

Unless a deluge of contributions arrive within the next two or three days this issue of the Newsletter will again be rather sparse although bulked out by two contributions which arrived one or two days after the Autumn 1980 issue had been despatched and a full fortnight after the target date. The UNIST Chemistry Department now has a Xerox machine with the reduction facility. Use of reduced copy would halve production costs and reduce the cost of postage but will make it quite impossible to include contributions which arrive after the last minute!

The target date for the Autumn issue will be Monday 28th September. Will all members try to ensure that their contributions will be delivered in Manchester by then.

A theme (A) on 'Emulsion Polymerisation' has been included for the first time in the programme for the 27th International Symposium on Macromolecules to be held in Strasbourg, France, 6 - 9 July 1981. Bob Fitch is to give the Main Lecture on 'Mechanism of Particle Formation, Chemistry at the Interface' but no details of the other contributions or posters (which are scheduled for one afternoon only) are available. There are 14 other themes and 27 other Main Lectures but the number of simultaneous sessions has been limited to five. The Registration Fee is FF 900 which includes the cost of Preprints of the Contributed Papers. Information from Service Organisation des Congrès, Palais de la Musique et des Congrès, Avenue Schutzenberger, F-67082, Strasbourg, France.

The big event of the year for the Group will be the biennial Gordon Research Conference on Polymer Colloids which is again to be held at Tilton School, New Hampshire, U.S.A. 12 - 17 July 1981. Details of the programme appear overleaf. The Group's Annual Business Meeting will be held during the Conference. The Conference Fee (which includes accommodation and meals) is U.S. \$ 200 and has to be paid 1 month in advance by all participants (including those from overseas). Air travellers will probably find it best to use the Chartered Bus which is provided (at an extra charge) leaving Logan International Airport in Boston at 4 p.m. on the Sunday to the Conference sites returning after lunch on the Friday reaching the airport about 3 p.m. Alternatively there are five return trips daily from the Continental Trailways Bus Terminal in Boston and the school is not far from the stop in Tilton. The address for registration is Dr A.M. Cruickshank, Gordon Research Conference, Pastore Chemical Laboratory, University of Rhode Island, Kingston, Rhode Island 02881, U.S.A.

The 12th Annual Lehigh Short Course on Emulsion Polymerization will be held June 8-17, 1981; Mohamed El-Aasser is dealing with registrations. The 4th Annual European Short Course will again be held in Davos, Switzerland, August 17-21, 1980 and Gary Poehlein is taking registrations for this. The Fee (excluding accommodation) for either course is U.S. \$500.

The S.C.I. Colloid and Surface Chemistry Group in collaboration with the Macro Group are holding a symposium on 'The Effect of Polymers on Dispersion Properties' in London 21 - 23 September. 22 papers (which will be preprinted) will be presented. Speakers include Tadros, Lyklema, Fleer, Napper, and Vincent. Registration Fee of £85 includes 3 lunches. Registrations before 4 September 1981 to Dr Th. Tadros, ICI Plant Protection Division, Jealott's Hill Research Station Bracknell, Berkshire, RG12 6EX, England.

The Macro Group have a one-day symposium on 'Continuous Emulsion Polymerisation' on the following day, Thursday 24 September 1981. Gary Poehlein will be the principal speaker supported by David Blackley, Brian Brooks (Loughborough), Henry Warson, M. B. Khan (Crown Paints), and Professor G.W. Pearson (Imperial College). The Registration Fee will be about £30 (including lunch). Applications to Society of Chemical Industry, 14 Belgrave Square, London, SW1X 8PS.

The Royal Society of Chemistry - Faraday Division - Colloid and Interface Science Group is arranging a one-day Informal Discussion on 'Emulsion Polymerisation' in London on Monday 14th December 1981 with Don Napper as the principal speaker. Further details are not yet available but inquiries might be made of the Group Chairman, Dr M.J. Jaycock, Chemistry Department, Loughborough University of Technology, Loughborough, Leicestershire, LE11 3TU, England.

As noted in her contribution the book on 'Emulsion Polymerization' which Pirmas has edited is in course of production by Academic Press but the date of publication does not yet seem to have been scheduled.

The papers given at last year's Lehigh Symposium on 'Emulsion Polymerization of Vinyl Acetate' are in course of publication by Applied Science Publishers Ltd. Publication of this book is scheduled for September 1981.

Professor Yeliseyeva has published a new book 'Polimernye Dispersii' (in Russian). The publishers are Chiniya, Moscow. 296 pages at R 3.40. Wiley's are investigating the possibility of sponsoring an English translation. Despite extensive publicity the Plenum Press translation of her earlier book still does not seem to have been actually published.

The papers presented at last year's A.C.S. Emulsion Polymerization Symposium are in course of publication and will appear in the A.C.S. Symposium Series. In the meantime preprint versions are available in 'Organic Coatings and Plastics Chemistry Preprints' 43 (1980) No. 2 although this issue may now be out of print. Dave Bassett says that the Symposium volume is scheduled for publication in June.

A. S. Dunn

process will pack rhombohedrally while coagulated doublets and triplets pack in a more random fashion.

It has been demonstrated that this particle exclusion mechanism could be used in formulating microvoid coatings for sealing the surface of the porous coating resulting in enhanced scrub resistance.

droplets with decreasing surface tension as a function of radial distance from the apex.

Calculations of the average theoretical orbit times for streamlines in evaporating droplets of three different surfactant systems are also presented for two limiting mass transfer cases, with comparison to experimental orbit times.

The segregation of small polymer latex particles to the upper and lower interfaces of mixed particle size latex films was found to be driven by the packing density of the larger particles in the film. If the void volume was too small to accommodate the number of small particles, they were excluded to the two interfaces provided they were small enough to fit between the interstices of the larger-diameter array. If the small particles were too large to fit through the interstices, the packing order of the larger particles was disrupted by the presence of the smaller particles.

The packing density of the large particles in the mixed latex films, or a single monodisperse latex, may be explained in terms of colloid stability theory, and experimental evidence is given supporting this explanation. Those particles remaining stable throughout the

17 FEB 1981

GORDON CONFERENCE ON POLYMER COLLOIDS

July 12-17, 1981

Tilton, New Hampshire

R. M. Fitch, Chairman, J. W. Vanderhoff, Vice Chairman

Sunday, July 12

Registration
Reception
Dinner

*from 2.30pm till 9pm.
6pm
9pm.*

Monday, July 13

A.M. Discussion Leader: W. Ropp, Hercules Research

9am

1. A. Rembaum, Clatech and Jet Propulsion Labs. Immunospecific Systems
2. P. Bagchi, E. Kodak, Rochester Adsorption of Immunoglobulins at a Model Latex/Aqueous Electrolyte Interface

P.M. Discussion Leader: B.R. Vijayendran, Celanese Polymers

7.30pm

3. G.B. Benedek, Massachusetts Inst. of Technology Measurements of the Cluster Size Distribution in a System of Coated Polystyrene Latex Spheres Cross-linked by Antibodies
4. Th. Tadros, ICI, Jealott's Hill, England Steric Stabilization and Adsorbed Polymers

Tuesday, July 14

A.M. Discussion Leader: H. Nomura, Fukui University

5. L. Landoll, Hercules Research with S. Ahmed & R. Fitch Amphiphilic, Surface-active Cellulose Derivatives
6. I. Michaeli, Weizmann Institute, Rehovot Polyelectrolyte Clusters

P.M. Discussion Leader: R. Potter, American Cyanamid

7. T.G.H. van de Ven, McGill Univ. Microrheology and Interparticle Interactions
8. F.J. Micale, Lehigh Univ. Electrokinetic Properties of Polymer Colloids in Aqueous and Nonaqueous Systems

by
Daniel Durbin

14 OCT 1970

ABSTRACT

The driving forces responsible for two interfacial phenomena have been identified in this study. The hydrodynamic circulation observed in evaporating surfactant droplets and the segregation of small diameter polymer latex particles to the interface of films dried from mixtures of large and small diameter latex particles.

Surface tension gradients radially extending across sessile surfactant droplet interfaces have been found to induce the hydrodynamic circulation within evaporating surfactant droplets. These surface tension gradients are a result of the concentration dependence of surface tension, geometry of the droplet, as well as the evaporation process.

A theoretical development is presented allowing calculation of the theoretical profile and hydrodynamic streamlines for sessile droplets possessing radial surface tension gradients. Drop profiles photographed during the evaporation process were found to possess inflections in the radius of curvature. These inflections are theoretically predicted for sessile

Wednesday, July 15

A.M. Discussion Leader: J. Goodwin, Univ. of Bristol

Short Contributions

10. Z. Adameczyk, Polish Academy of Sciences
Particle Deposition from Flowing Sols

P.M. Discussion Leader: A. Robertson, McGill Univ.

11. R.H. Ottewill, Univ. of Bristol
Neutron Scattering
12. Derek Rance, ICI, Welwyn Garden City
Colloidal Aspects of Vinyl Chloride
Polymerization

Thursday, July 16

A.M. Discussion Leader: I. Pifirma, University of Akron

13. Z.H. Liu, Inst. Photographic Chem.,
Academia Sinica, Peking
Thermodynamics of the Interface
14. J. Guillot, CNRS Laboratory of Organic
Materials, Lyon
Thermodynamic Approach to Emulsion
Copolymerization

P.M. Discussion Leader: R.M. Fitch, UConn.

15. J. Th. G. Overbeek, Van't Hoff Laboratorium
Rijksuniversiteit, Utrecht
Stability in Polar Organic Media

Friday, July 17

A.M. Discussion Leader: J.W. Vanderhoff, Lehigh Univ.

16. V.I. Yeliseyeva, Topchiev Inst. of Physical
Chemistry, Academy of Sciences, USSR
Regulation of Polymer Properties and
Particle Morphology
17. A. Klein, Lehigh University
Core-Shell Emulsion Copolymerization

in viscosity than the semi-continuous MMA-MAA latex in spite of the higher extent of neutralization. This was attributed to the dissolution of the latex polymer, which took place easily because of the lowered T_g , as well as to swelling in the semi-continuous latex upon neutralization.

A scheme of alkali-swelling and/or dissolving behaviors for latexes of the MMA-MAA copolymer system, the MMA-EA-MAA terpolymer system, and the corresponding crosslinked system was speculated, for both the batch with the semi-continuous latexes.

