7$ s^{-1} at ϕ=0.0006 to 0.001 from the DLS and reflection spectroscopy. Crystal growing process is beautifully explained by the classical diffusion theory of crystallization, though the restricted diffusion of the reacting spheres like as the fused metal systems should be taken into account. Crystal growth rates range from 2.9 μm/s to 20.7 μm/s, and increase substantially as the sphere concentration increases. The importance of the electrostatic intersphere repulsion through the electrical double layers and the cooperative fluctuation of colloidal spheres in the crystallization processes is supported strongly.

(12)"**Kinetic Analyses of the Colloidal Crystallization of Silica Spheres As Studied by the Reflection Spectroscopy**", T.Okuboand S.Okada, *J.Colloid Interface Sci.*, in press.

Reflection spectroscopy is made for the kinetic analyses of the nucleation and growth processes of colloidal crystals of silica spheres(110 nm in diameter) in the exhaustively deionized aqueous suspensions. Sphere concentrations range from 0.001 to 0.0025 in volume fraction(ϕ) for the nucleation and 0.0014 to 0.0036 for the crystallization process, respectively. Induction periods are from 1 to 500 seconds, and prolonged with decreasing sphere concentration. Nucleation rates are 10^{-3} to 10^5 $\mu m^{-3}s^{-1}$, and increase sharply as sphere concentration increases. The crystallization process has been observed from the sharpening and the increase of intensity in the reflection peaks for the suspension in a test tube, which stands still after being inverted. Crystal growth rates, v range from 2 to 15 μm/s, and decrease linearly as the reciprocal sphere concentration increases. Crystal growth rates represented by the number of the unit cells, u also increase as ϕ increases, ranging from 2 to 23 no. of unit cells/s. The importance of the electrostatic intersphere repulsion through the electrical double layers and the cooperative fluctuation of colloidal spheres in the crystallization processes is supported.

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

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

(14)"**Recent Advances in the Kinetic and Dynamic Properties of Colloidal Crystals**", T.Okubo, *Current Topics of Colloid Interface Sci.*, in press.

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

(15)"**Nonlinear Electro-Optics of Colloidal Crystals as Studied by the Reflection Spectroscopy**", T.Okubo, A.Tsuchida, S.Okada, and S.Kobata, *Current Topics in Colloid Interface Sci.*, in press.

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

Examination of Ellipsoidal Polystyrene Particles by Electrophoresis

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Starting with monodisperse spherical polystyrene particles ranging in diameter from 208 nm to 3.90 μm, a series of ellipsoidal particles have been prepared by a previously published stretching technique. Both spherical and ellipsoidal particles were examined by microelectrophoresis. The electrophoretic mobilities so obtained were converted into ζ-potential values using the Smoluchowski equation and an equation obtained by O'Brien and Ward from an analysis of the electrophoretic motion of spheroidal particles.

Introduction

There is a wealth of literature, on both experimental and theoretical studies of the electrophoresis of spherical latex particles.[1-14] In comparison, there are relatively few systematic electrophoresis studies of nonspherical particles. Basically the effect of orientation of the particle with respect to the direction of the external electric field needs to be addressed in the case of nonspherical particles. An early work on the motion of ellipsoidal particles immersed in a viscous fluid was given by Jeffery.[15] Theoretical analysis on electrophoresis of randomly oriented cylindrical particles has been reported by Henry[3] and subsequently extended by Overbeek[12,16] and others[17,18] in relation to elongated molecules of biological importance. Electrophoresis of spheroidal particles (both prolate and oblate) with thin double layers[19] and at low potentials[20] has also been investigated. More recently a theory of the electrophoresis of nonuniformly charged ellipsoids and dumbbell-shaped particles has been reported by Fair and Anderson.[21,22] Stigter[23] calculated, using a numerical iteration technique, the electrophoretic mobility of a cylinder with a polarized double layer in a univalent electrolyte. Morrison[24] and later Keh et al.[25,26] provided theoretical analyses of the electrophoretic motions of an infinite rigid insulating cylinder with a thin polarized diffuse layer. Keh's results[26] showed that a transversely oriented cylinder migrates at the same velocity as a sphere of the same radius. A theory for the dynamic mobility of nonspherical particles in an alternating electric field is now available from the work of Loewenberg and O'Brien.[27]

In recent work, well-defined monodisperse ellipsoidal polystyrene latex particles have been prepared.[28-30] It was found that the size and the axial ratio of these particles could be varied over a wide range and that the charge characteristics of these particles could also be controlled to a certain extent. In the present studies, these latices were used as a model of nonspherical particles and they were found well suited for examining the electrokinetic properties of prolate ellipsoidal particles.

Experimental Section

Materials. All water used for preparations was double distilled. Both sodium chloride and potassium chloride were analytical grade materials.

The materials used for the preparation of latices, SP12, RB5, and UK3, were the same as those described previously.[28,29] In the case of latex LP652, however, the poly(vinyl alcohol) (PVA) used was Aldrich material, 100% hydrolyzed with a molecular weight of ca. 115 000.[30]

The method of preparation of the ellipsoidal particles was as described previously.[28-30] Very briefly, monodisperse spherical polystyrene particles were mixed with a solution of PVA; a small sample of this dispersion was then placed in a shallow rectangular Perspex tray. After the water had evaporated, a thin PVA film was obtained with the spherical polystyrene particles embedded in it. Strips of this thin PVA film were then stretched[28] to preset draw ratios in an oil bath at 200 °C. The ellipsoidal particles thus formed were then recovered from the stretched film by

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New Information on the role of cofactor in PEO-type retention aid systems

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The flocculation of three colloidal dispersions (precipitated calcium carbonate (PCC), TiO_2 and a calcined clay) using a combination of polymeric flocculants and cofactors was investigated. The flocculants used were PEO (MW = 9 x 10^6), CPAM (a cationic copolymer of acrylamide) and POLYPAM-CO-PEG (a non-ionic comb copolymer (MW = 5 x 10^6) consisting of a polyacrylamide backbone with ~ 1mole % pendent PEG chains). The cofactors were based on poly(vinyl phenol-co-sodium acrylate) and poly(vinyl phenol-co-sodium styrene sulfonic acid). The amount of flocculation induced was dependent on the components present in each system. Cofactors containing sulfonic acid were more calcium ion tolerant than the cofactors containing carboxyl groups. These latter cofactors formed a precipitate when exposed to $\geq$ 0.6 mM Ca^{++}. Maximum flocculation of PCC was obtained by using POLYPAM-CO-PEG with a cofactor containing 23 mole % of sulfonated groups. TiO_2 was not flocculated when PEO was employed due to the adsorbed layer thickness of this flocculant being approximately equal to half the Debye screening length in 0.001 M NaCl. However, TiO_2 was flocculated by POLYPAM-CO-PEG and CPAM, the best flocculation being obtained when POLYPAM-CO-PEG was used with either a cofactor containing 19 mole % sulfonated groups, or with a cofactor containing 14 mole % acrylic acid groups. Overall, the easiest colloid to flocculate was the calcined clay; maximum flocculation being obtained when PEO was combined with a cofactor containing 19 mole % sulfonated groups. In general, the flocculation was most sensitive to the charge of the cofactors. It is proposed that the hydrophobic character of the vinyl phenol based cofactor is important. Hydrophobic interaction may be a part of the cofactor interaction with PEO and subsequent complex adsorption on surfaces.

Surface and Colloidal Properties of Hydrosilane Modified Stöber Silica

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Triethoxysilane (TES), $HSi(OEt)_3$ was used to functionalize Stöber silica and the resulting particles were characterized in acetone and water by light scattering, disk centrifugal photosedimentometry, microelectrophoresis, transmission electron microscopy, and ^{29}Si CP-MAS and ^1H MAS NMR spectroscopy. The thickness of the polymerized TES layer on the silica surface was found to be dependent upon the concentration of the TES solution used. Thus, 38 mM TES (polyTES38) and 75 mM TES (polyTES75) led to bound polyTES layers that were 7.6 and 8.2 nm thick, respectively. Using an initial concentration of 150 mM TES, polyTES150 coagulated in acetone as reflected by broad particle size distributions. In the pH range of 5.0 to 9.0, the polyTES38 particle diameter increased from 191-200 nm indicating a expandable polyTES layer existed in the interfacial region. ^1H MAS NMR spectra of polyTES38 showed narrowed ^1H line widths suggesting the presence of a mobile species on the silica surface. The critical coagulation concentrations (c_c's) determined for SiOH and polyTES38 using CaI_2 were 10 and 11.5 mM, respectively. Under aqueous conditions at low pH the polyTES layer collapsed due to the poor solvency of the polyTES chains whereas at

pH > 7 the polyTES segments were expanded due to intra/interchain electrostatic repulsion between the negatively charged polyTES segments and with the silica surface.

Effect of Shear on the Strength of Polymer-Induced Flocs

Anthony Yeung†, Andrea Gibbs, Robert Pelton*

Email:

Micromechanics was used to show that the rupture strength of polymer-induced flocs varied with the hydrodynamic conditions at which the flocs were formed. A maximum floc strength at an intermediate shear rate was observed. The overall performance of the polymeric flocculants, as determined by two independent methods, showed that the conditions for optimal flocculation did not coincide with those for maximum floc strength. The amount of flocculation was explained in terms of the competing effects of the particle collision frequency and the destructive hydrodynamic forces. The contributing forces to the floc strength are, however, more likely to be densification of the floc by shear and the weakening of reattachment strengths. The evidence presented here may be useful for explaining flocculation data which depart from the constant yield stress theory. Thus the notion of the floc strength varying with shear rate may offer an alternative to multilevel floc structure models in the description of flocculation kinetics.

