

Despite a number of substantial contributions from a number of members this is a rather thin issue again despite being bulked out by a couple of contributions which missed the deadline for the Spring issue and are unfortunately no longer such hot news as when they were written. Those who were at Miami Beach were supposed to remind each other to send off their contributions directly they got back but they seem to have failed to do so! Vivian Stannett has excused himself on the ground that he has no students working in this area at present: this is'nt really a good enough excuse because it is still possible to think about the topic! However he signs his letter as Dean which no doubt explains the lack of thoughts! Although this saves on postage and reproduction costs, members really must try to do better for the next issue: the deadline will be for copy to reach Manchester on or before Monday, 23rd April 1979.

The Abstracts of the Miami Beach Symposium papers appear in 'Polymer Preprints' as well as in the Abstracts of the Meeting. The papers are to be published by Plenum Press and the intention is that the book should appear by mid-March which will be very creditable if this schedule can be maintained.

The next meeting which is likely to be of interest to members is the International Polymer Latex Conference organised by the Plastics and Rubber Institute (11 Hobart Place, London SW1W 0HL) to be held in London 31 October, 1 and 2 November 1978. David Blackley and David Farmer are two of the Organising Committee of five. The contributed papers are being preprinted: authors include Napper, Dunn, Stenius, Ugelstad and Blackley. Plenary lecturers are W. White (Uniroyal, U.S.A.), R.H.Ottewill, E.G.Cockbain, K.O.Calvert, A.A.Feast, and J.W.Vanderhoff.

The 3rd International Conference on Surface and Colloid Science is to be held in Stockholm, 20-25 August 1979. Ottewill and Stenius are on the Scientific Committee and a Symposium on 'Polymer Colloids' under the chairmanship of John Ugelstad and another on Micellar Systems under the chairmanship of Per Stenius are included in the programme. Abstracts of proposed papers are required by 1st December, 1978. Further information from The Swedish Institute for Surface Chemistry, c/o Stockholm Convention Bureau, Strandvägen 7C, S-114 56 Stockholm, Sweden.

The Proceedings of the 50th Colloid and Surface Science Symposium held in Puerto Rico, 21-25 June 1976 have now been published (in 5 volumes!) by the Academic Press, New York. Volume 1 containing the Plenary and Invited Lectures also appeared in the Journal of Colloid and Interface Science 58 (1977). Included are the following papers by Group members.

S.G.Mason 'Orthokinetic Phenomena in Disperse Systems'	Vol. I p.293
R.H.Ottewill 'Stability and Instability in Disperse Systems'	Vol. I p.379
D.H.Napper 'Steric Stabilization'	Vol.I p.413
P.J.Stenius, J.B.Rosenholm, & M.R.Hakala 'Enthalpies of Lyotropic Liquid Crystalline Phases'	Vol II, p.397
R.M.Fitch & C. Gajira 'Polymer Colloids as Heterogeneous Catalysts'	Vol. III p.273
R.L.Rowell & R.S.Farinato 'New Values of the Light Scattering Intensity, Depolarization Ratio, and Anisotropy of Water'	Vol.III, p.545
D.B.Hough & R.H.Ottewill 'The Direct Measurement of Electrostatic Surface Forces'	Vol.IV, p.45
J.C.Brown, J.W.Goodwin, R.H.Ottewill, & P.N.Pusey 'The Determination of the Radial Distribution Function for Interacting Latex Particles'	Vol.IV, p.59
F.J.Micale, P.H.Krumrine, & J.W.Vanderhoff 'Electrophoretic Mobility Measurements by Continuous Particle Electrophoresis'	Vol.IV p.247
R.O.James & A.Homola 'Heterocoagulation of Amphoteric Latexes'	Vol.IV, p.363
A.J.McHugh, C.Silebi, G.W.Poehlein, & J.W.Vanderhoff 'Hydrodynamic Chromatography of Latex Particles'	Vol.IV, p.549

EFFECT OF POTASSIUM FATTY-ACID SOAPS UPON MECHANICAL STABILITY OF NATURAL RUBBER LATEX

27 SEP 1978

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It is well known that the mechanical stability of natural rubber latex is greatly enhanced by the addition of small amounts of water-soluble fatty-acid soaps. For example⁽¹⁾, the addition of as little as 0.3% of potassium laurate on the rubber can bring about an approximately 12-fold increase in mechanical stability.

Rather surprisingly, little published information seems to be available concerning the joint effects of both the level of the added fatty-acid soap and the chain length of the soap upon the stability of natural rubber latex. Almost the only published results pertaining to these matters seem to be those given by Cockbain and Philpott⁽²⁾ for the effect of the alkyl chain length of various straight-chain alkanoate soaps (octanoate to stearate) upon the mechanical stability of natural rubber latex at three molal levels of addition. The curves given by Cockbain and Philpott confirm that the amounts of fatty-acid soap which are required to increase the mechanical stability of natural rubber latex substantially are often very small. They also show that the molal effectiveness of the potassium fatty-acid soaps in enhancing the mechanical stability of natural rubber latex passes through a sharp maximum as the alkyl chain length of the soap is increased. The published curves suggest that the most effective soap is potassium decanoate, although they also show that potassium laurate is very effective in increasing the mechanical stability.

Cockbain and Philpott make little comment about the results they publish. In particular, they do not discuss the interesting effects of chain length of soap which are evident from their results. They do, however, draw attention to the very small amounts of added soap which are sometimes sufficient to produce a large effect upon the mechanical stability of natural rubber latex. Thus their results show that the mechanical stability of their latex was approximately doubled by the addition of as little as 0.1 millimole of potassium decanoate per 100 g. of latex solids. Assuming the molecular adsorption area of a fatty-acid soap anion to be 50\AA^2 , and also that the specific surface area of the latex was $10^5 \text{ cm}^2 \text{ g}^{-1}$, Cockbain and Philpott calculate that this amount of added soap would, even if wholly adsorbed, cover less than 5% of the surface area of the latex particles.

We have recently re-investigated in some detail the effects of added potassium fatty-acid soaps upon the mechanical stability of a high-ammonia centrifuged natural rubber latex concentrate. Mechanical stabilities were determined at 35°C and 55% total solids content using a conventional Klaxon mechanical stability test apparatus. The test was carried out according to the procedure specified in BS 1672:1972. The soaps used were potassium hexanoate, octanoate, decanoate, laurate, myristate, palmitate, and stearate. In order to give some opportunity for adsorption to be attained, the latex samples were allowed to mature for about three days at room temperature before determining their mechanical stabilities.