The changes in particle size which were measured by the dissymmetry method of light scattering did not seem to be able to reflect the swelling behavior in a highly swollen and/or dissolved latex, such as carboxylated latexes prepared by the semi-continuous process.

Effect of pH on the Adsorption of Immunoglobulin G on Anionic Poly(vinyl toluene) Model Latex Particles

29

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14650

Protein Adsorption on Latex Particles

Submitted for publication in J. Colloid and

Interface Science

¹ To whom all communications should be directed.

Abstract

The adsorption of a set of goat and rabbit immunoglobulin G's (Ig G) on the surface of a set of well-characterized, pH-independent, negatively charged poly(vinyl toluene) model latexes was studied as a function of pH. Highest adsorption occurred at the zero-point of charge (Z.P.C.) of the Ig G molecules at pH 7.8 and decreased linearly with both an increase and a decrease of pH. This indicated that the major driving force for the adsorption of the Ig G molecules is due to hydrophobic interaction rather than to charge interaction between the protein molecules and the latex particles. Consideration of

saturation area per adsorbed Ig G molecule at different pH values led to the conclusion that ionization-induced conformational changes in the Ig G molecule determine the extent of Ig G adsorption. Based on this, a model has been proposed for the conformations of adsorbed Ig G molecules on latex surfaces at the Z.P.C. and away from it. In accordance with this model, the saturation area-per-molecule of adsorbed Ig G as a function of pH correlates quantitatively with an end-on arm-collapsed "Y" conformation at the Z.P.C. of the protein, and an end-on arm-extended "T" conformation at pH values of 4.0 and 10.0, where the Ig G molecule is fully charged, cationically and anionically, respectively. Results of intrinsic viscosity measurements of rabbit Ig G solutions as a function of pH, at constant ionic strength, seem to support the proposed configuration changes of the Ig G molecule as a function of pH. Although the adsorption of Ig G molecules was irreversible at fixed pH values, it seemed to be quasi-reversible with pH cycling. A mechanism for this process has also been suggested, based upon conformational considerations.

by the serum replacement technique. The modified conductometric titration is composed of the following procedures: i) following a change in conductance after injection of excess NaOH into a sample latex; ii) after 24 hrs., back-titrating with HCl, the latex containing the excess NaOH; and iii) assigning the amount of carboxyl groups neutralized during a certain period of neutralization reaction to a location of carboxyl groups within the particles.

A simple diffusion theory indicated that the rate of neutralization reaction in the carboxylated latexes is dependent not only on the diffusion process, but also on the hydration of carboxylate groups and plasticization of water molecules.

The extraordinary increases in viscosity exhibited by the semi-continuous latexes with MAA contents of 15, 20, and 25% were attributed to the dissociated carboxyl groups with the attraction forces due to hydrogen bonds. In this special system the crosslinking seemed to have an insignificant effect to its viscosity behavior with pH.

The results obtained with the lower T_g latex system (incorporated with EA) indicated that the batch latex of this system exhibited a higher extent of neutralization and a higher increase in viscosity than the batch MMA-MAA latex; whereas the semi-continuous latex exhibited a much lower increase

ALKALI-SWELLING BEHAVIORS OF CARBOXYLATED LATEXES

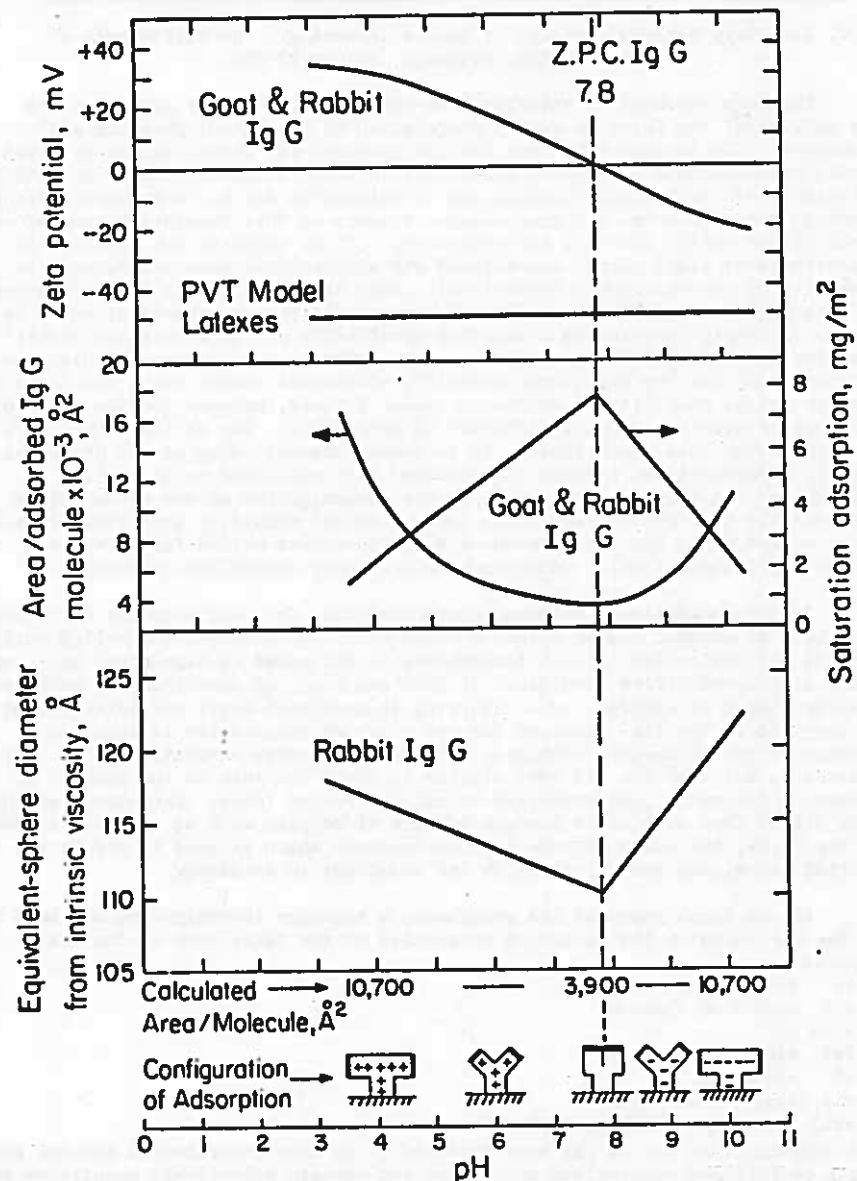
by
Shozo Nishida

14 OCT 1980

ABSTRACT

Methyl methacrylate (MMA)-methacrylic acid (MAA) copolymer latexes with MAA content from 5-25 weight were prepared as a model system of alkali-swellaible carboxylated latexes by means of two polymerization processes, i.e., batch process and semi-continuous process. The polymerization process was found to greatly influence the distribution of carboxyl groups in the final latex particles, which in turn influenced the alkali-swelling and/or dissolving behavior of the carboxylated latexes. The MMA-MAA copolymer latexes prepared by the batch process contained less uniform distribution of carboxyl groups inside the particle, and exhibited moderate increase in viscosity followed by slow decrease with increasing pH. The MMA/MAA copolymer latexes with similar composition prepared by the semi-continuous process, in which the rate of monomer feed was taken to be much less than the maximum rate of polymerization, contained more uniform distribution of carboxyl groups inside the particle, and exhibited great increase in viscosity followed by rapid decrease with increasing pH.

The distribution of carboxyl groups in alkali-swellaible carboxylated latex particles could be detected by the modified conductometric titration after cleaning



Comparison of the pH dependences of zeta potential, saturation adsorption, and area per molecule at the PVT latex/aqueous electrolyte ($2 \times 10^{-3} \text{ M KNO}_3$) interface and equivalent-sphere diameter of the Ig G molecule at 23°C with the proposed model of Ig G adsorption.

12 111 504

FURTHER STUDIES ON THE MECHANICAL DESTABILISATION OF NATURAL RUBBER LATEX

D. C. Blackley, National College of Rubber Technology, The Polytechnic of North London, Holloway, London N7 8DB.

The term "mechanical stability" as applied to a polymer latex denotes the ability of the latex to resist coagulation by mechanical shearing and turbulence. It is essential that latices intended for industrial application should have adequate mechanical stability, in order that they should be able to withstand such mechanical shearing and turbulence as may be encountered during pumping, transportation and processing. Readers of this Newsletter, and of our publications in the journals and elsewhere, will be aware of our interest in the effects of added soaps, surfactants and electrolytes upon the mechanical stability of natural rubber latex (1-5). What is not generally known (because we have not so far published any of the results of this programme of work) is that we are currently undertaking a detailed examination of the mechanical stability test for natural rubber latex itself. (Note that it is necessary to distinguish between tests for the mechanical stability of natural rubber latex and tests for the mechanical stability of synthetic rubber latices, because the two types of test are frequently somewhat different in principle.) Our ultimate objective in undertaking this investigation is to deepen understanding of the processes whereby a rubber latex becomes destabilised when subjected to mechanical influences. Although in the course of the investigation we are accumulating considerable information concerning the mechanical stability test itself, in a sense we are using the test procedure as a convenient method for effecting mechanical destabilisation under reasonably closely controlled conditions.

In the conventional high-speed-stirring test for assessing the mechanical stability of natural rubber latex, a known weight of latex of controlled solids content and controlled initial temperature is subjected to high-speed stirring under closely-specified conditions of size and shape of container, geometry of stirrer, speed of stirrer, etc. Stirring is continued until the latex begins to coagulate. The time required for the onset of coagulation is taken as a measure of the mechanical stability. There are several variants of this test in existence, but they are all very similar in their approach to the problem of assessing the mechanical stability of natural rubber latex. The points at which they differ from each other concern matters of detail, such as the solids content of the latex, the nature of the aqueous solution which is used to dilute the initial latex, and the way in which the end-point is detected.

In the first phase of the programme, a thorough investigation has been made of the way in which the following properties of the latex vary as the test proceeds:

- i) temperature
- ii) degree of foaming
- iii) pH
- iv) alkalinity
- v) viscosity
- vi) coagulum content
- vii) particle-size distribution

The investigation has so far been confined to an ammonia-preserved natural rubber latex centrifuged concentrate which does not contain appreciable quantities of secondary preservatives. The alkalinity of the latex is therefore due primarily to the presence of ammonia.