Aqueous biphase formation by mixtures of dextran and hydrophobically modified dextran

Jin Zhang, Robert Pelton*, and Lars Wågberg #

A series of modified dextrans was prepared by condensation of straight chain saturated C3, C4 and C6 fatty acids and the phase behavior of aqueous solutions of these materials with unmodified dextran was measured as a function of temperature, concentration and degree of substitution. At a constant degree of substitution the tendency towards aqueous biphase formation increased with the length of the hydrophobic substituent, the temperature and the molecular weight. Fluorescence studies of the modified dextrans with pyrene as a probe indicated the presence of hydrophobic micro-domains. Rheological study showed that there was no large scale association for C3 and C4 substituted dextran, mainly intramolecular association, however some intermolecular association existed for C6 substituted dextran. The results are compared with the behavior of the classical PEG/dextran biphase systems, and mechanisms driving phase separation are discussed.

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Partitioning of Polymer and Inorganic Colloids in Two-Phase Aqueous Polymer Systems

Steven M. Baxter, Peter R. Sperry*, and Zhenwen Fu

Langmuir 13, 3948 (1997)

The well-known phenomenon of partitioning of bioparticles in two-phase aqueous polymeric systems is extended to a variety of polymer (acrylic latex) and inorganic (TiO_2) colloidal particles. It is demonstrated that particle partitioning into a particular phase is controlled in rational ways by particle surface chemistry, viz., hydrophobicity, functional groups such as hydroxyl and carboxyl, and pH effects, in relation to the chemical nature of the water soluble polymers (WSPs) that comprise the phase separated system. WSPs include poly(ethylene oxide), poly(N-vinyl pyrrolidone), dextran, and a hydrophobe terminated water-soluble polyurethane based on polyethylene oxide. Mixtures of colloidal particles can be separated by selective partitioning.

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Contribution to IPCG Newsletter From Laboratoire de Chimie des Procédés de Polymérisation (LCPP-CNRS) and Unité Mixte CNRS-bioMérieux Lyon-France

(submitted by C. Pichot and A. Guyot)

1) Adsorption of Single stranded DNA fragments onto Aminated Latex Particles

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Abstract : A study of the adsorption behaviour of nucleic acid onto polymeric supports has been performed on the adsorption of polythimidylic acid oligonucleotide in the presence of aminated latex particles. Due to the presence of surface charges on the particles and the polyelectrolyte character of the oligonucleotides, it was observed that the electrostatic forces play a major role in the adsorption process. Strong adsorption was clearly evidenced together with a high affinity. A decrease in the adsorption was observed upon raising the pH. The contribution of hydrophobic forces was estimated using the various adsorption isotherms at various pHs, and extrapolating these results to zero surface charge density and to zero zeta-potential of the latex particles. The physico-chemical approach is centered on the conformation of the adsorbed oligonucleotide by investigating the effect of ODN chain length on the maximum adsorbed amount on the latex particles. It was found that the ODN adsorbs in the flat conformation irrespective of ODN nature so long as the support was oppositely charged.
(Langmuir 1997, 13, 701-707)

2) The effect of Triton X-405 on the Adsorption and Desorption of Single-Stranded DNA fragments onto Positively Charged Latex Particles

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Abstract : The influence of a nonionic surfactant (Triton X-405) on the adsorption behavior of single-stranded oligodeoxyribonucleotide (polythymidylic acid dT_{35}) onto cationic aminated polystyrene latex particles has been investigated. A preliminary study was performed on the adsorption of Triton X-405 onto these cationic particles, showing a maximum amount of c.a 0.5 mg m_2 at the plateau. Desorption of the nonionic surfactant even after an extensive cleaning procedure, was not completed indicating that probably low HLB species were still strongly adsorbed. The modification of the electrophoretic mobility of the latex particles together with the slight decrease in the colloidal stability suggested that the residual Triton X-405 molecules would adopt a flat conformation at the particles surface. Then, the adsorption behavior of dT_{35} onto precoated cationic latex was thoroughly examined under various conditions and compared with the case of bare latex particles. It was clearly evidenced that the residual adsorbed amount of nonionic surfactant

significantly affected the surface nature, especially above pH 8 (i.e., not far from the pKa of amino surface groups). It was interesting to notice that dT_{35} adsorption was strongly reduced at basic pH and that its desorption was favored using basic pH buffer containing Triton X-405 and high ionic strength. Kinetic exchange experiments were also performed using labeled $_{32}$P-dT_{35} and unlabeled ODN, indicating that the exchange took place with no marked differences between coated and bare latex particles.
(submitted to Langmuir)

3) Cationic amino-containing N-isopropylacrylamide-styrene copolymer particles : 1-Particle size and morphology vs polymerization process

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Abstract : Cationic hydrophilic copolymer latexes were synthesized at 70°C by batch or two-step emulsion-free emulsion polymerization of styrene (St), N-isopropylacrylamide (NIPAM), aminoethyl methacrylate hydrochloride (AEM) and using 2,2'-azobis (2-amidinopropane) dihydrochloride as initiator. At first batch polymerization kinetics were followed by gas chromatography revealing that NIPAM rapidly homopolymerized in a first step, before the polymerization of styrene started. Particle size analysis by quasielastic light scattering and transmission electron microscopy evidenced that monodispersed particles were obtained with the formation of poly[NIPAM] rich shell. Adding a few amount of the cationic monomer resulted in a strong decrease of the particle size without affecting the size monodispersity. When a shot process was used, size monodispersity was maintained, provided the monomer addition be performed at a relatively high conversion of the first step. The shell layer was largest with the shot process, but the presence of the amino-containing monomer dramatically affected the thickness. The use of transmission, scanning and atomic force microscopy techniques showed that these hydrophilic particles exhibited odd-shaped structures, the unevenness being dependent upon the process. Kinetic data and particle morphology information were inferred for discussing the polymerization mechanism of this system
(to be submitted to Colloid & Polymer Science)

4) Cationic amino-containing N-isopropylacrylamide-styrene copolymer particles : 2-Characterization and Colloidal stability

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ABSTRACT: In a previous paper, we demonstrated that monodisperse latexes could be synthesized by polymerization of styrene, N-isopropylacrylamide (NIPAM) and aminoethyl methacrylate hydrochloride (AEM) using 2,2'-azobis (2-amidinopropane) dihydrochloride initiator at 70°C. Particle size in the range 100-600 nm in diameter was controlled via the amount of NIPAM monomer introduced in the first stage of " batch " polymerization; the incorporation of the amino cationic conversion was performed using a shot addition of a NIPAM-AEM mixture at high conversion. The obtained latexes from the previous paper were then characterized as regards to particles size and distribution, surface charge density (using a colorimetric titration method), colloidal stability and

finally by electrophoretic mobility. The surface amino groups concentration originated from the functional monomer was found in between 12 to 25 µmol/g polymer. Using coagulation kinetics bellow and above the LCST allowed one to determine the critical concentration coagulation values of different latexes; the results have been discussed with respect to the surface charge density and actual thickness of the hydrodynamic layer.
(to be submitted to Colloid & Polymer Science)

5) Surface characterisation of amine-containing latexes by charge titration and contact angle measurements

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Abstract : The surface charge density and surface polarity of cationic polystyrene latexes containing amidine (derived from initiator residue) and amine groups (from functional monomer) have been investigated. The former characterisation was performed by ^{1}H NMR, conductometry, and two spectroscopic methods (UV, fluorescence) using either N-hydroxysuccinimide ester of 3-(2-pyridyldithio) propionic acid (SPDP) or fluorescamine, respectively. The whole methods leaded to surface charge density in the same range, mainly depending on the cationic monomer concentration and the chosen process. Despite poor accuracy, ^{1}H NMR confirmed the range of assayed functions. Conductometric experiments were found inaccurate, when titrating amidine group-containing latexes (batch process), because of this group tendency to be hydrolysed. On the contrary, for two-step latexes, then bearing mostly amine groups, conductometric titration was reliable. Results obtained from the fluorescent method and their combination with SPDP values allowed the discrimination between amidine and amine groups, both at the latex surface and buried in the particles. In batch process, increasing the functional monomer amount decreased the initiator residues tethered on the surface. "Core-shell"-like structure took place for latexes prepared with a shot-growth process, the shell containing most of the functional monomer added in the second process step. Both amidine and amine groups, resulting from the first step, were partly buried. Latex surface polarity was checked by contact angle measurements, and the different surface tension components obtained with the mean harmonic approximation method. The latex surface polarity was found not dependent on the amount of surface charge or the type of polymerization process. On the contrary, only the type of surface function was effective : the more acid the function, the more polar the latex surface.
(Submitted to Colloids and Surfaces)

6)Surface-functionalized polystyrene latexes with liposaccharide monomers : preparation, characterization and applications

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ABSTRACT

Latex particles bearing carbohydrate species have been prepared by emulsion copolymerization of styrene or methyl methacrylate in the presence of polymerizable liposaccharide surfactants :

11-(N-p-vinylbenzyl) amido undecanoyl maltobionamide (LIMA), 6-(2-methylpropenoyloxy) hexyl b-D-cellobioside (CHMA) and 10-(2-methylpropenoyloxy) decyl b-D-cellobiouronoside (CDMA). Due to their amphiphilic structure, these three monomers exhibit surface active properties in dilute solution and mesomorphic properties in concentrated solutions. Their incorporation onto latex particles has been performed according to a batch process or to a seed polymerization process. The presence of the carbohydrate residues at the particle surface was directly evidenced by NMR. The potential application of these functionalized latexes in the diagnostic field was evaluated by studying their interactions with bovine serum albumin, and by performing covalent binding of antibodies or single-strand DNA fragment on the surface.