The results are summarised in Figs. 1 and 2. In Fig.1, the level of added soap is expressed in moles per 100 grams of latex solids. In Fig. 2, the level of added soap is expressed as parts by weight per 100 parts of latex solids. In order to avoid confusion from the multiplicity of experimental points, Fig. 2 has been split into two parts: part (a) gives the results for the hexanoate, octanoate, decanoate and laurate soaps; part (b) gives the results for the remaining three soaps, with the results for the laurate soap repeated in order to facilitate comparison. In general, our results agree well with those of Cockbain and Philpott. Both sets of results show that large enhancements of mechanical stability can be brought about by small additions of certain fatty-acid soaps, and that, as the alkyl chain length of the soap is increased, so the effectiveness of the soap on a molecular basis passes through a maximum. The two sets of results differ in that, whereas those of

Cockbain and Philpott indicate that the maximum molecular efficiency is attained when the alkyl chain of the soap contains 9 carbon atoms, our results suggest that the maximum efficiency is attained with an alkyl chain containing 11 carbon atoms. However, from neither set of results can exact conclusions be drawn concerning the optimum alkyl chain length of the soap, since in neither case were results obtained for soaps which contain even numbers of carbon atoms in their alkyl chains. A further point of difference between the two sets of results is that, whereas those of Cockbain and Philpott suggest that soaps which contain 13, 15 or 17 carbon atoms in their alkyl chain have almost the same effect upon mechanical stability as does that which contains 7 carbon atoms, our results indicate that soaps which contain 13, 15 or 17 carbon atoms in their alkyl chain are significantly more effective than are those which contain 5 or 7 carbon atoms. We have also investigated the ability of potassium fatty-acid soaps to enhance the stability of natural rubber latex which has been chemically destabilised by (a) addition of potassium chloride, (b) addition of acetic acid, and (c) de-ammoniation to pH 8.5 by aeration. Again, the effect upon stability was assessed by means of the mechanical stability test. We have found that in each case the addition of fatty-acid soap brings about an increase in stability, and in each case the effect is at its optimum when the fatty-acid contains 9 or 11 carbon atoms in its alkyl chain.

Our results, and those of Cockbain and Philpott, present two obvious features for explanation: (1) large increases in mechanical stability can accompany relatively small additions of soap; and (2) the enhancement of mechanical stability passes through a maximum as the alkyl chain length of the soap is increased. Our present view is that the principal effect of the added fatty-acid soap is to mix with the fatty-acid soap anions which are already present in ammonia-preserved natural rubber latex, thereby possibly altering the character of the adsorbed layers present at the rubber-water interface. If, as is usually assumed, the fatty-acid soaps which confer stability upon unmodified natural rubber latex contain approximately 17 carbon atoms in their alkyl chains, then it is possible that they exist at the interface as essentially condensed films. It is further possible that, being condensed they are relatively inefficient in protecting the latex against mechanical destabilising influences. The effect of the added fatty-acid soap may therefore be to break up the condensed soap films already present at the rubber-water interface and thereby enhance their effectiveness in protecting the latex against mechanical destabilisation. This hypothesis explains immediately why small additions of soap can bring about large increases in mechanical stability. It also explains the existence of an optimum alkyl chain length for enhancement of mechanical stability. This optimum is seen as arising from the balance of two opposing tendencies as the alkyl chain length of the added soap is increased, namely, (a) increased tendency to be adsorbed at the rubber-water interface, and (b) a diminishing ability to break up condensed films of adsorbed soap already present at the rubber-water interface.

References

1. E. W. Madge, H. M. Collier and I. H. Duckworth, *Trans. Instn Rubb. Ind.*, 1952, 28, 15
2. E. G. Cockbain and M. W. Philpott, "Colloidal properties of latex", in "The Chemistry and Physics of Rubber-like Substances", ed. L. Bateman, Maclaren, London, 1963