Index (Contd.)

	<u>Page</u>
Preparation of Commercial Iron Oxide Dispersions (D.W. Timmons, L.M. Bennetch, M.J. Cantow, M.S. El-Aasser, F.J. Micale, J.W. Vanderhoff)	124
Colored Latexes: Preparation, Characterization, and Adsorption (Y.J. Shih, M.S. El-Aasser, J.W. Vanderhoff)	126
Theses Titles	

Index (Contd.)

	<u>Page</u>
Adsorption-Desorption Studies of Emulsifiers on Latex Particles (S. Maqsood Ahmed, M.S. El-Aasser, J.W. Vanderhoff)	61
Analysis of Latex Particle Size Using Hydrodynamic Chromatography: Improving Column Resolution in Nonporous Packed Systems (J. Viola, C.A. Silebi)	68
Hydrodynamic Chromatography--A Study of Latex Particle Recovery in Packed Bed Flow Systems (R. Thevenet, R.D. Rose III, C.A. Silebi, J.W. Vanderhoff)	70
Factors Affecting Stability in Continuous Particle Electrophoresis (R.V. Mann, F.J. Micale, J.W. Vanderhoff)	74
Modeling of Continuous Particle Electrophoresis (CPE): An Analysis of Hydrodynamic Stability (P. Vaughn, C.A. Silebi, F.J. Micale, J.W. Vanderhoff)	76
Study of Interaction Between Particle and Air Bubble in Flotation (K. Chiang, F.J. Micale)	83
Fundamental Studies of Effect of Particle Size on Critical Pigment Volume Concentration and Development of Model Latex Paint (A. Ranka, M.S. El-Aasser, J.W. Vanderhoff)	89
Interfacial Phenomena Occurring in Drying Surfactant Droplets (D. Durbin, M.S. El-Aasser, J.W. Vanderhoff)	91
Drying of Epoxy Latexes (B.I. Aremu, C.C. Ho, M.S. El-Aasser, J.W. Vanderhoff)	98
Coating by Electrodeposition (C.C. Ho, A. Humayun, M.S. El-Aasser, J.W. Vanderhoff)	103
The Effect of Thickener Displacement by Emulsifier on Dynamic Yield Stress of Thickened Latexes (J. Lin, M.S. El-Aasser, J.W. Vanderhoff)	114
Preparation and Characterization of Colloidal Iron Corrosion Products (M.H. Kang, M.J. Cantow, L.M. Bennetch, F.J. Micale, M.S. El-Aasser, J.W. Vanderhoff)	116

The temperature of the latex falls at first, presumably because the initial latex temperature is higher than that of the surroundings. But after a time the temperature begins to rise again and eventually exceeds the initial temperature. The latex foams considerably during the early stages of the test, but the foam then collapses progressively as the test proceeds. The pH of the latex falls approximately linearly with time of stirring, and this fall is attributable to loss of ammonia. The viscosity of the latex rises progressively as the test proceeds, quite apart from any enhancement of viscosity which may accrue from entrapment of air. The coagulum content of the latex increases only slightly until the end-point of the test approaches, when there is a sudden massive increase in coagulum content. The particle-size distribution of the coagulum-free part of the latex, as determined by Coulter Counter, gradually broadens as the test proceeds. The picture which these initial observations give is of a gradual increase in average particle size and broadening of the particle-size distribution, followed by catastrophic particle agglomeration as the end-point is reached. A plausible hypothesis is that the onset of mechanical destabilisation occurs when there are a few particles of sufficient size in the latex to agglomerate rapidly with smaller particles. Although mechanical destabilisation will be aided by the reduction in pH which accompanies loss of ammonia, this is thought to be a comparatively minor effect.

In the second phase of the programme, an investigation has been made of the effects of some of the important latex variables upon the mechanical destabilisation process. These variables include initial temperature and initial pH. An interesting and significant observation is that, within any one series of experiments (e.g., investigation of effect of initial pH), data for variables such as degree of foaming, viscosity and coagulum content can frequently be represented by a single "master curve" if they are plotted not against actual time of stirring but against "reduced" time of stirring, that is, against time of stirring relative to the time required to reach the end-point of the test.

We are also investigating the destabilisation process for natural rubber latex whose stability has been considerably enhanced by the addition of a small amount of a fatty-acid soap, and also for a natural rubber latex whose stability has been considerably reduced by the addition of an inorganic electrolyte. The indications at present are that the destabilisation process follows roughly the same course as that for unmodified natural rubber latex, except that the time scale is either lengthened or shortened according as the stability of the latex has been increased or diminished. We are also about to commence an investigation into the effect of the non-rubber constituents in natural rubber latex upon its mechanical stability. Of particular interest is the effect of proteinaceous substances, whose effect may be either to stabilise or to destabilise the latex against mechanical coagulation. For this aspect of the investigation, we are using a single batch of natural rubber latex, portions of which have been once, twice and thrice centrifuged. It is to be expected that, as the number of centrifugings increases, so the level of proteinaceous substances in the latex will fall, and the latex will more nearly approach a soap-stabilised dispersion of polyisoprene in water.

References

1. D.C. Blackley, b.N.M. Salleh and R. Twaits, Plastics and Rubber: Materials and Applications, 1977, 2, 117
2. D.C. Blackley, bt. A.A. Nor Aisah and R. Twaits, Plastics and Rubber: Materials and Applications, 1979, 4, 77
3. D.C. Blackley and M. Azas, Plastics and Rubber: Materials and Applications, 1980, 5, 57
4. D.C. Blackley and A.C. Haynes, Plastics and Rubber: Processing and Applications, 1981, 1, 73
5. D.C. Blackley, "Mechanical and chemical stability of polymer latexes", paper presented at A.C.S. Emulsion Polymerization Symposium held in Las Vegas, 24th - 26th August 1980

The Origin of the Carbonyl Content of Polyvinyl Alcohol

In their 1970 theory of vinyl acetate emulsion polymerisation (which was partly presented at the Lehigh Vinyl Acetate Emulsion Polymerisation Symposium in April and partly at the A.C.S. Symposium in September), Litt and Chang show that in contrast to the conclusions of most previous workers transfer to vinyl acetate monomer is mainly to the secondary hydrogens which is what might have been expected. The $\text{CH}_2\text{COCOOCH}_3$ radical does not reinitiate but is responsible for the termination of most polyvinyl acetate radicals. Consequently the polyvinyl acetate molecules will be expected to have one $\text{RCH}_2\text{CH}(\text{OAc})\text{CH}(\text{OAc})=\text{CH}_2$ end group. On hydrolysis this will become $\text{RCH}_2\text{CH}(\text{OH})\text{CH}(\text{OH})=\text{CH}_2$, which would be expected to isomerise easily to $\text{RCH}_2\text{CH}(\text{OH})\text{C}(=\text{O})-\text{CH}_3$, so that most polyvinyl alcohol molecules may be expected to have one end-group having an isolated ketone group. Unfortunately the u.v. absorption maximum of isolated ketone groups is below 200 nm and consequently is not readily observable with standard u.v. spectrophotometers. Polyvinyl alcohol samples do have two u.v. absorption maxima which are attributed to monoene and diene ketones. Hitherto it has not been at all clear how these structures arise although they may be attributable to adventitious oxidation during drying since the conjugated ketone content increases rapidly on heating in air. But the terminal ketone groups would be expected to promote the dehydrozation of adjacent residues.

Reaction with 2:4-dinitrophenyl hydrazine provides a possible method for determining the isolated ketone content of polyvinyl alcohol. Mr Abdul Ghani has succeeded in preparing, precipitating, and redissolving the 2:4 dinitrophenyl hydrazone of one sample of polyvinyl alcohol but unfortunately has so far not been able to reproduce the results having been unable to get a precipitate in later trials. However the result he has obtained is encouraging. The sample tested was 'Gohsenol' CH-17. The absorbance of a 0.50 % w/v solution of the polyvinyl alcohol 2:4-dinitrophenyl hydrazone at the maximum (369 $\text{m}\mu$) was 0.61 in a 1 cm cell. Taking the absorptivity to be $19\,700\text{ dm}^2\text{ mol}^{-1}\text{ cm}^{-1}$ (the value for acetone dinitrophenyl hydrazone in chloroform at 370 nm quoted by Burfield and Lay, *Polymer* 20 (1979) 620) this gives a concentration of $3.10 \times 10^{-5}\text{ mol dm}^{-3}$. The intrinsic viscosity of the sample in water at 25 °C was 0.8475 which using Borecniewica's calibration (*J. Polym. Sci.* 39 (1959) 63) for polyvinyl alcohol with a 13.4 mol % acetyl content gives $K_V = 1.63 \times 10^5$ whence the concentration of the solution of which the absorbance was measured would be $4.91 \times 10^{-5}\text{ mol dm}^{-3}$. Of course this sample does have a low content of conjugated carbonyl groups and the dinitrophenyl hydrazones of these have much higher absorptivities and the number-average rather than the viscosity-average molecular weight should be used to calculate the polymer concentration. Nevertheless this experiment provides prima facie evidence that a large proportion of polyvinyl alcohol molecules do have carbonyl end groups. With application of appropriate corrections, it should be possible to develop a colorimetric method of determining the frequency of long-chain branching in polyvinyl alcohol in conjunction with an osmotic determination of number-average molecular weight.