Recent Publications :

Emulsion-Free emulsion copolymerization of styrene with two different amino-containing cationic monomers-1 : Kinetic Studies, F. Ganachaud, F. Sauzedde, A. Elaissari, C. Pichot(in press, Journal of Applied Polymer Sciences)

Emulsion-Free emulsion copolymerization of styrene with two differentamino-containing cationic monomers-2 : Surface and Colloidal Characterization, F. Sauzedde, F. Ganachaud, A. Elaissari, C. Pichot(in press, Journal of Applied Polymer Sciences)

Polymer Colloids for Biomedical and Pharmaceutical Applications
C. Pichot, T. Delair, a. Elaissariin Polymeric Dispersions : Principles and Applications Edited by José M.Asua, NATO ASI Series E : Applied Sciences - Vol. 33

Fluorescence energy transfer study of the conformation of oligonucleotides covalently bound to polystyrene latex particles, M.T. Charreyre, O. Tcherkasskaya, M.A. Winnik, A. Hiver, P. Cros, C. Pichot, B. Mandrand, Langmuir, 3103, 13, n°12, 1997

ABSTRACTS OF PAPERS IN PRESS OR SUBMITTED FOR PUBLICATION (LCPP/CNRS)

MACROMOLECULES

Direct measurement of oligomers entry rate onto latex particles in an emulsion polymerization.

Catherine MARESTIN, Alain GUYOT, and Jérôme CLAVERIE

The coefficient of entry of MMA aqueous oligomers into polymer particles has been measured by direct EPR experiments. For this purpose, a stable spin trap (nitroxide free radical) was covalently grafted on the surface of a monodisperse latex. This seed has then been involved in a MMA emulsion polymerization. The trapping has been monitored by the decay of EPR signal. From the kinetics of entry, we have deduced an approximate coefficient of entry of 1.3 entries per particle and seconds. The influence of the particle size, initiator and surfactant concentration is currently under study.

Entrant oligomers have been collected after cleavage of the thermoreversible C-O bound. G.P.C and I.R. spectroscopy successfully have allowed to determine the nature of these oligomers. This method has enabled to measure the critical size z ($z = 5$) of MMA oligomers before entering a particle.

MACROMOLECULES

Living radical polymerization in emulsion

Catherine MARESTIN, Catherine NOËL, Alain GUYOT, and Jérôme CLAVERIE

Living radical polymerization in emulsion can be carried out with a nitroxide derivative, a convenient surfactant, potassium persulfate for initiator and styrene or an acrylate for monomer. The nature of the surfactant and of the nitroxide strongly determines the outcome of the reaction. In most cases, low conversion and/or flocculation are observed, probably because of the extraordinarily harsh conditions necessary to carry out this experiment (135 °C for several days). Nevertheless, the combination of aminoTEMPO and sodium dodecylsulfate (SDS) appears to generate satisfying results. The mechanism of the polymerization, still under sudy, resembles the mechanism of a miniemulsion, where the cosurfactant is generated in situ by hydrolysis of SDS.

The stabilization is further increased by starting the living polymerization with an hydrosoluble monomer such as styrene sulfonate. In this case, each polymer chain carries at least one sulfonate end-group.

P.A.T. POLYMERS FOR ADVANCED TECHNOLOGIES

REACTIVE SURFACTANTS IN HETEROPHASE POLYMERIZATION - PART XXI - KINETICS OF STYRENE DISPERSION POLYMERIZATION STABILIZED WITH POLY(ETHYLENE OXIDE) MACROMONOMERS

Patrick LACROIX-DESMAZES and Alain GUYOT*

ABSTRACT

The kinetics of styrene dispersion polymerization, using poly(ethylene oxide) macromonomers as precursors for the stabilization have been studied. Both the conversion of styrene and of macromonomers have been determined. The effect of various parameters such as the polarity of the medium, the nature and the amount of macromonomer and the concentrations of the reactants has been studied. Strong gel effect was observed, the main polymerization process taking place inside the particles where the average number of radicals per particle may be more than one thousand.

P.A.T.

REACTIVE SURFACTANTS IN HETEROPHASE POLYMERIZATION - PART XXII - INCORPORATION OF MACROMONOMERS USED AS STABILIZERS IN STYRENE DISPERSION POLYMERIZATION

The effect of several parameters on the incorporation yield of poly(ethylene oxide) macromonomers at the surface of the particles, for the dispersion polymerization of styrene in ethanol-water mixtures, has been studied. The reactivity of the macromonomer is a key parameter in the mechanism of stabilization of the micron-size polymer particles, because it determines partly the amount and the composition of the copolymer stabilizer available at any moment during the process. The polarity of the reaction medium also influences strongly the polymerization process: higher incorporation yield and grafting density were obtained in medium of lower polarity. Besides, a chain length of around 50 ethylene oxide units for the macromonomer were needed to produce stable monodisperse particles with a significant incorporation yield. Thus, an incorporation yield as high as 53% and a grafting density corresponding to a surface area of 232 Å²/molecule have been obtained in a one step process by using a methacrylate macromonomer. In an optimized two steps process resulting in monodisperse polymer particles, 80% incorporation yield with a very high grafting density (175 Å²/molecule) were reached. The particles with high grafting density (surface area lower than 600 Å²/molecule) could be transferred in water and exposed to a freeze-thaw cycle without massive flocculation, illustrating the efficiency of the steric stabilization.

COLLOID POLYMER SCIENCE

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Thiol-ended polyethylene oxide as reactive stabilizer for dispersion polymerization of styrene

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Abstract Radical dispersion polymerization of styrene in aqueous ethanol solutions was performed in the presence of a new reactive polyethylene oxide stabilizer with thiol end groups. This reactive stabilizer was compared to the more conventional poly (*N*-vinyl pyrrolidone). Particles size distribution, molecular weights and kinetics were investigated. Monodispersed polymer particles with diameter in the range 200–2000 nm were obtained depending on the amount of stabilizer used. In all cases, the polyethylene oxide (PEO) sequence of the dispersant was partly incorporated at the surface of the latex particles, but the grafting yield of polyethylene oxide chains was always limited and did not exceed 15%. Part of the stabilizer being unreacted or reacted with low molecular weight polystyrene remained in the continuous phase.

Key words Dispersion polymerizations – styrene – reactive stabilizer – molecular weight – particles size – incorporation yield

ENCAPSULATION OF INORGANIC PARTICLES BY DISPERSION POLYMERIZATION IN POLAR MEDIA: 1. SILICA NANOPARTICLES ENCAPSULATED BY POLYSTYRENE.

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Polymer encapsulation of small silica particles, using dispersion polymerization of styrene in aqueous ethanol medium with poly(N-vinyl pyrrolidone) (PVP) as stabilizer, is described. Silica particles, directly synthesized by the Stöber process in the aqueous ethanol medium, are either unreacted (hydrophilic character) or coated with 3-(trimethoxysilyl)propyl methacrylate (MPS) (hydrophobic character) which is chemically bound to the silica particles. When the bare silica particles are used as the seed, there is a strong tendency of the silica beads to cover the surface of the polystyrene particles and obviously encapsulation does not occur. On the opposite, when the silica surface is made hydrophobic by coating, the inorganic particles are entirely contained in the polystyrene particles as evidenced by microscopy techniques (TEM, SEM, AFM). It is shown that some polystyrene chains are then chemically bound to the silica particles, through the coupling agent MPS, and that only a small amount of bound polystyrene compared to the total polystyrene synthesized, is sufficient to obtain encapsulation of the silica particles with the entire amount of polystyrene synthesized during the polymerization. Under our experimental conditions, each polystyrene latex particle contains, in average, 4 to 23 silica beads depending, in particular, on the size of the silica. We believe that it is possible to control the composite particles size and morphology by a convenient choice of the composition of the system. Moreover, this new polymer encapsulation process could be used to synthesize other organic-inorganic composite particles, using for example other monomers or minerals.

COLLOID POLYMER SCIENCE

Reactive surfactants in heterophase polymerization for high performance polymers

Part I Synthesis of functionalized poly(ethylene oxide)-*b*-poly(butylene oxide) copolymers and their use as surfmer, inisurf and transurf in heterophase polymerization◆

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ABSTRACT

A variety of non ionic reactive surfactants have been prepared from block copolymer precursors. These precursors are formed from a commercially available polyoxyethylene glycol monomethylether as the hydrophilic sequence of the surfactant ; this product is used as initiator of living ring opening anionic polymerization of butylene oxide. Finally the reactive surfactants are obtained after proper functionalization of the precursor. The reactive surfactants are an inisurf with an asymmetric azo compound, a transurf with a thiol group, and a few surfmers with acrylic, methacrylic, styrenic and α-methyl styrenic reactive groups. These compounds have been engaged in styrene emulsion or dispersion polymerization. Several of them have been found to be useful for preparing stable latices.

J. APPLIED POLYMER SCIENCE

Reactive surfactants in heterophase polymerization. Part XVI. Emulsion copolymerization of Styrene - Butyl acrylate - Acrylic acid in the presence of simple maleate reactive surfactants.