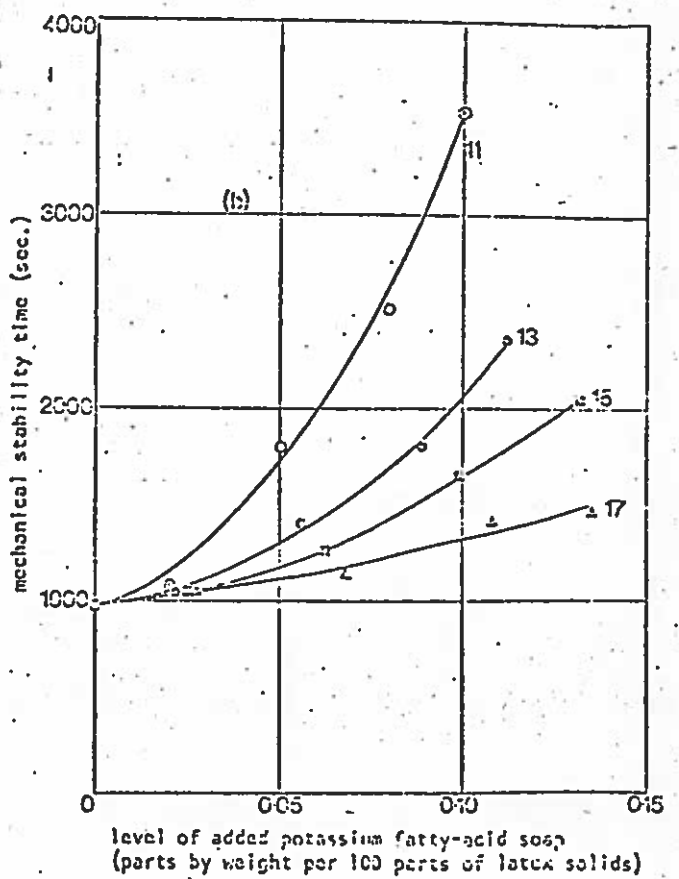
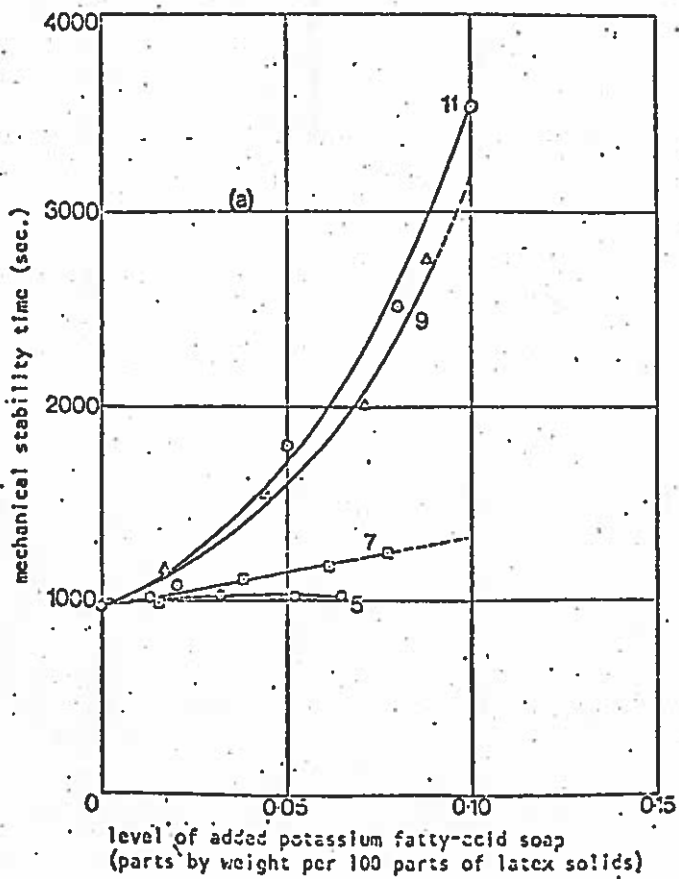
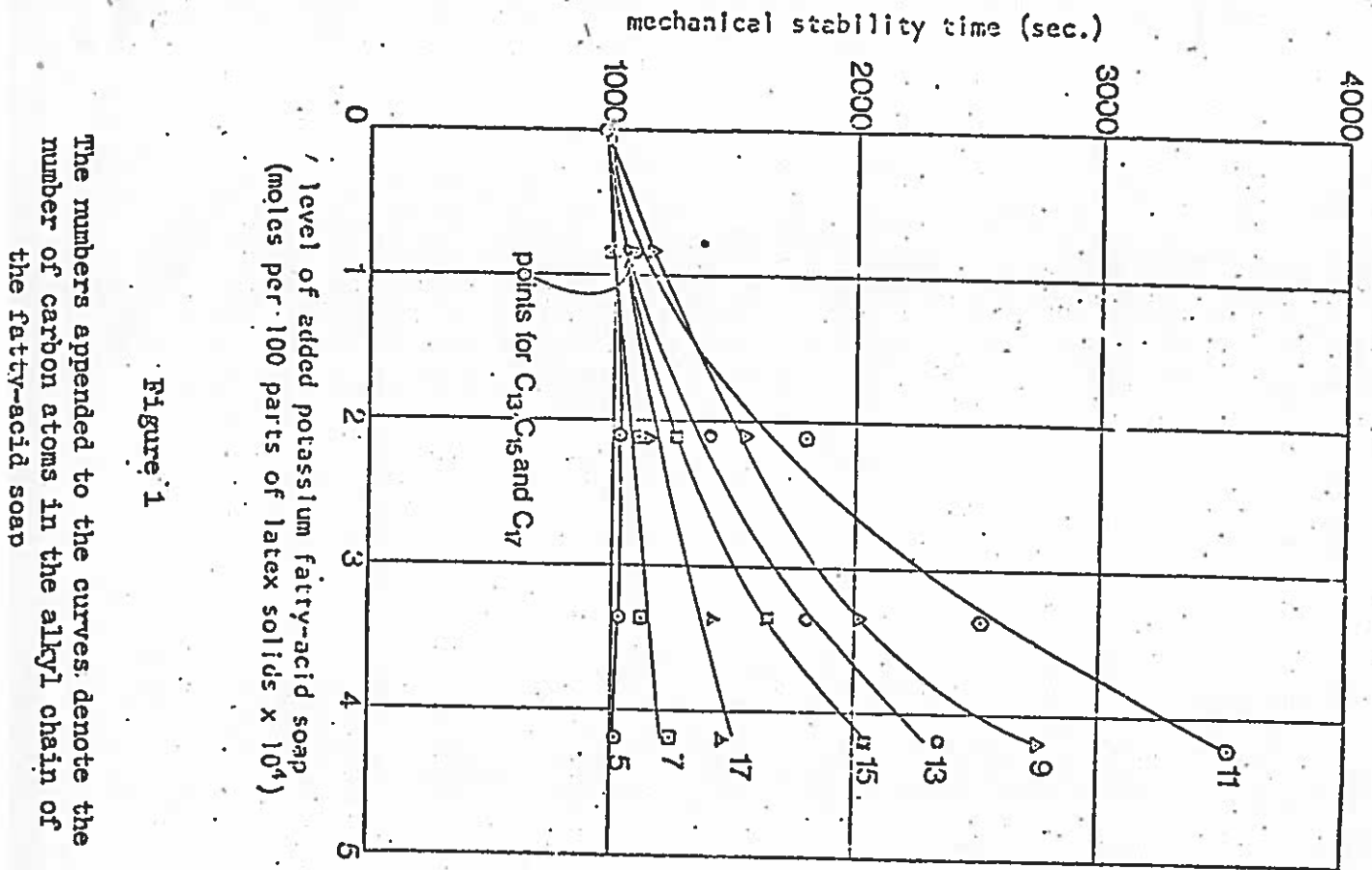


Figure 2



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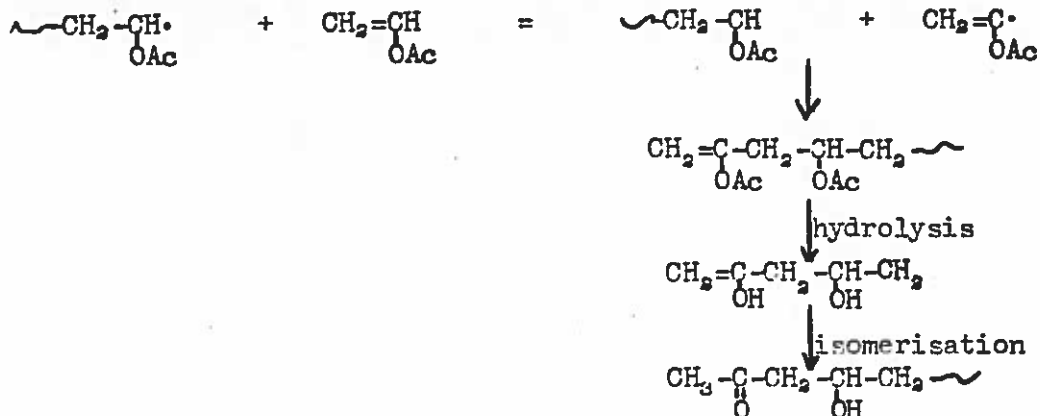
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Mr S. R. Naravane is now preparing his Ph.D. Thesis. He has been ultimately successful in obtaining a Post-doctoral Fellowship in the Department of Pure and Applied Chemistry of the University of Strathclyde with Professor J. N. Sherwood for work on the effect of impurities on the morphology of organic crystals. He would have preferred to stay in polymer chemistry but unfortunately none of the polymer groups seemed to be able to fund an appointment at this time.