Makromol. Chem., Rapid Commun. 1, 75-77 (1981)

75

Effect of the Presence of Traces of Water during the Polymerization of Vinyl Acetate on the Properties of Poly(vinyl alcohol) Obtained by Hydrolysis

Mohd. Heimi Mahmood, Rusli Abd. Ghani, Alexander S. Dune*

	Page
Emulsion Polymers Institute--Staff	1
Toward the Production of Large-Particle-Size Monodisperse Latexes (E.D. Sudol, M.S. El-Aasser, F.J. Micale, J.W. Vanderhoff)	4
Toward the Production of Large-Particle-Size Monodisperse Latexes--Swelling Study (C.M. Tseng, M.S. El-Aasser, J.W. Vanderhoff)	10
Separation of Latex Particles Using the Serum Replacement Cell (V. Lowry, M.S. El-Aasser, J.W. Vanderhoff)	13
Emulsion Polymerization in a Continuous Reactor (N. Pramojaney, G.W. Poehlein, A. Klein, J.W. Vanderhoff)	17
Kinetic Studies of Semi-Continuous Emulsion Copolymerization of Vinyl Acetate-Butyl Acrylate (T. Makgawinata, M.S. El-Aasser, A. Klein, J.W. Vanderhoff)	21
Inverse Emulsion Polymerization (F.V. DiStefano, M.S. El-Aasser, J.W. Vanderhoff)	26
Mechanism of Core-Shell Emulsion Polymerization (D. Stutman, A. Klein)	30
Production and Stabilization of Absorbent Beads by Suspension Polymerization (D. Bloom, M.S. El-Aasser, J.W. Vanderhoff)	32
Alkali-Swelling Behaviors of Carboxylated Latexes (S. Nishida, F. Loncar, M.S. El-Aasser, A. Klein, and J.W. Vanderhoff)	33
Effect of Successive Seeding on the Surface Charge Density of Monodisperse Latexes (E.D. Sudol, S.C. Misra, M.S. El-Aasser, J.W. Vanderhoff)	42
Preparation of Polystyrene Latex as a Model Colloid (A. Kamel, M.S. El-Aasser, J.W. Vanderhoff)	48
The Relationship Between the Electrophoretic Mobility and the Adsorption of Ions on Polystyrene Latex (C.M. Ma, F.J. Micale, M.S. El-Aasser, J.W. Vanderhoff)	54

papers are being prepared on his results. The work is being continued by one of the graduate students.

Dr. T. I. Min, Associate Professor of Chemical Engineering, Ajou Institute of Technology, Korea is spending a sabbatical year in our Institute. Dr. Min has good background in the area of characterization of copolymers by thin layer chromatography. He just started working on "Mechanism of Emulsification by Mixed Emulsifier Systems," and will also contribute to the core-shell morphology project.

Our 12th Annual Short Course on "Advances in Emulsion Polymerization and Latex Technology" will be held at Lehigh on June 8-12, 1981.

Polymer Colloids Group Newsletter
Contribution from The University of Connecticut

by R. M. Fitch

I have been on sabbatical leave since the first of January at the C.N.R.S. Centre de Recherches sur les Macromolécules in Strasbourg, France, and shall remain here until the IUPAC-Macro 81 meeting here in July. The "CRM" is world-renowned, of course, but it is not exactly a hotbed of activity in polymer colloids. Nevertheless, I have been treated very kindly here, and can certainly recommend Strasbourg as a place for a pleasant sojourn. Next door is the Ecole d' Application des Hauts Polymères (EAHP) at which some emulsion polymerization is being done under the direction of Profs. M. Lambla and A. Banderet. Incidentally these two gentlemen, along with K. A. Syed, published a paper in 1975 on the kinetics of the transport of free radicals across a planar interface separating two liquids: They used four combinations of water-soluble/oil-insoluble and oil-soluble/water-insoluble monomers (styrene and acrylamide) and initiators ($K_2S_2O_8$ and AIBN) along with three surface active agents. Transfer to surfactant, in some cases, was found to be an important mechanism for transport of radicals across the interface (European Polymer J. 12, 263-271 (1976)).

Here at the CRM Mme. Françoise Candau is successfully engaged in the formation of inverse polyacrylamide microemulsions by the photoinitiated polymerization of an acrylamide monomer microemulsion. Many others have previously attempted to do this without much success (except J. Herz et al. - also of the CRM- who polymerized soap-like monomers: J. Polym. Sci., Part C (4) 1275 (1963)). Candau's secret is that she has employed a monodisperse, amfifilic block copolymer as the surfactant. She is to give a short communication on this at the Gordon Conference.

There is another C.N.R.S. center at Lyon (Villeurbanne), the Laboratoire des Matériaux Organiques under Alain Guyot. He and his coworkers C. Pichot and J. Guillet are doing some excellent work on the theory and engineering of emulsion co-polymerization. Guillet will discuss his work at the Gordon Conference also.

Inspired by the recent theoretical and experimental work of Hansen and Ugelstad, we have taken renewed interest in this old problem. We are encouraged by the possibility of finding experimental values for critical parameters, especially the critical degree of polymerization for homogeneous nucleation (our DP_{crit} , M and U 's j_{cr}) as a function of monomer, end-groups, etc. The experiment is an extension of the one employed by Watson and Fitch in which intensity light scattering is used to follow particle formation and growth. A diagram of an improved apparatus is shown in the accompanying figure. The differential detection mode, suggested to us by Prof. Gerson Kegeles of UConn, allows one to obtain higher signal-to-noise ratios. By using appropriate frequency filters, we can have continuous photoinitiation in the blue region whilst detecting only the red.

The requirements for extreme purity in terms of dust and reactive contaminants mean that reproducibility has been difficult to achieve. Nevertheless we observe great differences in behavior as a function of the concentration of sodium dodecyl sulfate (SDS) until the CMC is exceeded, when the activity of SDS becomes constant. This is shown in the figure, in which four levels of SDS have been investigated, two above the CMC (1.6×10^{-2} and 6.4×10^{-2} M). All curves represent replicate runs.

The theoretical curve, from the NUFT theory (Hansen-Ugelstad, based on the earlier Fitch-Tsai), represents an attempt at curve-fitting in which the $M-U$ condition $A=1$ applies:

$$k_{cj} = k_p^M v_p^j a_j / E_j \quad \text{for } n = 0$$

$$k_{cj} = (k_p^M + k_{tp}^* / v_p) v_p^j a_j / E_j \quad \text{for } n = 1.$$

The Morton equation is used for particle swelling by monomer, and the radical concentration is determined from the capture kinetics. The Rayleigh ratio, R_{90} , increases with time because of particle growth by polymerization and coagulation. The value of $j_{cr} = 53$ was chosen on the basis of some of our earlier work.

There are still too many adjustable parameters. More experiments with other initiators, monomers and surfactants will be required to sort things out.

Surface Analysis by ^{13}C -nmr (P. Tarcha)

In an earlier publication (Gajria, Tarcha and Fitch) we showed that acrylate latexes bearing surface sulfate and sulfonate groups in the M^* form undergo autocatalyzed hydrolysis. The rates were found to be zero order with respect to polymeric ester, and first order in surface strong acid concentrations. We proposed a mechanism involving a "surface reaction zone" in which the ester concentration would remain constant over long periods of time. D. Bassett had earlier examined a couple of our partially hydrolyzed colloids and concluded that they were similar to his copolymer latexes which were thought to have carboxylic acid-rich shells.

M. S. El-Aasser, A. Klein, and J. W. Vanderhoff
Lehigh University

We have currently 26 active projects, the titles are included in the attached Index of our Graduate Research Progress Reports, issue No. 14, which was published on August 1, 1980. We have few copies left of the reports available for distribution to the members of the Polymer Colloid group on a first come first serve basis. However, if any member is interested in a particular project, we will be pleased to provide you with a copy of the progress report on that project.

Two of our graduate students have just finished their Ph.D. theses: Daniel Durbin on "Interfacial Phenomena Occurring in Drying Surfactant Droplets and Polymer Latex Films;" and Shozo Nishida on "Alkali-Swelling Behaviors of Carboxylated Latexes." Dr. Durbin accepted a job with Shell Co., Research and Development Group in Houston, Texas, and Dr. Nishida will be returning to his company, Japan Synthetic Co. Both will be leaving as of November 1, 1980. Copies of the abstracts of the two theses are included.

Dr. C. C. Ho, who spent the past nine months of his sabbatical at our Institute, will be returning back to the University of Malaya on November 1, 1980. Dr. Ho worked on the "Kinetics of Film Growth and Film Formation of Epoxy Latexes by Cathodic Electrodeposition Process." Two

Report from Vivian T. Stannett
Chemical Engineering Department
North Carolina State University
Raleigh, NC 27650

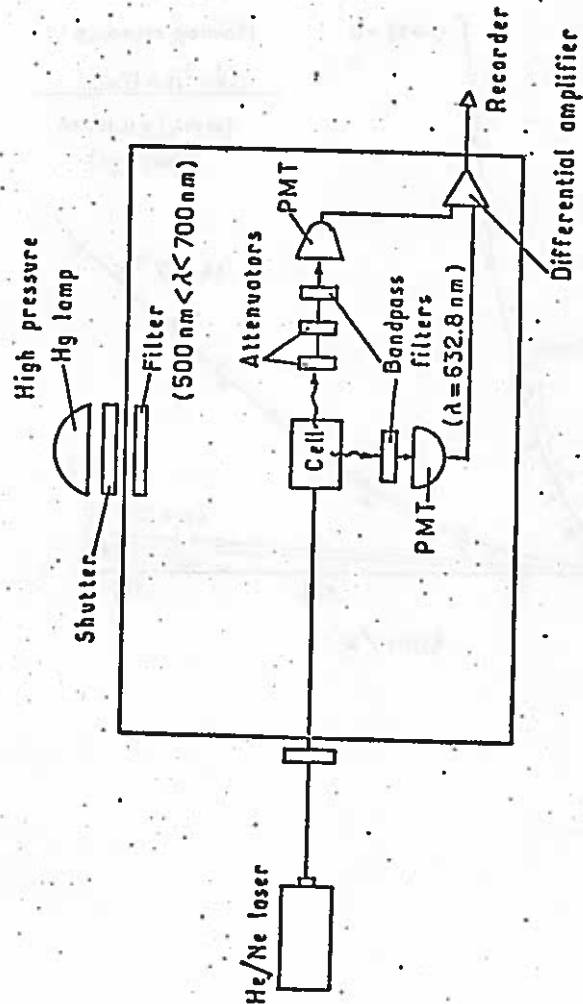
Vivian is pleased to say that after a considerable "lapse from grace" he has started up some radiation induced emulsion polymerization work again. With his colleague, Professor E. P. Stahel, he has rebuilt the pilot plant flow system [see e.g., Tsai, Stahel and Stannett, J. Appl. Poly. Sci. 23 2701-2710 (1979)]. Two subjects, the emulsifier concentration dependence of the rate of polymerization (with sodium lauryl sulfate) of vinyl acetate and the relative rates and other behaviour with anionic, nonionic and cationic emulsifiers with vinyl acetate are under study.

Preliminary results show a 0.41 ± 0.2 order with emulsifier in good agreement with the literature but less than the earlier results (1969!) for the same author. The rates were in the order anionic > nonionic > cationic emulsifiers. Since highly stable cationic latices can be obtained using radiation initiation, this subject will be studied in more detail.