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ract:

This study deals with the influence of copolymerizable surfactant on the stability of ces. Two main reactive surfactants, one anionic and one non ionic, both containing a tive part issued from maleic anhydride, have been engaged in seeded emulsion merizations of styrene co butyl acrylate co acrylic acid. The importance of the merization conditions clearly appears through the incorporation yield of the surfmers: n good conditions are used, this yield can be as high as 75%. Once stable latices are hesized, with a high incorporation of the surfactant, the stability of the colloid (against ze thawing cycles or in the presence of concentrated divalent electrolyte solutions) is thus atly improved.

words: STYRENE - ACRYLIC COPOLYMERS
EMULSION POLYMERIZATION
REACTIVE SURFACTANTS
MALEATE DERIVATIVES

Feature article

Acta polymerica

"Reactive surfactants in heterophase polymerization"

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ABSTRACT

This paper sumarizes the work carried out during 3 years in a Network of the program "Human capital and Mobility" of the European Union CHRX 93-0159 entitled "Reactive surfactants in heterophase polymerization for high performance polymers". A serie of about 25 original papers are to be published in the open litterature under the general title of this feature article from Part I to Part XXV.

Synthesis of an amphiphilic triarm star copolymer based on polystyrene, poly(ethylene oxide) and poly(methyl methacrylate) - Micellization behavior.

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Abstract

The synthesis of an amphiphilic triarm star copolymer based on polystyrene, poly(ethylene oxide) and poly(methyl methacrylate) blocks has been achieved by a novel strategy which consists in the preparation of a diblock copolymer, polystyrene-block-poly(methyl methacrylate), having a protected anionic initiator group at the junction of the two blocks. After deprotection, this function is activated by a coloured and weakly basic carbanion. The generated alcoholate initiates the ethylene oxide anionic polymerization. Early studies demonstrate the formation of micelles with weakly higher sizes and greater aggregation numbers than polystyrene-block- poly(ethylene oxide) of the same blocks molecular weights.

Introduction

In addition to linear ABC triblock copolymers, the synthesis of starblock copolymers with sequences of different natures has been one of the challenges in anionic polymerization for the last few years. This type of copolymers is commonly called heteroarm, miktoarm and triarm starblock copolymers. Except for a very recent result[1], the existing methods[2,3] have not allowed the fixation of a hydrophilic sequence in such star terpolymers.

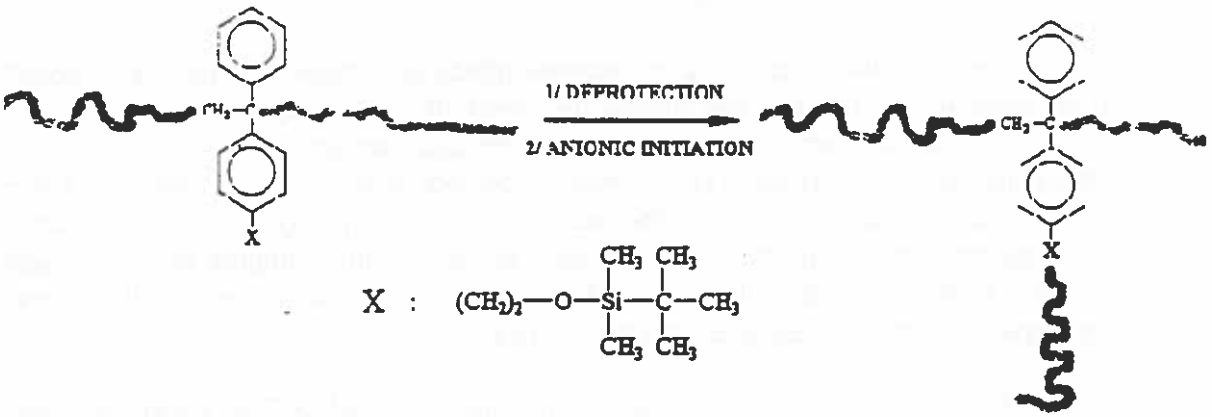
In order to obtain amphiphilic triarm star copolymers, we developed a new route of synthesis consisting in two successive initiation steps on a 1,1-diphenylethylene derivative located at the end of a first block.(Scheme 1).

The strategy is based on the use of a core molecule bearing a protected anionic initiating function. First a diblock copolymer of styrene and methymethacrylate, containing this core molecule in its centre is prepared. After deprotection and several purifications steps of the diblock copolymer PS-block-PMMA, the central function is activated to initiate the anionic polymerization of the third monomer (Ethylene oxide).

Because of the lack in results and theories for the micellization behavior of such starblock copolymers , the aim of our studies was first to answer to some basic questions : do star copolymers form micelles ?, and then, what are the order of magnitude for major characteristics like diameter and aggregation number of the micelles ?

We investigated the micellization behavior of PS-PMMA-PEO starblocks copolymers in water, with dynamic light scattering and viscosity measurement to demonstrate the presence of micelles and their sizes, and to get the aggregation number respectively.

Scheme 1 : Schematic representation of the star terpolymer synthesis with the protected anionic initiator in a PS-PMMA copolymer.



Experimental part

Anionic polymerization was carried out in a flamed glass reactor under nitrogen atmosphere. Styrene, ethylene oxide and methylmethacrylate were first stirred over sodium, butyllithium and triethylaluminium respectively and then distilled under reduced pressure just before polymerisation.

1-(4-(2-tert-butyldimethylsiloxy)ethyl)phenyl-1-phenylethylene has been synthesized according to a procedure described in the literature[5].

Size exclusion chromatography was carried out in THF (1 ml/ mn) at 25°C using a Waters 150C liquid chromatograph equiped with three Lichrogel columns (Merck) (PS 400, PS 40, PS 10) and a refractive index detector coupled with an UV detector. The size exclusion chromatography was calibrated with PS-standards. ^{1}H NMR spectra were recorded on a 250 MHz spectrometer (Bruker AC 250) using $CDCl_3$ as a solvent. Dynamic light scattering was performed on a COULTER N4, in water at 20°C. Vicosity measurements were performed in a Ubbelhode viscosimeter at 20°C.

Results and discussions

Styrene is polymerized at -78°C in tetrahydrofuran using cumyl potassium as an initiator. After one hour, the core molecule [1-(4-(2-tert-butyldimethylsiloxy)ethyl)phenyl-1-phenylethylene] is added to the living chain ends and the typical red colour of the polystyryl anion changes to the deeply dark-red colour of the living diphenylethylene derivative. Twenty minutes later, methylmethacrylate is added into the reactor at -78°C to the solution which turns immediately to yellow.

The polymerization of this diblock copolymer is then terminated by addition of methanol. Aliquots of the polymeric solution were taken after each stage for characterizations. The diblock copolymer is precipitated into a mixture methanol / eau (80/20, v/v).

Size-exclusion chromatography (SEC) shows relatively narrow molecular weight distribution for the polystyrene block bearing the core-molecule and for the diblock copolymer. The molar composition of the copolymer is determined by proton nuclear magnetic resonance (^{1}H NMR) analysis. The Mn values of each sequence can be then calculated.

Deprotection[6] of the core molecule will generate the hydroxy function needed for the polymerization of the third monomer.

For the third step, the polystyrene-block-poly(methylmethacrylate) copolymer is introduced in the reactor and thoroughly dried by several cycles of dissolution in dried tetrahydrofuran and removal of the solvent under high vacuum.
Dried and degassed solvent (THF) is then condensed on this purified material in the reactor at -78°C. The anionic activation is obtained by addition of diphenyl methyl potassium dissolved in tetrahydrofuran to the diblock copolymer solution, until a slightly brilliant orange colour persists. Ethylene oxide is then distilled into the reactor which is left for three days at room temperature in order to complete the polymerisation.

The characteristics of starblocks copolymers PS-PMMA-PEO are given in table 1.

Table 1 : Characteristics of starblocks copolymers PS-PMMA-PEO

Material	PS : wt.-% [a]	PMMA : wt.-% [a]	POE : wt.-% [a]	Mn (g · mol) [b]	Mw/Mn [c]
Star Copolymer 1	20.7	13.4	65.9	19300	1.16
Star Copolymer 2	44.9	28.7	26.4	9000	1.27
Star Copolymer 3	33.7	22.1	44.2	11800	1.20
Star Copolymer 4	47.7	30.8	21.5	8400	1.26
Star Copolymer 5	25	16.2	58.8	16000	1.21

a) Weight percentages calculated using ^{1}H NMR analysis.
b) Calculated using ^{1}H NMR analysis and Mn of the PS precursor determined by size exclusion chromarography (SEC)
c) Estimated from SEC

Those copolymers are now good material to start the investigation of the micellization behavior.

All micellar solutions in water are prepared by dialyse to avoid the formation of aggregates. The copolymers are first dissolved in a mixture of tetrahydrofuran, methanol and water (50/25/25, v/v/v). This addition of methanol prevent the formation of hydrogen links between water and the PEO sequences.

Micellar solutions are filtred before and after dialyse to avoid dust. Size diameter particles (weight distribution) are determined by Dynamic Light Scattering at 20°C using a COULTER N4.

Different values for the PS-PMMA-PEO triarm starcopolymers prepared and for PS - block - PEO are given in table 2.

The comparison between the different values indicates for both diblock and triarm copolymers, an increase in the diameter of the micelles with the molecular weight of the hydrophilic sequence PEO.

Moreover, it seems that micelles formed from PS-PMMA-PEO star copolymers, have diameters weakly greater than for diblocks PS-b-PEO with PEO sequences of the same lenght.

Tab. 2 : Diameter of the structures ("micelles"?) formed in water by the triarm star copolymers.