Naravane's work on the application of ^{13}C n.m.r. spectroscopy to the analysis of the structural differences between different preparations of similar grades of polyvinyl alcohol has produced some very interesting developments. We obtained two samples, one a sample of Goshenol GH-17 and the other an ostensibly similar grade from another manufacturer which had been found to give an entirely different latex viscosity (8900 c.P. instead of 16 300 c.P.) when substituted for the Goshenol sample in a standard vinyl acetate polymerisation recipe. The samples had the same D.T.A. melting point so that they did not differ in the average size of the residual acetyl blocks. Infra-red spectra and X-ray powder diffraction photographs also appeared identical. The u.v. absorption spectra (which arise from conjugated unsaturated ketonic structures) did differ somewhat but it was difficult to see what connection there could be between this and the observed difference in the properties of the polyvinyl acetate latices prepared using the samples. The fine structure (attributable to tacticity) of the ^{13}C n.m.r. spectrum also was identical: however the ratio of the intensities of the CH and CH_2 peaks (which would be expected to be 1:1) did differ and was not 1:1 in either case. Moreover the intensity of the C=O resonance appeared to indicate a carbonyl content twice as large as attributable to the acetyl content. The explanation seems to be that the samples differ in the extent of long-chain branching and that chain transfer in the vinyl acetate polymerisation produces end-groups which isomerise to form carbonyl groups on hydrolysis. There is a well-known sequence of polymer-analogous reactions in which polyvinyl acetate is completely hydrolysed and the resulting polyvinyl alcohol reacylated. The molecular weight falls in the first cycle but subsequently remains constant demonstrating the presence of hydrolysable branches attached through acetyl groups in the original sample. We understood that the polyvinyl alcohol obtained was substantially linear but this belief does not seem to have any actual evidence to support it! On the contrary evidence has been published recently which shows that extensive non-hydrolysable branching also occurs by transfer to C-H and CH_2 bonds as well as CH_3 bonds.

Nozakura, Morishima, and Murahashi (J. Polym. Sci. A-1, 10 (1972) 2781) polymerised ^{14}C labelled vinyl acetate in the presence of unlabelled polyvinyl acetate which was cross-linked with polyurethane bonds: homopolymer could easily be separated from the cross-linked graft polymer which could then be solubilised by quantitative cleavage of the urethane links with hydrobromic acid. They found that non-hydrolysable branches are formed 2.4 times as frequently as hydrolysable branches at 60 °C and 4.8 times as frequently at 0 °C.

Although these authors argue that transfer to monomer is largely to the primary hydrogens of the acetyl group, one might have expected on the basis of the general principles of free-radical chemistry that transfer to the tertiary hydrogen of the methine group would be predominant.



Since chain transfer is the dominant method of polymer chain termination in the vinyl acetate polymerisation a significant concentration of isolated ketone end-groups might be anticipated. Although the ketone group may induce dehydration of adjacent vinyl acetate residues, quantitative estimation of the concentration of mono- and diene ketones from the u.v. spectra indicates that this is normally a comparatively minor effect. Unfortunately the relaxation time of carbonyl carbon atoms is too long compared with the pulse delay time used to obtain the ^{13}C n.m.r. spectra for the determination of carbonyl content from these spectra to be reliable. On the other hand a standard chemical procedure tried proved to be insufficiently sensitive to determine the low concentration of carbonyl groups involved. A determination of the carbonyl content (excluding that of the residual acetyl groups) would give a lower limit of the number of branches per polymer molecule provided the occurrence of oxidation can be excluded.

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Effect of Homologous Series of Alkyl Sulfate Surfactants on the Emulsion Polymerization of Styrene. I. Equal Total Concentrations

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Synopsis

There is evidence in the literature that the rates of emulsion polymerization increase by a large factor as the alkyl chain length increases for a homologous series of surfactants. However, the area occupied by a surfactant molecule in a saturated monolayer at the polystyrene/water interface is independent of chain length for alkyl sulfates so that, on the basis of Gardon's theory, equal rates of polymerization would be expected when equal concentrations of surfactants are used. There is a large increase in the number of polymer latex particles formed and in the rate of emulsion polymerization as the surfactant concentration is increased through the critical micelle concentration; this accounts for the large increases reported, because the lower members of the homologous series are below their critical micelle concentrations in most of the published studies. When a common concentration is chosen that is above the critical micelle concentration even for the lowest member of the series, only a relatively small increase in latex particle number and rate of emulsion polymerization with alkyl chain length of the surfactant is observed. This is attributable to an increase in the concentration of surfactant micelles. Good agreement with Gardon's theory is obtained when the concentration of micellar surfactant is used instead of the total surfactant concentration.

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On the Applicability of Gardon's Equations for the Calculation of Particle Size in Emulsion Polymerisation*

Alexander S. Dunn and Walid A. G. R. Al-Shahib

Gardon's revision of the Smith-Ewart theory of emulsion polymerisation makes it possible to calculate the average particle size of the latex produced from the conditions used for the polymerisation at least for monomers with a low monomer transfer constant. Good agreement has been found between the calculated particle sizes and the turbidity averages measured by light scattering for polystyrene latices prepared with various emulsifiers. However the theory neglects the effect of the ionic strength of the aqueous phase although Gardon's own results show this to be a significant parameter: increase of ionic strength increases the average size of the latex particles by reducing electrostatic stabilisation. The difference between the total and the micellar surfactant concentration is significant for surfactants with relatively high critical micelle concentrations and a considerable improvement in agreement between measured and calculated particle sizes is found when the concentration of micellar surfactant is used in the calculation. The theory requires the reaction rate to depend on the $3/5$ th power of the concentration of micellar surfactant and although this would appear to have been satisfactorily verified experimentally, replotting of the extensive series of precise results published by Bartholome, Gerrens, Herbeck and Weitz shows that the double logarithmic plot is not actually linear. This is probably the result of a slow change of micelle size as the surfactant concentration is increased.

* Presented at the SCI Plastics and Polymer Group Symposium on 'Control of Particle Size in Emulsion Polymerisation' in London on 23 November 1976.

24 MAY 1978
Postmarked 18 May
May 10, 1978

Newsletter Contribution

Further work has been carried out on the sulfonation of Polyvinyl benzyl chloride (PVBC) latex, to produce high levels of surface charge density. Infra-red spectroscopy on the supernatant fluid after centrifuging shows the presence of appreciable quantities of polyelectrolyte. This indicates that high extents of sulfonation cause the detachment of polysulfonate chains. Since this polyelectrolyte is not removed during ion exchange, its sulfonic acid groups contribute to the strong acid titer of the latex. High surface charge densities reported in a preprint are due in large part to the detached polyelectrolyte.