Two chapters have been written since the last report. 1. "Radiation Induced Emulsion Polymerization" by V. Stannett for the book "Emulsion Polymerization" edited by Dr. Irja Piirma, Academic Press. 2. "The Radiation Induced Emulsion Polymerization of Vinyl Acetate" by V. Stannett, R. R. Challa, J. H. Drew and E. P. Stahel for the book "Emulsion Polymerization of Vinyl Acetate" edited by Mohamed S. El Asser and John W. Vanderhoff, Applied Science Publishers, Ltd.

I am afraid they are too bulky to send out but if anyone is especially interested and it is legal, I will be glad to send them a copy!

Vivian
May 6, 1981.



Contributed by Dr F. L. Saunders

MORPHOLOGY AND PROPERTIES OF TWO-STAGE LATEX PARTICLES

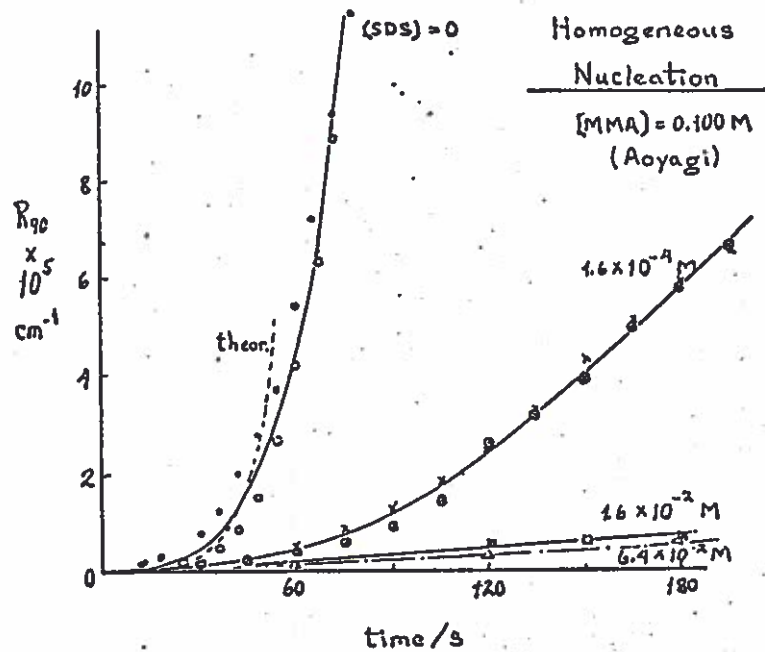
27 MAY Recd

Do Ik Lee
Designed Latexes & Resins
Dow Chemical U.S.A.
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U.S.A.

ABSTRACT

The morphology of two-stage (styrene/styrene-butadiene) latex particles was studied as a function of stage ratio (polymer phase ratio), molecular weight, S/B copolymer composition, polymerization sequence, and polymerization conditions, using electron microscopy with the osmium tetroxide staining method. Their film-forming, thermal, and mechanical properties were evaluated and compared with those of their corresponding homogeneous and blended (polystyrene and S/B) latexes. The morphological features were mainly structures resulting from phase separation rather than the core-shell morphology expected from surface polymerization with no interpenetration. Depending on the molecular weights of the polymers involved, the second-stage polymer phase-separated either as microdomains within the first-stage polymer phase or completely from the first-stage polymer phase. The minimum film formation temperature of two-stage latexes was found to be more affected by the continuous polymer phase in the particles than the polymer phase ratio, unlike that of blend latexes. Two or more glass transition temperatures (T_g) were observed by DTA. Intermediate T_g 's between those of S/B copolymers and polystyrene were shown by those two-stage latex particles composed of either small size microdomain phases or two continuous phases. The mechanical properties of two-stage latexes were similar to those of their corresponding blends, but their efficiency of reinforcement was much greater than that of the blends.

A presentation based on this work was given at the 2nd Japan-Korea Joint Symposium on Polymer Science and Technology held at Kyoto, Japan, October 20-22, 1980.





DEPARTMENT OF CHEMISTRY

The Commonwealth of Massachusetts
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Amherst 01003

May 5, 1981

13 MAY Recd

In recent years, our research has been very heavily concerned with a natural polymer, coal, and the interaction with the very complicated system which does include polymeric materials and to which we add other polymeric materials amongst other chemical reagents. The second system is either No. 6 fuel oil or a variety of other oils of various molecular weight and composition. The principal thrust of our work has been in the development of stabilizers for mixtures of coal and oil as fuels for electric power generation but more recently we have been drawn into studies of highly loaded slurries of coal and water for the same purpose. A number of ideas growing out of this work have considerable carry-over to systems of interest to the polymer colloid group. I hope to be able to give some insight into this at the upcoming Gordon Conference on Polymer Colloids. Below are listed two papers (1,2) that were presented at the ACS Meeting in Atlanta and two papers (3,4) that were presented at the Third International Conference on Coal-Oil Mixture Combustion Technology held recently in Orlando. The titles of these papers give some insight into the fruits of our efforts.

1. R. L. Rowell and B. J. Marlow, "The Intrinsic Specific Volume of Pulverized Coal Particles", Abstracts, 181st ACS Meeting, Atlanta, March, 1981.
2. S. R. Vasconcellos and R. L. Rowell, "Microelectrophoretic Investigation of the Influence of Surfactant Structure on the Zeta Potential of Dispersions of Powdered Coal in n-Heptane and Benzene", Abstracts, 181st ACS Meeting, Atlanta, March, 1981.
3. B. J. Marlow and R. L. Rowell, "Stability and Rheology of Coal-Oil Mixtures and Coal-Water Mixtures", Third International Symposium on Coal-Oil Mixture Combustion, Orlando, Florida, April 1-3, 1981.
4. R. L. Rowell, J. J. Kosman, S. K. Batra and T. Tsai, "Stabilization of Coal-Oil Mixtures by Chemical Additives", Third International Symposium on Coal-Oil Mixture Combustion, Orlando, Florida, April 1-3, 1981.

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13C-nmr was chosen as a means of exploring this further and to see whether a "core-shell" structure was being formed by the hydrolytic process. The technique allows one not only to determine relative quantities of various pendant groups and the nature of their closest neighbors, but also to gain information concerning segmental mobilities. We have used polymethyl acrylate (PMA) in all of these experiments. It is rubbery at room temperature, but the reorientational motions are slow compared to the nmr relaxation times. Thus a ¹³C nucleus feels the effects of local magnetic fields in all directions, so that the peak is so broad that it is indistinguishable from background noise. As hydrolysis proceeds the polymer becomes more hydrophilic, and the chain segments move in a faster, solution-like manner. The local magnetic fields become time-averaged, and the ¹³C peak narrows and rises above the noise.

We observe a rudimentary hump at around 178 ppm (corresponding to carbonyl carbon) after ¹³C hydrolysis, indicating a certain degree of solvation of the particle, whether on the surface or uniform is not known. The -COOH and -COOCH₃ carbons are unresolved until ca. 20% hydrolysis has taken place. If reaction from the surface inwards were occurring, this would represent the hydrolysis of very many "monolayers" of polymer, each of which should be highly solvated. In such a case one would expect the peaks to be relatively sharp and well resolved even at low extents of reaction.

A good spectrum is shown in the accompanying figure, corresponding to 32% hydrolysis of the PMA particles. Only 1.5 - 3.0% of the carboxyl groups are found as soluble polymer in the serum. The observed effects are exhibited by polymer attached to the particles. The kinetics are shown in the attached figure: the overall rate of the autocatalyzed hydrolysis remains zero order at 90°C for at least 6 1/2 weeks at which time it is 65% hydrolyzed. The peak areas (normalized to an internal standard) for ester and carboxyl groups change with time in a manner again suggesting that hydrolysis does not occur in a thin shell zone. In that case one would expect the amount of ester to be relatively small and constant with time.

Our tentative conclusion is that the reaction zone constitutes considerably more than a thin shell, i.e. water and protons penetrate rather freely into unhydrolyzed, rubbery PMA. Some of the polymer (near the surface?) becomes highly swollen and plasticized by water only after ca. 15 - 20% hydrolysis. The kinetics remain zero order for extremely long periods of time, after a brief initial period of rapid reaction.

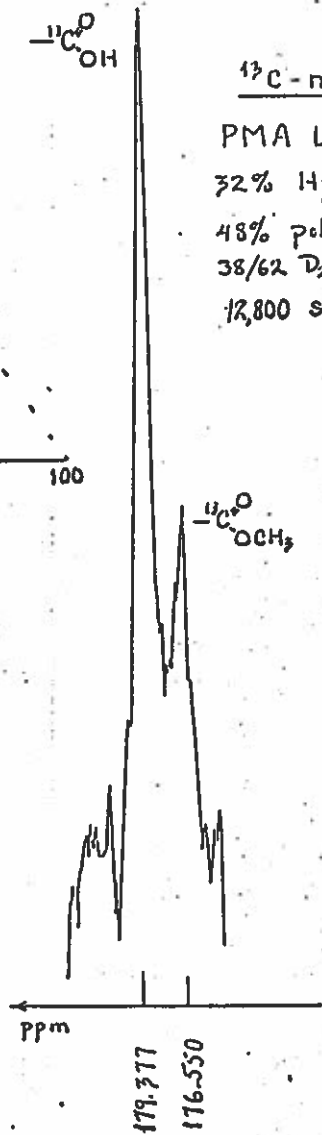
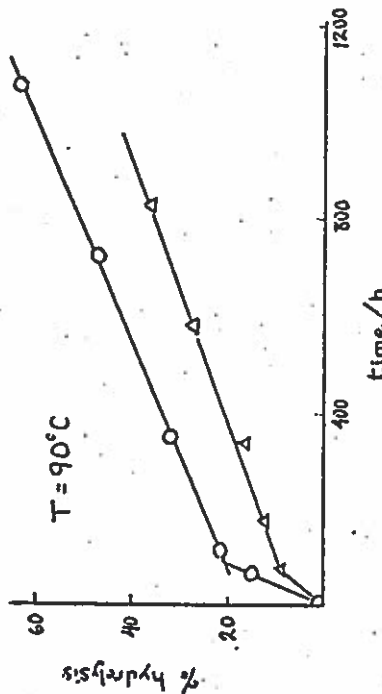
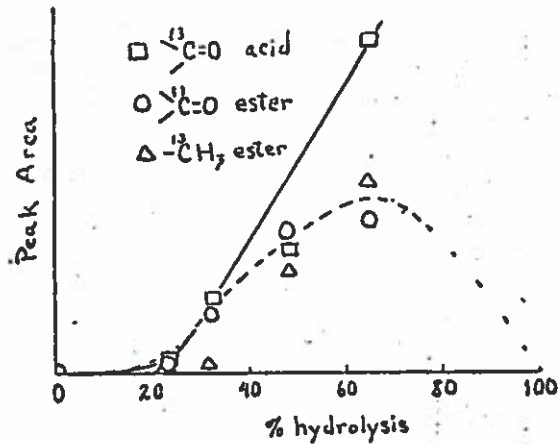
Polymer Colloid Group Newsletter
Contribution from University
of Akron

5 MAY 1964

Reported by I. Piirma

^{13}C -nmr

PMA Latex
32% Hydrolysis
48% polymer in
38/62 $\text{D}_2\text{O}/\text{H}_2\text{O}$
12,800 scans



Our latest investigations have concentrated in a field which one could summarize as: Surfactant effects on the kinetics of emulsion polymerization. Following the unusual results obtained with a non-ionic emulsifier Emulphogene BC-840 (reported at the Las Vegas Emulsion Polymerization Symposium) we are doing some follow-up work with other chemically similar surfactants.