Copolymer	Mn (PS) (g / mol)	Mn (PMMA) (g / mol)	Mn (POE) (g / mol)	SDP in weight (nm)
Star Copolymer 1	4000	2600	12700	31.2
Star Copolymer 2	4000	2600	2400	20
Star Copolymer 3	4000	2600	5200	20.4
Star Copolymer 4	4000	2600	2400	40.2
Star Copolymer 5	4000	2600	9400	30.7
PS-b-POE 1	4000		3950	18.4
PS-b-POE 2	4000		11000	29.1
PS-b-POE 3	4200		16900	31.6
PS-b-POE 4	4700		20200	36.5

SDP that we obtained are in good agreement with the usual sizes of micelles. So, we can conlude that PS-PMMA-PEO triarm starblock copolymers are able to form such structures in water.

According to the theory of Einstein[7], knowing the hydrodynamic radius R and intrinsic viscosity $[\eta]$ of micelle allows the calculation of its molecular weight and then the aggregation number Z. (table 3).

Tab. 3: Characteristics of the micelles formed with the triarm starblock copolymers.

Copolymer	Mn[a] (g/mol)	R[b] (nm)	$[\eta]$[c] (cm^3/g)	Molecular weight of micelles $*10^{-6}$ (g / mol)[d]	Z[e]	$k_1 - k_2$[f]
Star Copolymer 1	19300	15.6	15.63	1.54	80	0.481
Star Copolymer 3	11800	10.2	8.35	0.80	68	0.478
Star Copolymer 4	8400	10	8.32	0.76	90	0.489
Star Copolymer 5	16000	15.35	16.65	1.37	86	0.463
PS-b-POE 3	21100	15.8	47.03	0.53	25	0.462
PS-b-POE 4	24900	18.25	79.20	0.48	20	0.433

a) Calculated using ^1H NMR analysis and Mn of the PS precursor determined by size exclusion chromarography (SEC)
b) Determined by DLS
c) Calculated according to the method of HELLER[8] with the viscosity values (determined with the Ubbelhode viscosimeter)
d) Calculated according to the theory of EINSTEIN[7]
e) Molecular weight of the micelle / molecular weight of the copolymer
f) Coefficients in the theory of HELLER[8] ($k_1 - k_2 = 0.5$)

The results obtained show that the triarm starblock copolymers PS-PMMA-PEO associate in water in structures whose characteristics are close to micelles.

Moreover, moderate viscosity data demonstrate the compacity of these associates and let us suppose that micelles formed from triarm starblock copolymers PS-PMMA-PEO adopt a core-shell structure in good agreement with theories about amphiphilic diblock copolymers.

Conclusion

We developped a new strategy to synthesize triarm starblocks copolymers with low polydispersities in weight and composition. According to this method, different PS-PMMA-PEO triarm starblock copolymers have been obtained with a variation in the lenght of the PEO. To fill the lack of results in the micellization behavior of such copolymers, we started a study in water which demonstrated the formation of micelles with a core-shell structure.

Works are in progress to elucidate the conformation of the hydrophobic sequences in the core and then to show the influence of the star architecture.

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Surface morphology of polypyrrole core/polyacrolein shell latex by atomic force microscopy (AFM)

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Seeded emulsion and/or dispersion polymerizations are used for synthesis of homopolymer latexes with a narrow particle diameter polydispersity and for latexes with core-shell morphology with core and shell composed of different polymers. Depending on the actual system (nature of seed latex and monomer, mode of monomer addition, initiator, and reaction medium) propagation proceeds in seed particles swollen with a second monomer, or is initiated in solution from which the growing macromolecules precipitate, when their chain length exceeds the critical one, and may be adsorbed onto the seed particles. In the case when this adsorption is thermodynamically unfavorable, or kinetically hampered, new particles are nucleated and when such particles do not coalesce with the primary ones this step of polymerization yields the mixture of two homopolymer latexes. Regardless of the actual mechanism of particle formation, once the outer shells are created, they also could be swollen with a monomer, providing the new environment for propagation.

In principle, there are two possibilities for the initial stage of shell formation by adsorption of macromolecules of a second polymer (with still propagating or with terminated active centers). These macromolecules could be adsorbed: (i) randomly onto the surface of the seed support, (ii) or in a way leading to clusters covering densely only fragments of seed particles. In the former case the surface of seed latex would be gradually modified during polymerization, whereas in the latter one, it would be composed of the covered and free patches. Still very little is known on the arrangement of polymer macromolecules during initial stage of their adsorption. However, there are some indirect evidences suggesting formation of the patched structures in the case of adsorption of protein macromolecules.

Recently, we reported on synthesis of polypyrrole core / polyacrolein shell latex (P(P-A)) by radical polymerization of acrolein carried out in presence of the polypyrrole seeds [1]. The polypyrrole seed particles, obtained earlier in the red-ox polymerization, were positively charged. Macromolecules of polyacrolein, formed in radical polymerization initiated with $K_2S_2O_8$, were equipped with negatively charged sulphate end groups, resulting from the incorporation of initiating radical anions. Electrostatic interactions facilitate adsorption of polyacrolein macromolecules onto the surface of polypyrrole support. However, during this process the positive charge of the polypyrrole core particles steadily decreases. Consequently, the amount of polyacrolein which could be attached to polypyrrole seeds is limited because, at the moment of full compensation of the positive charge of polypyrrole seeds with the negative charge of the polyacrolein shell, the core-shell particles loose their electrostatic stabilization, aggregate, and precipitate from suspension [1]. Therefore, the P(P-A) latexes forming stable suspensions are interesting as model particles with limited thickness of the shell. In this paper we describe our observations of surfaces of P(P-A) particles by atomic force microscopy (AFM). We expected that, for this system, it will be possible to discriminate between the two conceivable modes of adsorption of polyacrolein macromolecules, namely, the random one and the adsorption with formation of polyacrolein patches.

Atomic force mmicroscopy observations indicated that surface of the polypyrrole seed particles is smooth. On the other hand, we found that surfaces of the P(P-A) particles were unevenly coated with polyacrolein, forming the patchy structures. Analysis of cross sections of 20 P(P-A) particles (an example is shown in Figure 1) allowed us to measure thickness of these layers which was found equal 1.6 ± 0.2 nm. Apparently, attraction between macromolecules of polyacrolein in the surface layer is high and the enthalpy of formation of polyacrolein macromolecule clusters is sufficient to compensate, at least, the negative entropy change due to ordering of these macromolecules.

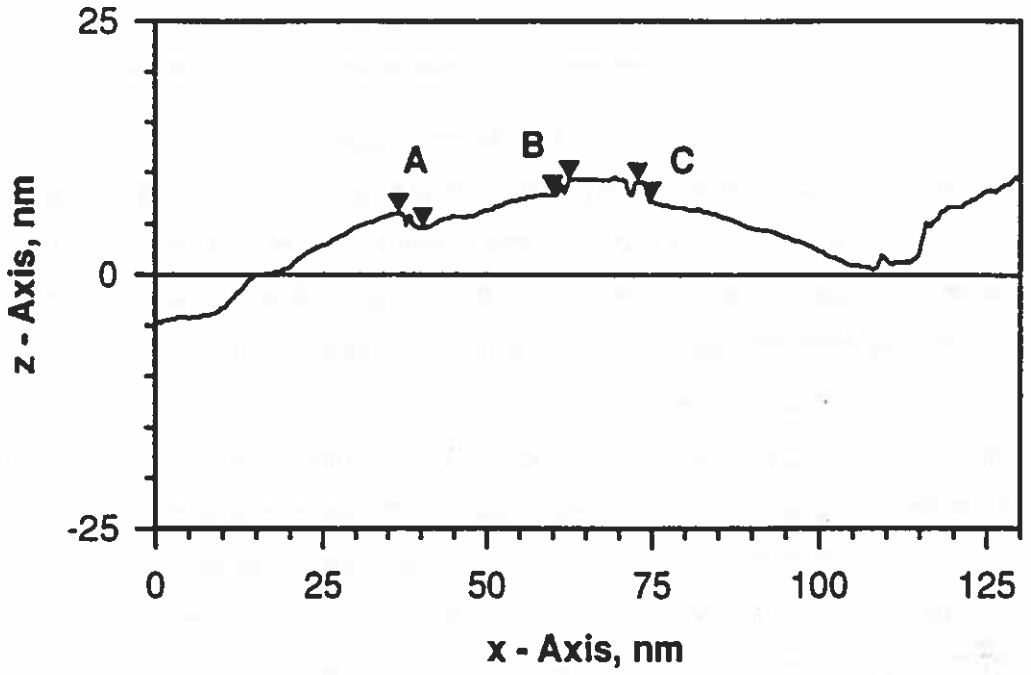

Figure 1 An example of the "cross section" of a fragment of P(P-A) particle reconstructed from the AFM image. Vertical distance between the pointers equals 1.39 nm (A), 1.51 nm (B), and 1.97 nm (C).

References: 1. B.Miksa, S.Slomkowski, Colloid Polym. Sci. 273, 47-52

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Cryogenic SEM Studies on the Latex Film Formation

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Previous studies identified three main stages of latex film formation. In the first stage, the solvent (water) evaporates, forcing latex particles close together. In the second stage, latex particles crowd to the solvent surface and menisci form across the interstices between the particles. In the third stage, solvent disappears from between the interstices and the latex particles begin to coalesce and fuse. Only the final stage of particle coalescence, fusion and film formation can be examined *in situ* with conventional scanning electron microscopy. Evaporation of solvent in earlier stages of film formation scatters the electron beam and interferes with images.