Attempts were made to prepare crosslinked PVBC, and to subject the latex to milder sulfonation conditions, in order to produce latices with high surface charge densities which are free of polyelectrolyte contaminant. Uniform PVBC latices were produced incorporating 2 to 9% divinylbenzene as crosslinking agent. Electron-microscopic examination of the latex showed no change in particle size as a result of sulfonation. Sulfonation at 55°C with a 1:4 ratio of surface Cl to SO_3^- gave surface charge densities of ca. 2×10^{-3} charges/ A^2 after washing and centrifuging. Results to date indicate that it is possible, by mild sulfonation of crosslinked PVBC latex, to augment the surface charge substantially while producing moderate amounts of polyelectrolyte. It appears feasible to remove this polyelectrolyte either by repeated centrifuging and washing, or by the Nucleopore filtration technique recommended by the Lehigh group.

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PSEUDO EMULSION POLYMERIZATION*

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* This paper is being submitted for publication prior to the ACS Meeting Introduction to be held in Honolulu in April 1979.

Redox polymerization techniques are well known in the field of emulsion polymerization technology, but the elucidation of mechanism is scarce in the literature. In this paper, we will describe PEP (Pseudo Emulsion Polymerization) latices of high acid containing termonomer systems, using a fast redox initiator. The feature difference between conventional and PEP emulsion polymerization mechanism is in the main locus of propagation. In the first case, it occurs in the monomer swollen polymer particle, and in the latter, data support water phase polymerization followed by particle formation via homogeneous nucleation. Homogeneous nucleation may well be the mechanism for particle formation for many relatively water soluble monomers, but it stops for most systems between 10-30% conversion, after which polymerization takes place predominantly in the particles (1, 2, 3). In the PEP system, water phase polymerization predominates throughout the reaction, homogeneous nucleation is proposed for particle formation mechanism and the monomer swollen particles serve only as monomer reservoirs.

The PEP latices when neutralized form polyelectrolytes. They belong to the technologically significant class of polymers generally used as thickeners for practical latex coatings. Latex thickening is not just an enhancement of the water phase viscosity, but has been postulated as being due to network formation between particles by the polyelectrolyte molecules (4). When the stand-off distance between particles is less than the length of the expanded water soluble molecule, and there is free surface for adsorption, then linkage occurs (5). It is shown in this paper that styrene-butadiene latex thickening is dependent on the termonomers used for the PEP. The termonomers, depending upon their reactivity with methacrylic acid, regulate the vicinal acid placements in the backbone and, therefore, also vary the length of the expanded polyelectrolyte molecule. The ability to thicken a given latex is correlated with intrinsic viscosities and the computer generated probabilities for vicinal acid block formation. It is hypothesized that the electrostatic component of chain extension is affected (reduced) by ion binding and that ion binding increases with vicinal acid placements in the polymer backbone.

Experimental

Terpolymers of the following composition by weight: 66/28/6 methacrylic acid/ethyl acrylate/termonomer, were prepared in a 3 liter resin kettle, equipped with mechanical stirrer, reflux condenser, thermometer and gas inlet tube. Under a blanket of nitrogen, the ingredients of the reaction were charged with agitation in the following order:

- 1626.6 g distilled water
- 2.475 g sodium dodecyl benzene sulfonate, (Siponate DS-10) from Alcolac, Inc.
- 7.4 g n-butanol
- 325.7 g methacrylic acid
- 138.1 g ethyl acrylate
- 29.6 g termonomer
- 0.016 g divinyl benzene (60%)
- 1.97 g of a 10% ammonium persulfate solution from E. M. Sargent Chemical Co.
- 3.29 g of a 0.1% ferrous sulfate solution from J.T.Baker Chemical Co.

After all the above ingredients were introduced and well dispersed,

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2.46 g of a 10% freshly prepared sodium hydrosulfite solution (Lykopen from Rohm and Haas) was introduced. The reaction was started at 20°C and generally between 12 minutes to 360 minutes the temperature peaked, indicating the completion of the reaction.

Thickening experiments used a carboxylated styrene-butadiene latex. The surface average particle diameter was $0.17\mu^2$ and the carboxyl surface charge density was 8.5×10^{-10} mol of COOH/cm. The latex characterization was carried out by electron photomicroscopy and the surface charge density measurements followed the techniques of Vanderhoff (6). The latex was commercially available as GAF 1400 at 50% solids.

The PEP thickened latex was measured with an LVF Brookfield viscometer using Spindle No. 4 at 12 rpm. In each case, the PEP/styrene-butadiene weight ratio was 1:100 and total solids concentration was 36%. The measurements were carried out at pH 7 using ammonia neutralization. The viscosity measurements were found to be reproducible to ± 100 cp.

Intrinsic viscosities were determined in 0.2M sodium chloride solution of ammonia neutralized PEP. The method is described elsewhere (7).

Results and Discussion

The types of termonomers investigated with the corresponding Alfrey-Price Q and e reactivity parameters, reaction rates, intrinsic viscosities and latex viscosities are shown below:

METHACRYLIC ACID-ETHYL ACRYLATE-TERMONOMER SYSTEMS

<u>Termonomer</u>	<u>Termonomer</u>		<u>Intrinsic Viscosity</u>	<u>Brookfield Visc., cp</u>	<u>Reaction Rate % Conv/min.</u>
	<u>Q-Value</u>	<u>e-Value</u>			
Styrene	1.0	-0.8	12.7	18,600	5.0
Acrylamide	1.12	1.19	13.9	14,000	3.3
Acrylonitrile	0.60	1.2	13.4	11,750	2.2
n-Butyl vinyl ether	0.087	-1.2	11.9	9,900	8.3
Isobutyl vinyl ether	0.023	-1.77	12.0	8,200	5.6
Vinylpyrrolidone	0.14	-1.14	12.0	6,950	0.3
Diethyl maleate	0.059	1.49	14.7	6,800	3.0
Mono ethyl hexyl maleate	0.05	1.5	14.0	5,800	5.0
Triethoxyvinylsilane	0.023	0.04	5.0	3,600	2.5
Vinyl acetate	0.028	-0.22	9.2	3,430	3.7