Another group of surfactants under study are polymeric in nature, chemically either random copolymers, graft copolymers or block polymers. It is too early to report anything on the results, since they are rather inconclusive.

A third phase of this study includes polymerizable surfactants, i.e. surface active materials with vinyl endgroups. These materials are, of course, expected to behave like comonomers and provide stability to the latex.

also

A note of interest to all:

The book "Emulsion Polymerization" to be published by Academic Press, Inc. is ready for typesetting. It contains 12 chapters with contributions by our colleagues: Blackley, Dunn, Force, Hamielec, Hansen, Napper, Nomura, Ottewill, Pochlain, Stannett, Ugelstad, Yeliscyeva and including some co-authors. A 13th chapter was planned, but Dr. Vanderhoff has so far not finished the writing of it.

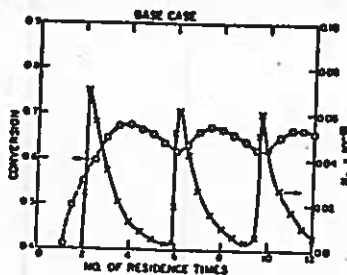


Figure 2a: Conversion and number of particles N_p versus number of residence times for a single CSTR where $\theta = 3600$ secs., $[I] = .01$ mole/L., $[S] = .01$ mole/L

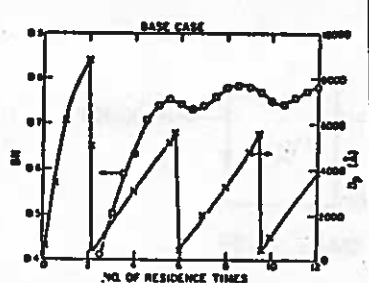


Figure 2b: Average number of branch points per polymer molecule B_n and average particle diameter D_p versus number of residence times for a single CSTR where $\theta = 3600$ secs., $[I] = .01$ mole/L., $[S] = .01$ mole/L.

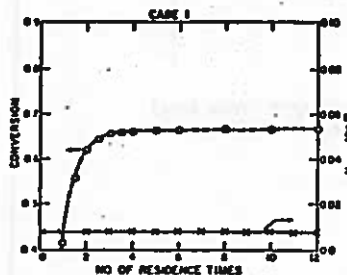


Figure 3a: Conversion and number of particles N_p versus number of residence times for the new configuration where $\theta_1 = 300$ secs., $\theta_2 = 3600$ secs., split = .2, and $[I] = .005$ mole/L., $[S] = .0075$ mole/L in the product.

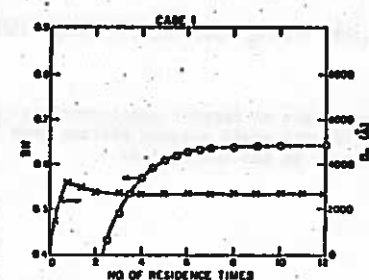


Figure 3b: Average number of branch points B_n and number average particle diameter D_p versus number of residence times for the new configuration where $\theta_1 = 300$ secs., $\theta_2 = 3600$ secs., split = .2, and $[I] = .005$ mole/L., $[S] = .0075$ mole/L in the product.

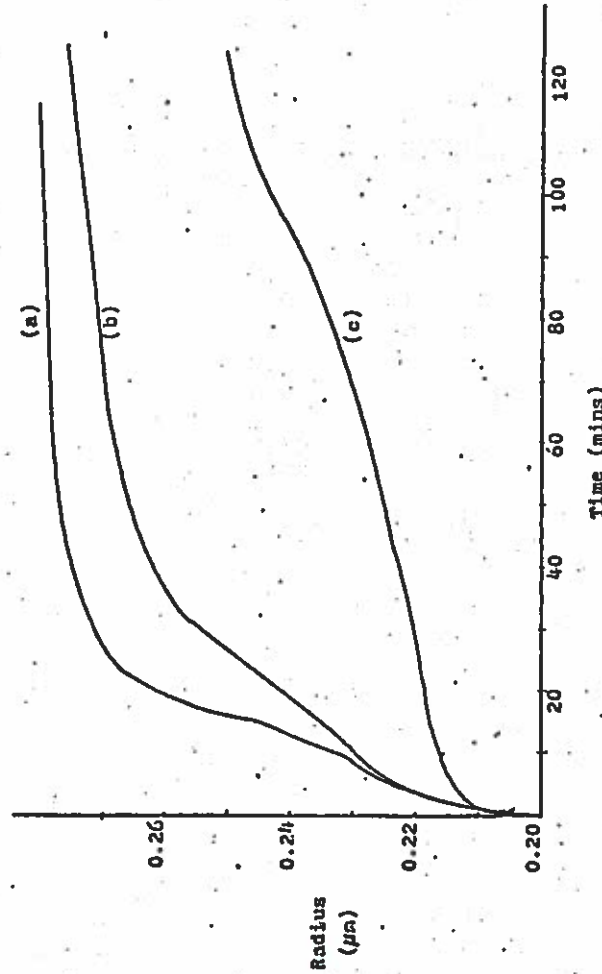
KINETICS OF THE DIFFUSION OF SMALL MOLECULES ACROSS POLYMER MONOLAYERS
 Shu-jan Liang and Robert M. Fitch, Dept. of Chemistry/Institute of Materials Science, The Univ. of Connecticut, U. 136, Storrs CT 06268, USA

A new method for following the diffusion kinetics of small molecules into polymers and liquids involves measurement of the time-dependence of the angular light scattering intensity exhibited by a monodisperse colloid during swelling by the diffusant. The colloidal particles may be comprised of glassy or rubbery polymer or of a liquid. The experiments are conducted at constant external diffusant activity. Characteristically, after the first few minutes the diffusion rate becomes dependent upon the "surface barrier", i.e. the concentration gradient at the interface. When polymers are adsorbed at the interface the diffusion is retarded to an extent which apparently depends upon the chain conformations and the magnitude of polymer-diffusant interactions. Slow changes over periods of several days in conformations in the surface polymer have thus been observed. Comparison of these light scattering results have been made with those obtained by ultracentrifugation and quasi-elastic light scattering.

(See attached figures)

CHEMICAL REACTIONS AT THE INTERFACE IN POLYSTYRENE COLLOIDS. R.M. Fitch
 Dept. of Chemistry, The Univ. of Connecticut, Storrs, CT. 06268, USA
 and Prakash K. Mallya, Polysar Corp., Sarnia, Ontario, Canada.

Polymer colloids bearing chemically functional groups at the surface of the particles may act as heterogeneous catalysts or as chemical reagents. They have the advantages of high specific surface area, sphericity of the particles, extremely narrow particle size distributions and a high degree of control in their synthesis: glassy or rubbery polymer particles may be formed with $-COOH$, $-SO_3H$, $-OSO_3H$, $-OH$, or $-NR_2^+X^-$ groups at various average surface spacings. An example of heterogeneous catalysis will be given in which the hydrolysis of sucrose is studied in the presence of polystyrene colloids bearing surface sulfonate and hydroxyl groups. The second order rate constants are on the order of 50 times higher than those found for the same reaction catalyzed by chemically identical, but physically different ion-exchange resin particles; they were up to 79% greater than the sulfuric-acid catalyzed rate constants. The presence of surface $-OH$ groups had no effect on the rates. It appears that although it is the H^+ counterions which act as the principal catalyst, participation by surface $-SO_3^-$ groups is also involved. Other surface reactions will also be discussed.

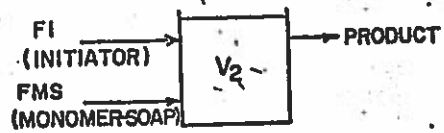


Swelling curves of PS-B2 latex in 3 vol% TIF aqueous solution:

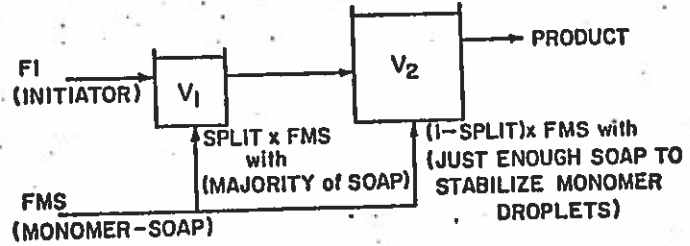
(a) surfactant free, (b) PMA-CEA-I coated and (c) HN-HEC' coated.

* poly(acrylic acid - cetyl/eicosyl acrylate)

† hydrofobically modified hydroxyethyl cellulose



BASE CASE



NEW REACTOR CONFIGURATION.

Figure 1: Comparison of reactor configurations: Single CSTR (Base Case) vs. same size CSTR with small seeding reactor (New Reactor Configuration) showing flow pattern in the two systems.