Freezing and cry-techniques lower vapor pressure and overcome electron beam scattering. In this study, we examine "wet" microstructures with cryo-SEM after freeze fracturing the sample and compare them to air-dried films at ambient temperature with conventional SEM. These include film formation during the flocculation process, latex-pigment interaction in the dispersion and consolidation fronts of the drying latex suspension. We demonstrate how the extent of electro-static and electro-steric stabilization affects all three stages of the film formation. Previous studies of latex film formation have focused only on forces between latex particles. This study investigates the influence of pigment particles on film formation.

A detailed description of the cryo-SEM system used in this study can be found in (1). The main barrier to high resolution cryo-SEM is water-vapor condensation on cold samples. The conduction-cooled stage shown in Figure 1 has a large surface area cold trap in close proximity to the sample. This reduces the partial pressure of water and thus reduces the impingement rate of water molecules. Figure 1 also includes a cryo-SEM picture of a carboxylated poly(styrene-butadiene) latex dispersion at 20 wt% in water. The sample was dip coated on a Mylar film, air dried for 20 seconds, frozen in liquid ethane, transferred to the metal-coating chamber, etched at 173 °K for 10 min, coated with 4nm of chromium by thermal sublimation, and imaged in a JEOL JSM-840

SEM. Thread-like material between the latex microspheres is solute that was forced to ice grain boundaries during freezing. We etched only dip-coated samples to remove ice that condensed on them after freezing. We examined formation of consolidation fronts of latex dispersions at various ionic strengths.

Samples can also be fractured under cryogenic conditions. These samples do not require etching because we fracture them in high vacuum (10^{-4} torr). Figure 2 is cryo-SEM of a carboxylated poly(styrene-butadiene) latex and ground calcium carbonate dispersion at 80 wt% particulate solids with ratios of 1:9 latex: $CaCO_3$. This image clearly demonstrates that latex particles associate with calcium carbonate particles, creating a dispersion of carboxylic acid-stabilized $CaCO_3$ particles.

In this work, we demonstrate that one can deduce colloidal forces present in all stages of latex film formation with high-resolution cryo-SEM.

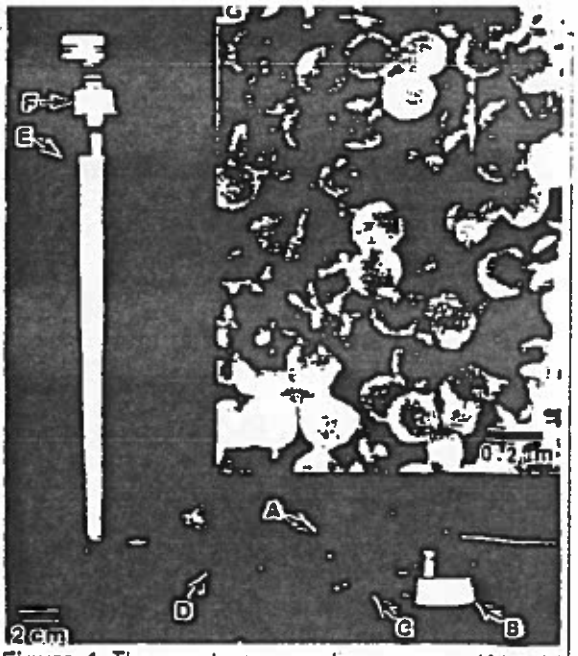

Figure 1 The conduction-cooling system. (A) cold trap, (b)Telfon-insulated stage, (C) copper braid, (D) copper rod, (E) liquid-nitrogen vessel, (F) ceramic insulator, (G) a 20 wt% suspension of a carboxylated poly(styrene-butadiene) latex.

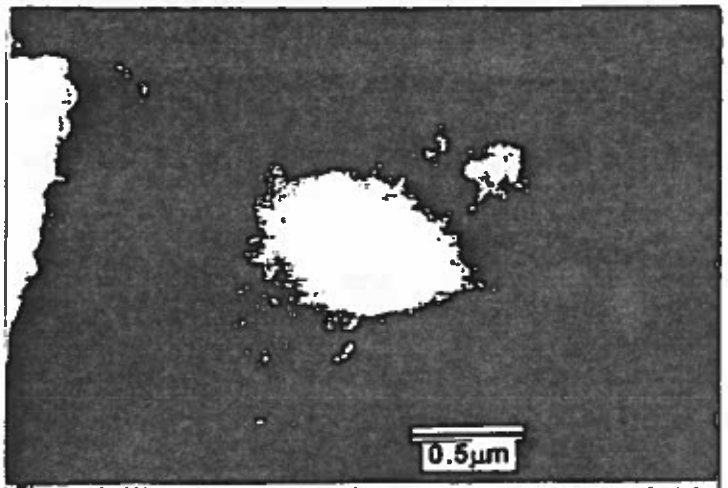

Figure 2 Wet microstructure of one part latex to 9 parts $CaCO_3$ dispersion at 80% total solids with cryo-SEM after freezing and fracturing.

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Contribution to the International Polymer Colloids Group Newsletter 1997

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Heterophase Polymerization in Poly(ethylene glycol) as Dispersions Medium

The use of poly (ethylene glycol) azo initiators (**PEGA** initiators where the postponed number refers to the molecular weight of the poly(ethylene glycol), cf. Figure1, offers the unique possibility to carry out heterophase polymerizations in poly(ethylene glycol) (**PEG**) as dispersion medium where the dispersion medium and the stabilizer are chemically very similar. In case of a PEG with a molecular weight of 200 g mol^{-1} the polymerization can be carried out in the same equipment as in case of water as the viscosity between water and PEG200 is not that much different.

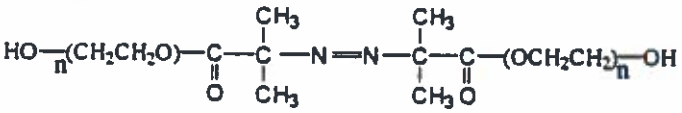


Figure1: Structure of PEGA initiators
n=4,5 PEGA200

Generally, the particles polymerized in PEG200 are smaller than those prepared in water. Changing the dispersion medium from water to PEG200 has especially in the case of the initiation with PEGA200 a strong influence on the average particle size as well as on the PSD, see Figure 2 and Figure 3, respectively.

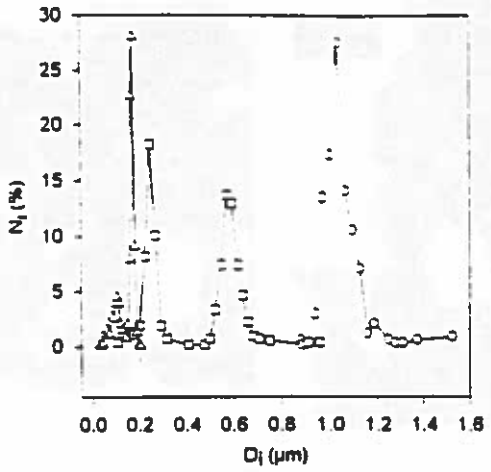


Figure 2 PSD estimated from enumerating TEM pictures of PS particle polymerized with PEGA initiators with varying PEG chain lengths in water
circles - PEGA200, D_N = 1047 nm, D_W = 1068 nm,
squares - PEGA2000, D_N = 440 nm, D_W 600 nm,
triangles - PEGA10000, D_N = 150 nm, D_W = 167 nm, D_I = 226 nm

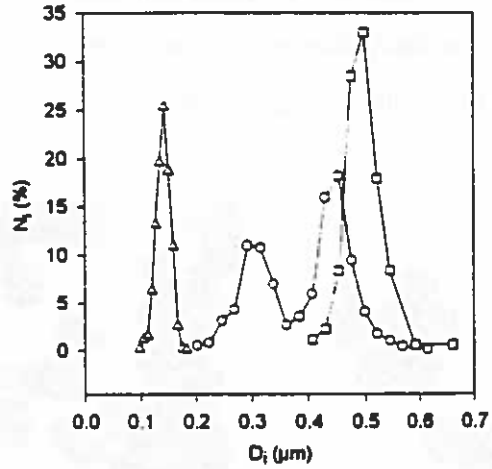
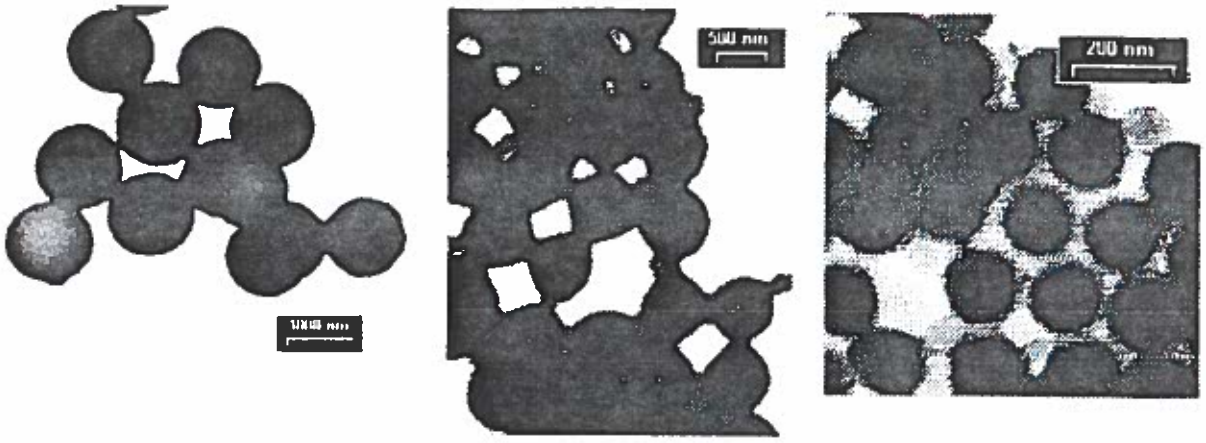