The large variation in reaction rates based on the relatively small amount of termonomers was surprising. Taking the acrylamide containing termonomer system, it was found that the reaction rate was proportional to the -0.3 power of the surfactant concentration. The decrease in reaction rate with increasing anionic surfactant level has not as yet been reported for emulsion polymers. For mixed surfactant of anionic and non-ionic type, a reduced rate over the anionic surfactant system for vinyl acetate polymerization was found (8). The reduced rate was attributed to decreased free radical diffusion into the particle due to the dense interfacial mixed surfactant film. In order to establish the locus for polymerization, seeded experiments were studied. In Fig. 1, the electron photomicrographs of the seed and seeded particle size distributions are shown. Twenty percent of the formulation solids were replaced by seed in the original recipe. The seed and seeded latex particle size distributions are practically identical, the weight average particle radii are 0.043μ and 0.039μ , respectively. These data indicate that polymerization is not taking place within the particles but must occur in the aqueous phase. This was supported by further evidence that in the presence of hydroquinone, 700 ppm-2000 ppm, the hydroquinone partitions all in the oil phase and polymerization is unaltered, while generally, in conventional emulsion polymerization this dose of free radical scavenger would have short stopped the reaction. All evidence supports water phase polymerization with the implication that the surfactant has an effect on the interfacial mass transfer of monomers solubilized and part-

ditioned in the oil phase. For the copolymer of methacrylic acid ethylacrylate, the rate dependence or surfactant level is much higher than for the acrylamide terpolymer, -0.69 vs -0.295 . The indication is, therefore, that ethylacrylate partitions into the polymer particle and is released through the adsorbed surfactant film at the interface. The adsorbed surfactant at the particle interface must also prevent radical entrance since there is no measurable polymerization within the particles. In order to assess the role of the termonomer in this interfacial mass transfer controlled reaction scheme, 6% of each monomer component in the styrene termonomer system was withheld and slow added in 15 minutes. The 0.5% neutralized to pH 7 viscosities were monitored as a convenient and easy measure of any change. The results are shown in Table 1. The plus signs indicate slow additions. The lowest viscosities are obtained when styrene is slow added. Styrene and ethyl acrylate are most likely in the oil phase. The large viscosity differences obtained in Table 1 were hypothesized to be due to the effect of the termonomer on the sequencing distribution of acid in the chain. It is known that in poly(methacrylic acid) ion binding can be as high as 60% (9). It is hypothesized that the termonomer will lower the degree of acid block formation and, hence, reduce on binding and increase the effective length of the neutralized molecule. In order to test this hypothesis, the probabilities for acid-acid link formation were calculated from the Q and e values for the monomers (10). A plot of the latex viscosities as a function of these probabilities is shown in Figure 2 for all the termonomers studied. The trend for lower viscosities at higher probability values coincides with expectations based on ion binding hypothesis. Obviously, molecular weight will also influence the extended chain length. This effect, however, is thought to be compounded with the effect of acid sequencing. Namely, at the same molecular weight, increasing ion binding will yield lower viscosity. Consequently, at the same level of ion binding, increasing molecular weight will increase viscosity. In order to demonstrate this, it was necessary to decompose the viscosity effect into molecular weight and electrostatic components. Contour maps in viscosity were charted in terms of intrinsic viscosity (molecular weight dependent) and probability values for acid-acid formation (the electrostatic component). From the contour maps, the latex viscosity as a function of the electrostatic (probability for acid-acid linkage) and molecular weight (intrinsic viscosity) could be plotted as a family of curves shown in Figure 3. It can be seen that at a given molecular weight, increasing the electrostatic component increases viscosity and, at a given acid sequencing, the molecular weight similarly increases the viscosity. This effect is very similar to the solvent effect in viscosity measurements for macromolecules. The solvent-polymer interaction, analogous to the electrostatic component, or acid sequence distribution, tends to regulate chain extension, irrespective of molecular weight.

References

- (1) R. M. Fitch and C. H. Tsai, "Polymer Colloids", R. M. Fitch, Ed., N.Y., Plenum, 1971, pp. 73-102.
- (2) V. T. Stannett, A. Klein, M. Litt. British Polymer J. 7, 139 (1975).
- (3) V. I. Yeliseyeva, S. A. Petrova, A. V. Zuikov, J. Polymer Sci. Symp. No. 42, 63 (1973).
- (4) G. L. Brown, B. S. Garrett, J. Appl. Polymer Sci., 1, 283 (1959).
- (5) R. W. Kreider, Official Digest, p. 1243, Nov. 1964.
- (6) J. W. Vanderhoff, F. J. Micale, M. S. El-Aasser, W.C. Wu, ACS Polymer Preprints 16(1), 125 (1975).
- (7) P. W. Allen, Techniques of Polymer Characterization, London, Butterworth 1959, pp. 194-195.
- (8) D. H. Napper, A. G. Parts, J. Polymer Sci. 61, 113 (1962)
- (9) A. Oth, P. Doty, J. Phys. Chem. 56, 43, (1952).
- (10) L. D. Maxim, C. H. Kuist, M. E. Meyer, Macromolecules 1, 86 (1968).

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FIGURE 1. Particle Size Distributions of Seed and Seeded Latex.

Seed
Seeded latex

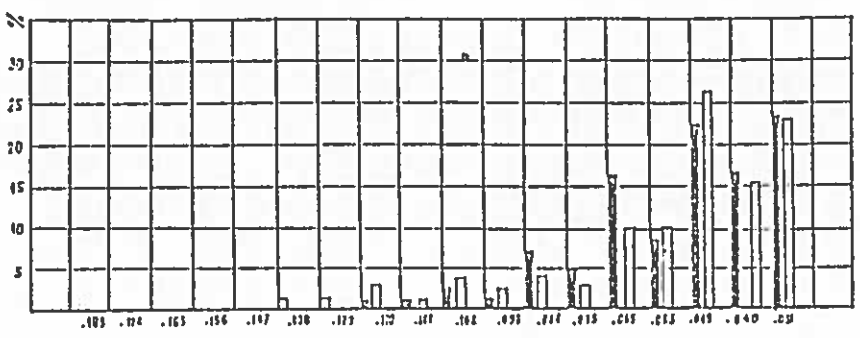


FIGURE 2. Calculated Probability of Acid-Linkage vs Latex Thinning

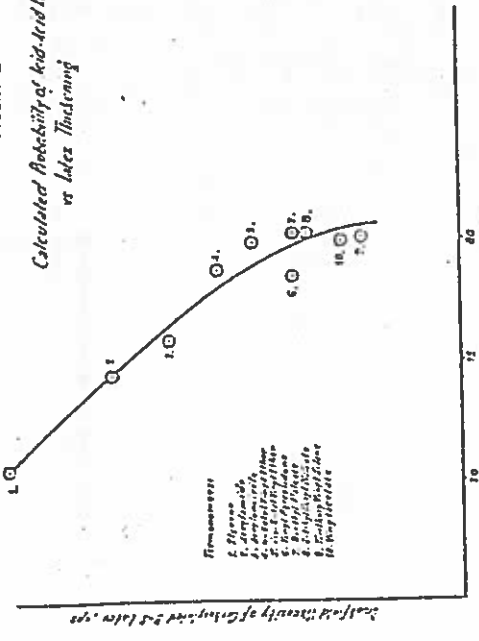


FIGURE 3. Latex Viscosity Dependence upon Intrinsic Viscosity and Probability of Acid-Linkages (Iso Viscosity Contour Smoothed Values)