28 APR Recd

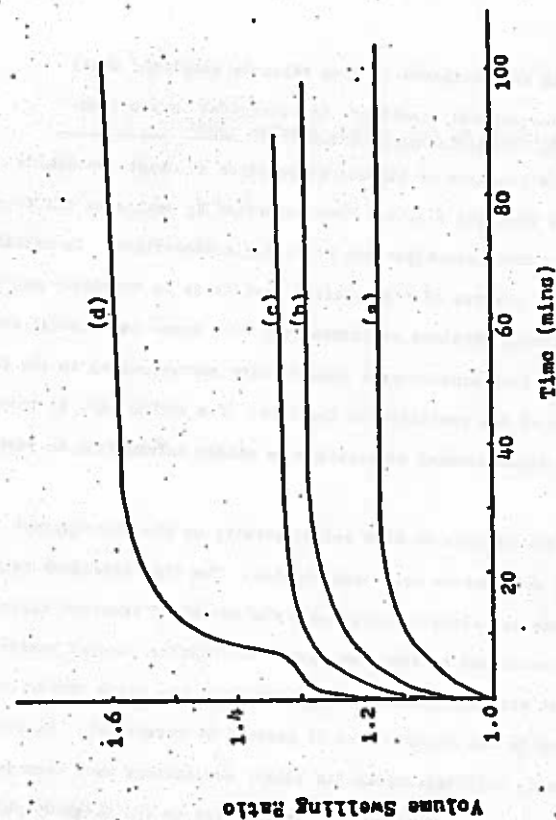
COLLOID RESEARCH AT McMASTER UNIVERSITY - RECENT DEVELOPMENTS.

1) Continuous Emulsion Polymerization of Vinyl Acetate

A dynamic model for molecular weight and branching development in the continuous emulsion polymerization of vinyl acetate has been developed. It has been used to design a continuous reactor train for the production of poly(vinyl acetate) latices which can operate with minimal oscillations. Figures 1, 2 and 3 illustrate the improved stability one can obtain with the use of split flow and a small prereactor for particle nucleation.

The work reported herein was done in collaboration with Dr. J.F. MacGregor and Mr. M. Pollock, McMaster University.

(Contribution to Polymer Colloids Group Newsletter, from Dr. A.E. Hamielec, Department of Chemical Engineering, McMaster University, Hamilton, Ontario, Canada).



Swelling curves of polystyrene latex (PS-P2) in p-dioxane aqueous solutions; volume swelling ratio vs. time for (a) 2 vol%, (b) 8 vol%, (c) 30 vol% and (d) 40 vol%.

S.G. Mason, A.A. Robertson and T.G.H. van de Ven
Pulp and Paper Research Institute of Canada
and
Department of Chemistry, McGill University

The following are abstracts of some recently completed work:

1. Rheo-optical transients in spheroidal suspensions.
(a thesis by G.M. Cerda, October 1980)

The behavior of bimodal suspensions of oblate spheroids undergoing simple shearing flow has been described by analyzing the frequency spectra of orientation-dependent macroscopic properties. In particular, the frequency spectra of rheo-optical transients in turbidity and angular light scattering obtained experimentally from mono- and bimodal suspensions of human and frog erythrocytes showed peaks corresponding to the dominant frequencies of the particles in the flow. The method can, in principle, be applied to multimodal dispersions to obtain information on particle geometry.

The effects of high polydispersity on the rheo-optical transients of sheared suspensions have been studied. The time-dependent behavior of such systems is neither determined by the period of rotation defined by the mean axis ratio nor by the mean period of rotation amongst particles, but by the most probable period of rotation (i.e. the value corresponding to the maximum in the distribution of periods of rotations). Rheo-optical transients in polydisperse kaolin (clay) suspensions have been experimentally obtained. Here the oscillations, in contrast to the slightly polydisperse suspensions studied previously, are highly damped. Frequency spectra obtained from these experiments have peaks near $2/\tau_m$, where τ_m is the most probable period in the ensemble.

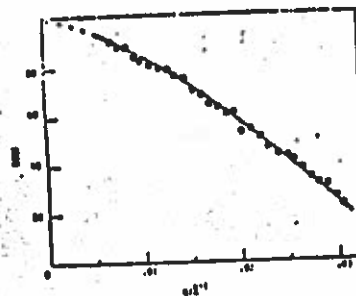


Figure 1: $I(Q)$ vs Q for a poly-deuterostyrene latex (0.12) in 100% D_2O

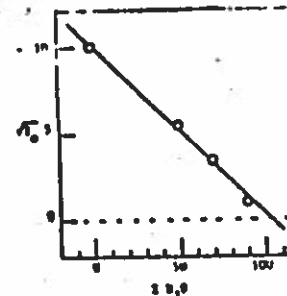


Figure 2: $\sqrt{I_0}$ against ϕ_{D_2O} for a poly-deuterostyrene latex

Observations made in 90% D_2O were interpretable in terms of a scattering shell of hydrogenated material, since the particle was virtually contrasted out under these conditions. The dimensions obtained for the thickness of the shell were of the same order as the value obtained for the apparent thickness of the adsorbed layer by photon correlation spectroscopy. It is possible that the adsorbed layer has a larger spatial extension and contains a very high percentage of solvent. This experiment demands good counting statistics and although the initial objectives were achieved, it needs to be repeated with longer count times.

Interaction between Adsorbed Layers of PVA

The poly-deuterostyrene latex with an adsorbed layer of PVA in 90% D_2O was concentrated to 10% latex by volume using osmotic compression of the latex in a dialysis bag. At this concentration the system formed a stiff gel. The spectrum obtained using D11 with a sample-detector distance of 2.53 m and an incident beam of wavelength 13.78 Å is shown in Fig.3. It is clear that structural peaks are present and since the particles have essentially been contrasted out these must correspond to diffraction from the interacting layers (shells) of adsorbed PVA molecules. It seems possible that at these higher concentrations, the adsorbed layer is less solvated and consequently has a higher contrast in 90% D_2O .

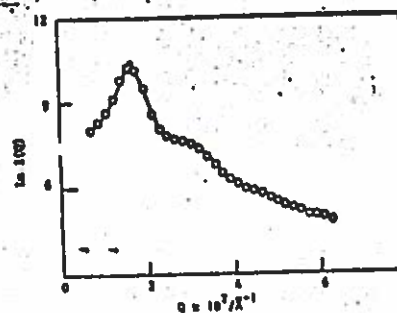


Figure 3: Interacting polydeuterostyrene - PVA system (10% latex). Results obtained in 90% D_2O .

Conclusion

The experiments were successful in establishing the feasibility of carrying out neutron scattering experiments on this type of system. However, some time was lost due to malfunctioning of the air conditioning unit and it is clear that the experiments need long counting times to obtain good statistics.

References

1. Experimental report O7-05-238 I.L.L. 1978.
2. F.W. Cain, R.H. Ottewill and J.B. Smith, Disc. Faraday Soc., 1978, 65, 33.
3. J. Hearn, R.H. Ottewill and J.M. Shaw, Brit. Polymer J., 1970, 2, 116.
4. M.J. Carvey, Th.F. Tadros and B. Vincent, J. Coll. and Interface Sci., 1974, 49, 57.

Theory

From these data $S(Q)$ as a function of Q can be obtained for particles interacting under various conditions ranging from long range electrostatic interactions (soft sphere) to short range steric interactions (hard sphere). Using various models for the interaction computer simulation can be used to obtain $S(Q)$ values for comparison with experimental data.

Conclusion

Small angle neutron scattering shows considerable promise as a means of obtaining information about the modes of interaction between particles in concentrated colloidal dispersions.

2. Adsorption of Polymeric Molecules on Polydeuterostyrene Latices

Introduction

In previous work the adsorption of a deuterated surface active agent (sodium dodecanoate) on to polystyrene latex particles has been examined in some detail. (1) using the contrast variation technique. It was of considerable interest to extend this work to examine the adsorption of water soluble polymers on to the surface of a latex particle. However, since fully deuterated polymers are not readily available whereas polydeuterostyrene is relatively inexpensive, it was decided to reverse the procedure and use polydeuterostyrene latices in combination with a hydrogenated water soluble polymer, a poly-vinylalcohol-poly-vinylacetate copolymer (PVA). The latter material had been used in previous studies on direct measurements of interaction between macroscopic polymer coated surfaces (2).

In the present work the objectives were:-

- a) to characterize the poly-deuterostyrene latex
- b) to examine the adsorption of PVA on a poly-deuterostyrene latex by the contrast variation technique
- c) to concentrate the latex particles with adsorbed layers of PVA to a high volume fraction so that interaction occurred between the adsorbed layers.

The Poly-deuterostyrene Latex

The preparation of a poly-deuterostyrene latex (JCS) containing particles with a very narrow distribution of sizes was successfully accomplished using previously developed methods (3). Examination of this latex using D11, with a sample-detector distance of 10.51 m, and an incident wavelength of 7.0 Å gave the spectra shown in Fig.1 after substitution of background and correction for detector efficiencies. These data, which were obtained with the latex in H_2O , after computer fitting gave a particle diameter of 16.1 nm. This compared with a value of 19.3 nm (Z-average) obtained by photon correlation spectroscopy.

A series of contrast variation experiments with this latex gave the plot of $\sqrt{I_0}$ against D_2O shown in Fig.2. From this plot it can be seen that the contrast match point of a polydeuterostyrene latex is close to 100% D_2O .

Poly-deuterostyrene Latex + an Adsorbed Layer of PVA

Experiments were carried out using a 12 latex containing 3.2 mg cm^{-3} of PVA, a concentration range which it was anticipated from the literature would correspond to a monolayer of PVA on the particles (4). Photon correlation measurements carried out on this sample gave a hydrodynamic diameter of 59 nm thus providing strong evidence that the spatial extension of the PVA molecule from the surface was of the order of 20 nm.

S.A.N.S. experiments under variable contrast conditions gave the following results:
a) in 100% H_2O the particle diameter obtained was close to that of the base particle. This was anticipated since the coherent scattering length of the PVA molecule was close to that of the base particle.

Finally, the influence of the rotary Brownian motion on the rheo-optical transients of sheared spheroidal suspensions is considered by using simulation procedures such as those employed previously to analyze rheological properties and memory loss. The rotary Brownian motion induced two effects: damping of oscillations and a shift in the extreme of the oscillations resulting in variation in the apparent mean period of rotation. Experiments with human erythrocytes at low Brenner number confirmed such behavior. Also a system with strong rotary Brownian motion was observed for which the rheo-optical transients showed monotonic changes.