Figure 3 PSD estimated from enumerating TEM pictures of PS particle polymerized with PEGA initiators with varying PEG chain lengths in PEG200
circles - PEGA200, D_N = 391 nm, D_W = 433 nm,
squares - PEGA2000, D_N = 496 nm, D_W 502 nm,
triangles - PEGA10000, D_N = 141 nm, D_W = 144 nm, D_I = 265 nm

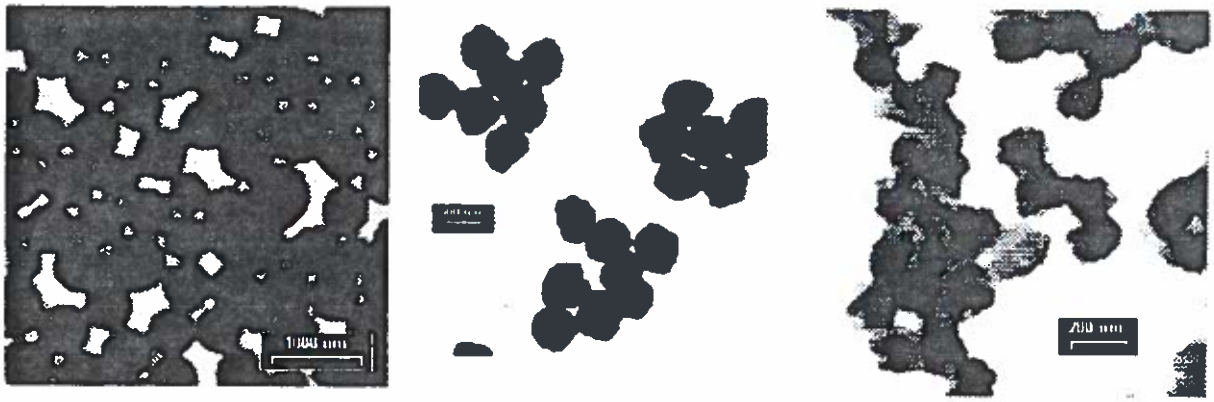
In the case of PEGA200 the average size of the particles prepared in water is twice the size of the particles polymerized in PEG200. Furthermore, in the case of water as dispersion medium the particles prepared with PEGA2000 are smaller than those prepared with PEGA200, but in PEG200 this order is reverse. Another interesting point is that the particles polymerized with PEGA200 in PEG200 possess a bimodal PSD whereas in water as dispersion agent PEGA2000 as well as PEGA10000 lead to a bimodal PSD.

The TEM pictures depicted in Figure 5 illustrate very clearly that the heterophase polymerizations in PEG200 lead to non-spherical particles if PEGA2000 or PEGA10000 are used. The reference system, the polymerizations in water, leads for all PEGA initiators to almost spherical particles (cf. Figure 4).



a b c

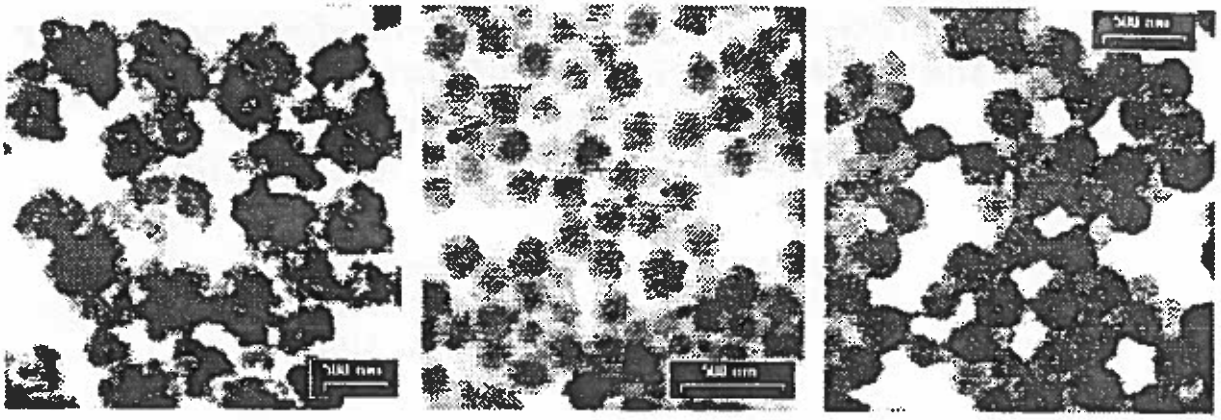
Figure 4 TEM photographs revealing the „crew cut" nature of particles prepared with PEGA200 (a) and the more and more hairy nature of the particles prepared with PEGA2000 (b) and PEGA10000 (c), respectively



a b c

Figure 5 TEM pictures of PS particles polymerized in PEG200 as dispersion medium with PEGA200 (a), PEGA2000 (b), and PEGA10000 (c) as initiator

The universality of the occurrence of non-spherical particles in PEG200 as a solvent, if covalently bound PEG chains with a molecular weight well above 200 g mol^{-1} are present, has been shown by performing polymerization with PEGA200 as initiator in the presence of PEG macromonomers (MM2000, MM4000, and MM8000). Indeed, the shape of the particles obtained is non-spherical (cf. Figure 6).



a b c

Figure 6 TEM pictures of PS particles polymerized in PEG200 with PEGA200 as initiator and in the presence of PEG macromonomers MM2000 (a), MM4000 (b), and MM8000 (c), respectively

Furthermore, the TEM pictures of Figure 6 prove the impression that with increasing PEG chain length of the macromonomers the shape becomes less and less indented. The reason for this behavior is at the moment not completely clear, but is possible attributed to the different bendability of thin layers of shorter and longer tethered chains. An alternative explanation might be given by the fact that the reactivity of PEG macromonomers in copolymerization decreased with the PEG pendant chain length [1]. Assuming that the same relation is valid for the polymerization system investigated here, the surface density of the PEG chains should be the lowest in case of MM8000, the interface energy highest, and hence a more smoother particle surface might be favored. The TEM pictures shown in Figure 6 also reveal with increasing PEG chain length a tendency of these chains to crystallize onto the particle interface. This is clear indicated by the vanishing of any curvature in the interstitial volumes.

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This is part of a paper submitted to *Macromolecular Chemistry and Physics*:

"Initiators based on Poly(ethylene glycol) for Start Heterophase Polymerizations: Generation of block copolymers and new particle morphologies."

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Characterization by Fluorescence Energy Transfer of the Core of Polyisoprene-Poly(methyl methacrylate) Diblock Copolymer Micelles. Strong Segregation in Acetonitrile

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(submitted to Macromolecules)

Abstract: Fluorescence decay measurements of the rate of non-radiative direct energy transfer has been employed to characterize the core and the core-corona interface of polyisoprene-poly(methyl methacrylate) (PI-PMMA) diblock copolymer micelles in acetonitrile. These micelles consist of a core of the insoluble PI-blocks and a corona of the soluble PMMA-blocks. The block copolymers are labeled, at the block junction, with a single fluorescent dye, either a donor chromophore (phenanthrene) or an acceptor chromophore (anthracene). Micelles were prepared in which the components are randomly mixed. Because the polymers are junction-labeled, the chromophores are naturally confined to the interface of each micelle. Fluorescence decay measurements show that the donor emission displays a non-exponential decay profile due to energy transfer. Analysis of these data indicate that energy transfer takes place on a flat spherical surface, which implies a strong segregation between PI and PMMA in the micelle. From the data analysis, a micellar core radius of (7.1 ± 0.7) nm is calculated from which a micellar aggregation number of 80 ± 16 is obtained.

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Communication: Micelle formation by block copolymers when dissolved in a solvent selective for one of the blocks has been studied for many years. [3] The techniques of small-angle X-ray [4] and small-angle neutron scattering [5] have often been used to obtain structural information about block copolymer micelles. This report concerns micelle formation of diblock copolymers of polyisoprene (PI) and poly(methyl methacrylate) (PMMA) in acetonitrile (CH3CN). Acetonitrile is a modestly good solvent for PMMA, which forms the corona. PI is insoluble in acetontrile and comprises the micellar core. We wish to show how the technique of direct dipole-dipole energy transfer (DET) can be utilized to characterize the morphology of the core.

The synthesized PI-PMMA diblock copolymers are labeled at the junction with a single fluorescent chromophore. Our donor chromophore (D) is phenanthrene, the acceptor chromophore (A) is anthracene, and the polymers are singly labeled. The PI-PMMA samples have number-averaged degrees of polymerization of (N_{PI}:N_{PMMA}) 150:470 (D-labeled), 150:550 (A-labeled).

In order to utilize DET to characterize the core, the A- and/or D-labeled chains need to be randomly mixed in any given micelle. The D- and A-labeled polymers were therefore first dissolved in dichloromethane, which is a good solvent for both blocks. The solvent was then evaporated in a N_2(g) stream to yield a thin film which was dried under vacuum at 50°C. The solid mixture, when dissolved in acetonitrile, yields the desired mixed micelles, with, as we will show, D and A restricted to the core-corona interface.