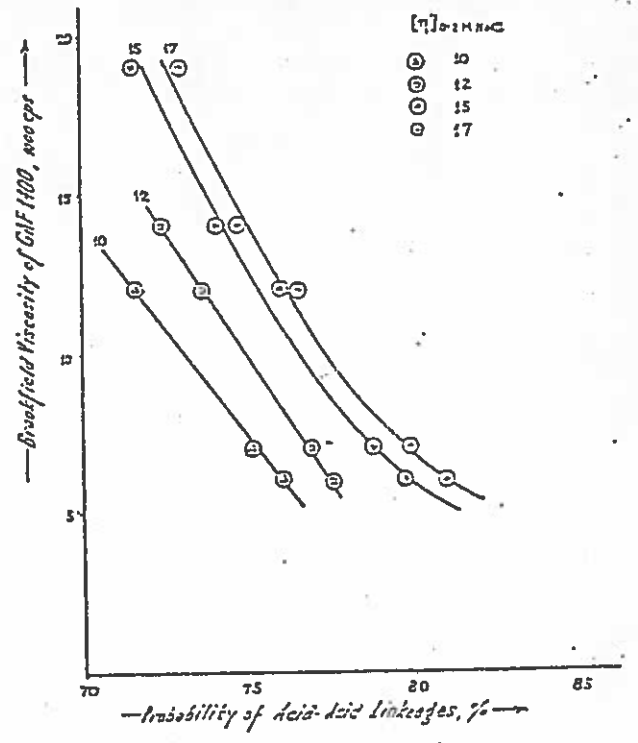


TABLE 1. EFFECT OF GRADUAL ADDITION ON VISCOSITY

Gradual Addition*			0.5% Visc. cps
MAAc	Concn.	Tempn.	
-	-	+	148
-	+	-	1300
+	-	-	1280
+	-	+	120
-	+	+	30

* 6% of Total Change in 15 minutes.

not type
on this line



McGill
University

Department of Chemistry
Pulp and Paper Building

26 SEP 1978

Contribution to the Polymer Colloid Group Newsletter

September 1978

S.G. Mason and A.A. Robertson

The following are some of the areas related to polymer colloids in which there have been activity and progress in recent months.

First, there have been further developments in the studies of the interaction of colloidal particles in shear flow being conducted by Takamura.

1. Models of Doublets of Rigid Spheres Having Fixed Separation Distance with Independently Rotating Particles. In the previous newsletter we reported on the periods of rotation, T , of macroscopic models of doublets having a fixed distance of separation, h , between the sphere surfaces but with the particles able to rotate freely at various shear rates, G , in Couette flow. In agreement with theory it was demonstrated that the measured value of TG of such doublets were significantly higher than those of rigidly connected spheres at the same h . To gain a better understanding of the effect of such relative rotation of the individual spheres on the TG values of doublets, measurements of the angular velocities of the doublet axis and of the individual spheres were undertaken.

This has been done in a model system by marking individual 3mm spheres to make their independent rotation observable and connecting them by either a rigid or slightly restrictive coupling. It was possible to observe the theoretical TGs of 41 and 17.4 for the doublet rotation of freely rotating spheres and rigidly coupled spheres respectively and an intermediate value of 28.8 for a doublet of spheres with partially restricted rotation.

2. Models of Triplets with Independently Rotating Particles. The studies of model doublets have been extended to investigate the effects of independent particle rotation on the configuration of the spheres of a triplet. Macroscopic models of triplets of rigid particles having a fixed h but with independently rotating spheres were made by adding another freely rotating sphere to model doublets by means of a small metal wire loop.

The experiment was initiated with the orientation of a triplet (abc) initially linear and aligned in the direction of flow. Upon shearing, the particles formed a triangular configuration due to compressive stresses in the flow, and the angle abc between spheres a and c continued to decrease until they appeared to touch. Since interparticle forces were absent in this model triplet, the angle started to increase again as the particle became subjected

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to tensile stresses but never reached 180° with the initial linear configuration. From these observations it is presumed that, in the case of a triplet in which adjacent particles are in the secondary energy minimum, the closed triangular configuration may be the only stable one in shear flow.

3. Diffusion of Spherical Particles in Poiseuille Flow. Drs. Foister and van de Ven have been examining the ways in which the diffusion of particles subject to Brownian motion is affected by an external field. The mean square displacement in unit time of spherical Brownian particles in simple shear flow has been calculated on the basis of the convective-enhanced diffusion that is due to the coupling of convective motion in the flow direction and diffusion in the direction of the velocity gradient.

In plane Poiseuille flow we expect similar behavior but no exact solution of the convective diffusion equation is available, so in order to calculate the mean square displacement we have made use of the fundamental Langevin equation for the motion of a spherical particle subjected to random thermal forces and an external Poiseuille velocity field.

The equation that has been derived is now being tested experimentally, using the travelling microtube technique.

4. The conductometric titration of latexes as a means for distinguishing and evaluating the various surface groups contributing to electrical stability and electrokinetic properties has been examined in some detail by Labib. The extension of the procedure to include back-titrations and the comparison of conductometric and potentiometric titrations indicates that the conventional identification of weak-acid end-points is often wrong or misleading. The stoichiometric end-point is obscured by the changing distribution of ions between bulk and surface during titration by concurrent dissociation and double layer effects. It is proposed that a pragmatic identification of the weak-acid end-point in conductometric titration is obtained by the extrapolation of the curve for excess alkali back to its intersection with a horizontal line drawn through the strong-acid end-point conductivity.

POLYMER COLLOIDS AT SYDNEY UNIVERSITY

Reporter: D. H. Napper

SEP 1978

Seeded Emulsion Polymerization

In our previous report, we mentioned that Brian Hawke had measured the first order radical annihilation (probably exit) rate constant for styrene by following the approach to the steady state in seeded systems. This has now been done for a series of different particle sizes. The results to date suggest that the rate constant varies as $1/r^2$, not, as has often been hypothesised, as $1/r$. The $1/r^2$ dependence can be justified theoretically using diffusion theory.

A second aspect of this project has involved kinetic relaxation studies. We were confronted with an apparent paradox: Brian's results unequivocally showed that \bar{n} could be less than 0.5 for styrene in the steady-state yet this is not possible theoretically if termination is exclusively second order, as has been claimed by Ley, Schneider and Hummel. Stephen Lansdowne has therefore repeated their γ -irradiation experiments using seeded emulsion polymerizations, rather than their ab initio systems.