The observations made in this work contribute to a better understanding of the transient rheo-optical properties of flowing suspensions.

2. Deposition of Brownian particles onto cylindrical collectors. (by Z. Adamczyk and T.G.H. van de Ven, submitted for publication).

A theoretical analysis is presented enabling prediction of particle deposition rates from a dilute suspensions of Brownian particles flowing past an isolated cylindrical collector as well as through a fibrous filter. Complete transport equations, taking rigorously into account specific surface interactions (dispersion and double-layer forces) and external forces (gravity and electrostatic), were solved numerically for a variety of conditions characteristic for suspensions and aerosols. From these solutions the dimensionless mass transfer number (deposition rate) is predicted as a function of dimensionless parameters introduced, characterizing the flow intensity and the colloidal and external force fields. The

numerical calculations predict an appreciable increase in the deposition rate, up to an order of magnitude, when strong attractive double-layer forces are acting between the particle and the collector surface. This effect is especially well pronounced in the region near the forward stagnation point and for larger particles ($\approx 1 \mu\text{m}$ when the Peclet number $Pe > 1$).

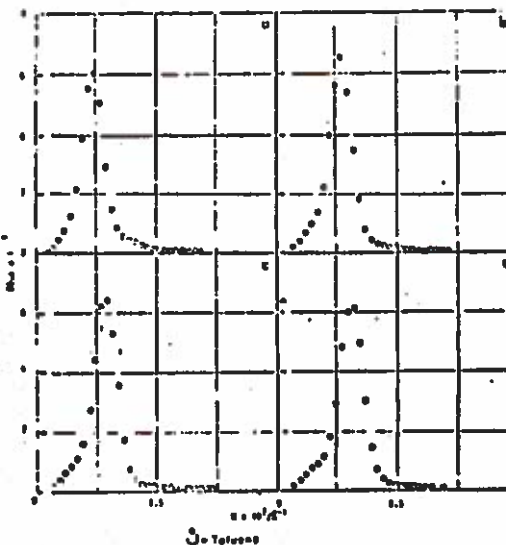


Figure 3
 Ion-exchanged polystyrene lattices at low electrolyte concentrations and volume fractions of H_2O :
 a) 0.11; b) 0.14;
 c) 0.21; d) 0.24.

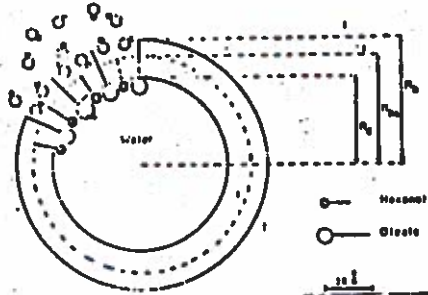


Figure 4
 Schematic diagram of a microemulsion droplet

More concentrated systems of the same type of microemulsion showed evidence of strong interaction and gave a pronounced peak $S(Q)$ whose intensity and position depended on the volume fraction of water in the system. A typical example is shown in Figure 5.

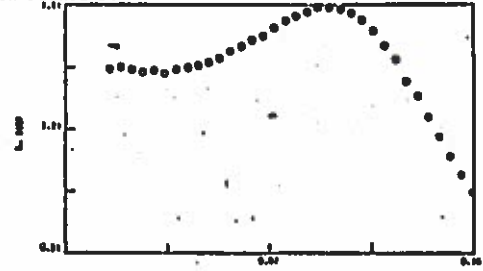


Figure 5
 In $I(Q)$ against Q for a toluene-oleate-hexanol D_2O microemulsion. Volume fraction of $\text{D}_2\text{O} = 0.23$.

These data were obtained on D17 using a sample-detector distance of 1.41 m at $\theta = 2^\circ$ with an incident neutron beam wavelength of 12.2 \AA , thus giving a Q range of 0.01 \AA^{-1} to 0.14 \AA^{-1} .

Kinetics of Emulsion Polymerization

Re-entry

We have continued our studies on the seeded emulsion polymerization of styrene in order to establish the role of re-entry of free radicals in these systems. It is possible by using relatively small particle sizes to increase the importance of exit processes. By varying the number of seed particles in the system, the role of re-entry can be studied. The results appear to be quite conclusive that complete re-entry of free radicals does not occur with styrene. In some systems, the results suggest that the cross-termination of exited free radicals with free radicals generated in the aqueous phase via the initiator is almost complete. This is in accord with the known rapidity of heterotermination reactions compared with homotermination reactions. In other systems, however, both re-entry and heterotermination in the aqueous phase appear to occur.

Polymerization of Miniemulsions

We have performed kinetic studies on emulsions of the type developed by Ugelstad and co-workers that display droplet polymerization. We have confirmed that, under suitable conditions, their conclusion that the locus of polymerization is primarily the droplets, is correct. The radical capture efficiency by droplets, however, appears to be significantly less than the corresponding value for particles, leading to a significant reduction in the rate of polymerization compared

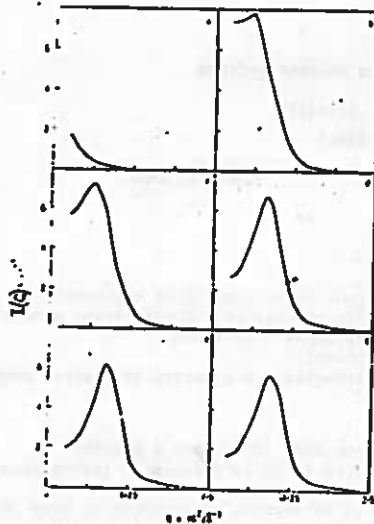


Figure 1

$I(Q)$ against Q for PDDA latices stabilised by PHS chains in dodecane at various core volume fractions:-
 a) 0.01; b) 0.20; c) 0.25; d) 0.32;
 e) 0.39; f) 0.45.

- 24

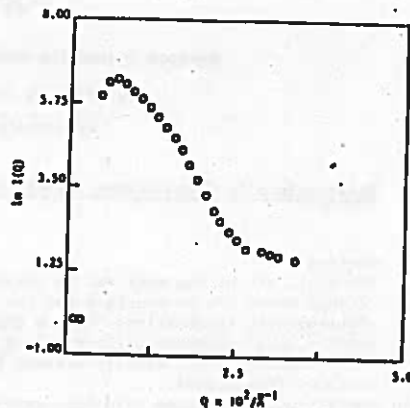


Figure 2

$\ln I(Q)$ against Q for a polystyrene latex at a volume fraction of 0.01 in 10^{-3} mol dm⁻³ sodium chloride solution.

In this type of system addition of ion-exchange resin to the system lowers the electrolyte concentration to a very low value ($\sim 10^{-5}$ mol dm⁻³) and the strong electrostatic repulsion between the particles causes the particles to form into an ordered array which behaves as a Bragg diffracting lattice. This is illustrated in figure 3.

These results were obtained on D11 using a sample detector distance of 10.53 m and an incident neutron beam of wavelength of 4.90 Å. Results over a more extended range of Q were obtained on D17.

Data of this type on such concentrated colloidal dispersions would be quite impossible to obtain by any other technique.

Microemulsions

Before commencing the study of interactions between microemulsion droplets of water in toluene stabilised by sodium oleate and hexanol, preliminary studies were carried out on the structure of the microemulsions by examining the small angle scattering of the systems made with D₂O and then with D-toluene. These studies confirmed that the structure of the microemulsion droplet was that shown in Figure 4.

with seeded systems. This may well be associated with the different extents of solvation of the hydrophobic tail in the two cases, making replacement of a surfactant molecule in the droplet by an oligomeric free radical more difficult.

Neutron Scattering Studies on Polymer Latices

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113 OCT 1980

1. Interactions in Concentrated Dispersions

Introduction

The basic aim of the work was to obtain a deeper understanding of the types of interactions which are responsible for the stability of colloidal dispersions, namely:-

- i) electrostatic interactions between charged particles (repulsive),
- ii) van der Waals dispersive interactions (attractive),
- iii) steric interactions, usually arising from macromolecules adsorbed or grafted onto surfaces (repulsive).

Four basic types of systems have been examined:-

- a) polymer latices, with a poly methylmethacrylate core (PMMA) and a grafted stabilising layer of poly-12-hydroxystearic acid (PHS) in dodecane - interaction by a steric mechanism,
- b) polystyrene latices, with charged particles in an aqueous environment at very low salt concentrations - interaction by an electrostatic mechanism,
- c) polystyrene latices, with an adsorbed layer of polyvinylalcohol in an aqueous environment - interaction by a steric mechanism,
- d) micemulsions of water in toluene and dodecane, stabilised by a mixed adsorbent layer of oleate ions and hexanol.

In the interaction mode the intensity of scattering $I(Q)$ is given by,

$$I(Q) = \text{Const.} \cdot \phi \cdot P(Q) \cdot S(Q)$$

where $P(Q)$ = the particle scattering factor, $S(Q)$ = the structure factor and ϕ = the volume fraction. An examination at low volume fractions for the latex particles gives the form of $P(Q)$ and since ϕ is known then,

$$S(Q) = \frac{I(Q)}{\text{Const.} \cdot \phi \cdot P(Q)}$$

PMMA Latices

Figure 1 shows the results obtained on a PMMA latex in dodecane, with a mean particle core diameter of 65 nm, at a series of volume fractions. These data were obtained using D11 at a sample-detector distance of 10.53 m using an incident beam of wavelength 0.80 Å. Figure 1a was obtained using a very dilute latex [$\phi = 0.01$] so that the latex was in a non-interactive situation. Figures 1b to 1f were obtained over the volume fraction range 0.20 to 0.45. At 0.20 an $S(Q)$ effect can be clearly seen and as the volume fraction increases the $S(Q)$ peak becomes dominant.

Polystyrene Latices

These experiments were carried out using a latex with a number average particle diameter of 440 Å as determined by electron microscopy. Figure 2 shows the plot of $\ln I(Q)$ against Q obtained with this latex at a volume fraction of 0.01 in 10^{-2} mol dm⁻³ sodium chloride solution. These conditions were utilised in order to obtain the form of $P(Q)$ for this latex. A Guinier analysis of the data using a computer fitting procedure gave a mean particle diameter of 351 Å.