The fluorescence decay measurements employed the single photon timing technique, where the donor was excited at 300 nm, and its emission was monitored at 348 nm. Figure 1 below displays the fluorescence decay curves ($I_D(t)$) for the micellar solutions, where the fraction of A-labeled polymer increases from 0 (curve a) to 0.78

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3 Tuzar, Z.; Kratochvíl, P. in *Surf. Colloid Sci.*, Vol. 15; Matijevic, E., Ed.; Plenum Press: New York, 1993; pp. 1-83.

4 Jada, A.; Hurtrez G.; Stiffert, B.; Riess, G. *Macromol. Chem. Phys.* **1996**, *197*, 3697.

5 Mortensen, K.; Brown, W.; Almdal, K.; Alami, E.; Jada, A. *Langmuir* **1997**, *13*, 3635.

(curve g). The total polymer concentration was kept at 0.25 wt %. Note that in the absence of acceptors, the decay is exponential, with a donor lifetime (τ_D) of 45.5 ns. In the presence of acceptors, the donor decay is faster because of energy transfer.

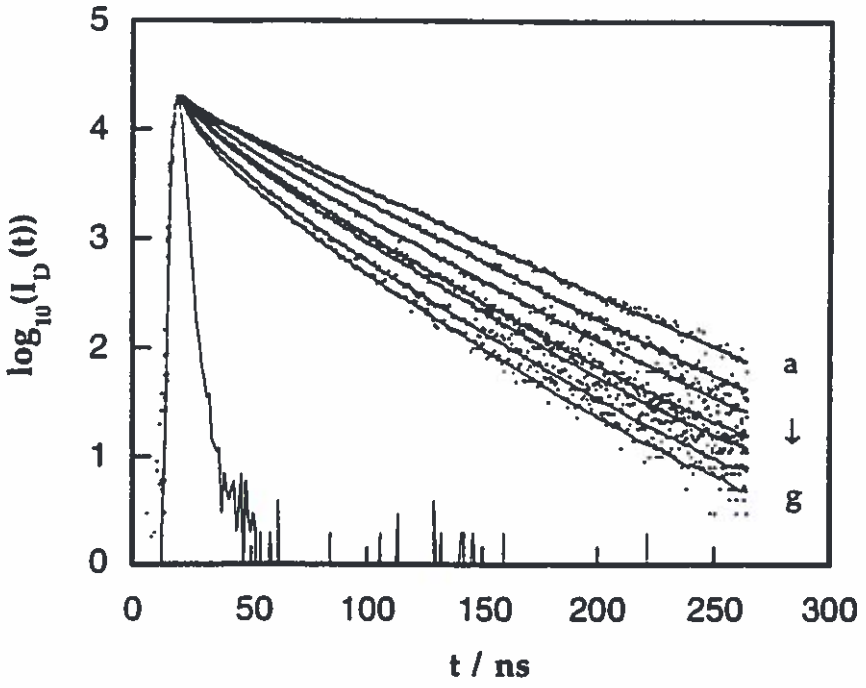

Figure 1. Time-resolved fluorescence decay measurements of 0.25 wt % dye-labeled PI-PMMA micellar solutions. The donor chromophore, phenanthrene, is excited at 300 nm, and the donor emission is observed at 348 nm. The fraction of the acceptor dye, anthracene, varies from 0 (trace a) to 0.78 (trace g).

It has been shown that the donor fluorescence decay contains information about the distribution of distances between donors and acceptors, which in turn is related to the morphology of the space in which DET takes place. $I_D(t)$ may be written as [6,7]

$$I_D(t) = I_D(0)\exp\{(-t/\tau_D)\}\exp\{-g(t)\} \quad ; \quad g(t) = P(-t/\tau_D)^{\beta} \qquad (1)$$

where P is a parameter proportional to the local concentration of acceptors (c_A); $\beta = \Delta/6$, where Δ is the dimensionality of the system in which DET takes place.

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When the DET is restricted to the surface of a sphere, i. e., when donor and acceptor are attached to the surface of a perfect sphere of radius R_{core}, then $\beta = 1/3$ (or $\Delta = 2$) and eq 1 will be simplified to

$$g(t) = P(-t/\tau_D)^{1/3} \quad ; \quad P = 0.339 f_A N_{agg} (R_0/R_{core})^2 \tag{2}$$

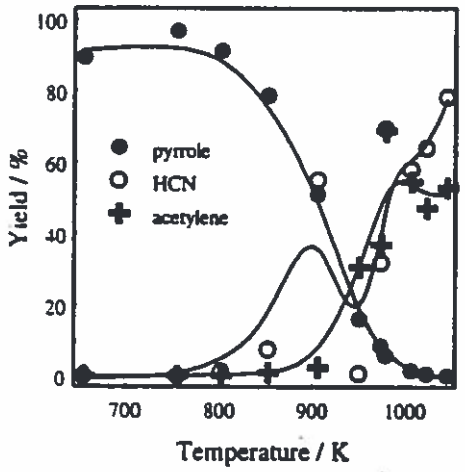
where $f_A = c_A / (c_A + c_D)$ is the mole fraction of the acceptor labeled chains, and N_{agg} is the micelle aggregation number. R_0 is a constant depending on the D-A pair and is here equaled to (2.3 ± 0.1) nm.

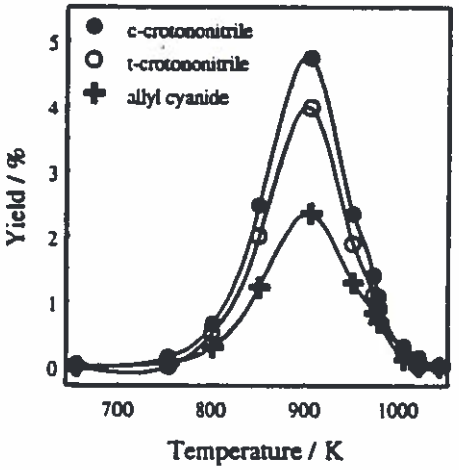
Eq 2 indicates that when the block junctions (or the dyes) are restricted in a two-dimensional geometry then the inteface between PI and PMMA is "sharp" and it is possible to obtain an estimate of the micellar core radius and aggregation number.

When the data of Figure 1 are fitted to the expression (1), two fitting parameters, β and P, are recovered. We obtain $\beta = 0.345 \pm 0.034$. This corresponds to a dimensionality of $\Delta = 2.07 \pm 0.20$, and within the experimental uncertainty, $\Delta = 2.0$. Thus, the interface is sharp, on the scale of < 1 nm (< 0.5 R_0). When the decay curves are fitted to the expression (2) (β fixed to 1/3), similar P values are obtained.

From the slope in a diagram of P, obtained with β fixed to 1/3, versus the fraction of acceptor labeled polymers f_A, the product $N_{agg} (R_0 / R_{core})^2 = 8.37 \pm 0.10$ is obtained. If we assume that the core is comprised only of the insoluble PI block, the aggregation number may be expressed as $N_{agg} = (4(R_{core}{}^3(_{PI}N_{AV}) / (3M_n{}^{PI})$, where the molecular weight of the PI block $M_n{}^{PI} = (10.3 \pm 0.6)\text{x}10^3$ g/mol, $\rho PI = 0.913$ g/cm^3 is the density of bulk PI and N_{AV} is Avogadro's number. Combining the two expressions for N_{agg}, we obtain $R_{core} = (7.1 \pm 0.7)$ nm, and $N_{agg} = 80 \pm 16$.

In summary, one is able to utilize the technique of direct non-radiative energy transfer (DET) to characterize the morphology of the core of block copolymer micelles in selective solvents. For the PI-PMMA/CH_3CN system considered here, the PI segments strongly segregate from the solvent by forming a sharp interface with a compact spherical shape.


Yield / %
Temperature / K
pyrrole
HCN
acetylene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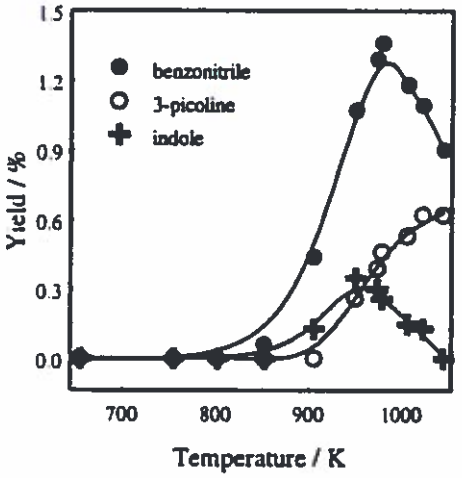
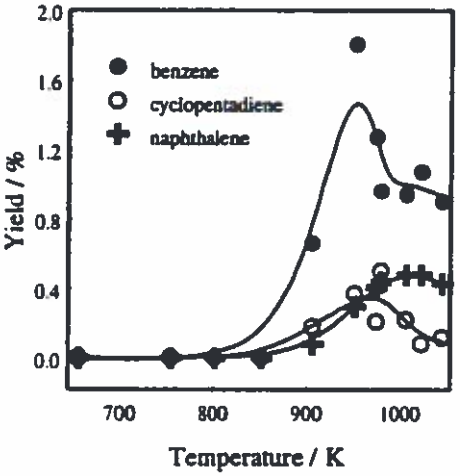
Temperature / K
c-crotononitrile
t-crotononitrile
allyl cyanide


Yield / %
Temperature / K
benzonitrile
3-picoline
indole


Yield / %
Temperature / K
benzene
cyclopentadiene
naphthalene