There is no question that the decay rate in these well-controlled experiments is first order, not second order, at least for styrene. Moreover, the first order rate constants calculated from these relaxation studies are in excellent agreement with those observed by Brian Hawke for chemically initiated system. This allows us to assert that the results of Ley, Schneider and Hummel must be treated with extreme caution for they appear to contain serious artifacts.

Contribution to Polymer Colloid Group Newsletter

by M. Nomura
Dept. of Industrial Chemistry, Fukui University, Fukui JAPAN

Rate of Emulsion Copolymerization

In order to elucidate the kinetic picture of emulsion copolymerization, it is necessary to solve two problems, that is, to make clear the effects of initial initiator, emulsifier and monomer concentrations on the number of polymer particles produced and the rate of polymerization per particle. For this purpose, it will be easy and reasonable to solve these problems separately. From this view point, I have been theoretically and experimentally studying what factors and how affect the rate of polymerization per particle.

The following are the outline of the paper to be given at the 12th Autumn Meeting of The Society of Chem. Engrs, Japan, Oct.9-11.

Part I: Mathematical model for emulsion copolymerization

Hypothesis:

- (1) A particle contains not more than two radicals.
- (2) Instantaneous termination takes place when the second radical enter the particle which contains a radical.
- (3) Only monomer radicals can escape and reenter the particles.
- (4) No distinction is made between radicals with and without an initiator fragment.
- (5) Reactions in the water phase is considered negligible

Elementary Reactions and their rates

(1) Initiation of radicals in the water phase

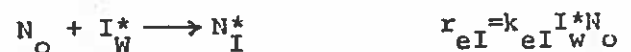


(2) Entry of radicals from water phase into particles

(i) Instantaneous termination:



(ii) Activation of polymer particle;

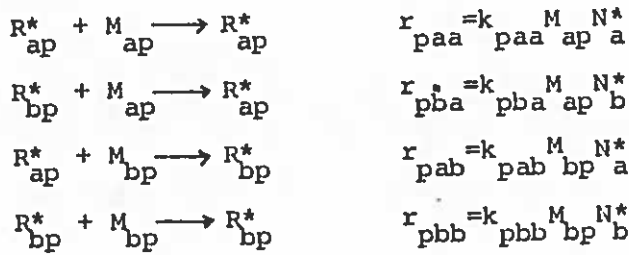


(3) Initiation in the polymer particles

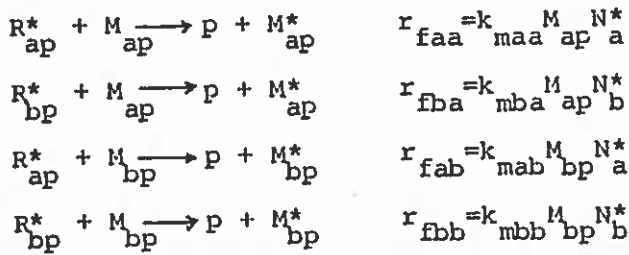


<u>Nomenclature</u>	
subscripts, w and p mean water and polymer particle phases	
I, I [*]	: initiator and initiator radical
f	: initiator efficiency
k _d	: rate constant of initiator decomposition
M _a , M _b	: A, B-monomer and its concentration
M _a [*] , M _b [*]	: A, B-monomer radical
R _a [*] , R _b [*]	: polymer radical with A, B monomer unit at radical end
N _a [*] , N _b [*]	: polymer particle containing R _a [*] , M _a [*] and R _b [*] , M _b [*]
N _I [*]	: polymer particle containing I [*] radical
N _o	: polymer particle containing no radical
N [*]	: polymer particle containing radical
γ _a	: reactivity ratio = k _{paa} /k _{pab}
γ _b	: reactivity ratio = k _{pbb} /k _{pba}

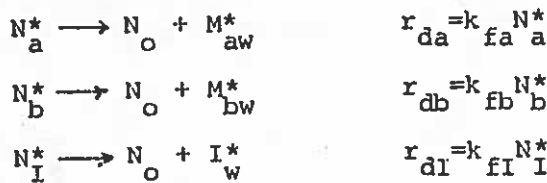
(4) Propagation in the polymer particles:



(5) Chain transfer to monomer in the particles:



(6) Desorption of radical out of polymer particle:



According to the reaction scheme shown above, we have a following set of differential equations by taking material balance for respective species. Furthermore, we apply steady state method to them,

$$dR_w^*/dt = r_i + k_{fa} N_a^* + k_{fb} N_b^* + k_{fI} N_I^* - (k_{ea} M_{aw}^* + k_{eb} M_{bw}^* + k_{eI} I_w^*) N_T = 0 \quad \text{-----(1)}$$

where $R_w^* = M_{aw}^* + M_{bw}^* + I_w^*$ (radical concentration in water phase)

$$dN_I^*/dt = k_{eI} I_w^* N_o - (k_{ia} M_{ap} + k_{ib} M_{bp}) N_I^* - (k_{ea} M_{aw}^* + k_{eb} M_{bw}^* + k_{eI} I_w^*) N_I^* - k_{fI} N_I^* = 0 \quad \text{-----(2)}$$

$$\begin{aligned}
 dN_a^*/dt = & k_{ia} M_{ap} N_I^* + (k_{pba} + k_{mba}) M_{ap} N_b^* + k_{ea} M_{aw}^* N_o - (k_{pab} + k_{mab}) M_{bp} N_a^* \\
 & - (k_{ea} M_{aw}^* + k_{eb} M_{bw}^* + k_{eI} I_w^*) N_a^* - k_{fa} N_a^* = 0 \quad \text{-----(3)}
 \end{aligned}$$

$$\begin{aligned}
 dN_b^*/dt = & k_{ib} M_{bp} N_I^* + (k_{pab} + k_{mab}) M_{bp} N_a^* + k_{eb} M_{bw}^* N_o - (k_{pba} + k_{mba}) M_{ap} N_b^* \\
 & - (k_{ea} M_{aw}^* + k_{eb} M_{bw}^* + k_{eI} I_w^*) N_b^* - k_{fb} N_b^* = 0 \quad \text{-----(4)}
 \end{aligned}$$

Since high molecular weight polymers are produced in an ordinary emulsion copolymerization system, it is reasonable to consider that the 3rd, 5th and 6th terms in Eqs(3) and (4) are not dominant. Furthermore, if we assume that the rate of the initiation step(3) is very rapid, the values of N_a^* and N_b^* would be much greater than that of N_I^* and hence, we get the following approximate equation from Eqs.(3) or(4).

$$(k_{pba} + k_{mba}) M_{ap} N_b^* = (k_{pab} + k_{mab}) M_{bp} N_a^* \quad \text{-----(5)*}$$

Since $k_p \gg k_m$ in usual case,

$$k_{pba} M_{ap} N_b^* = k_{pab} M_{bp} N_a^* \quad \text{-----(5)}$$

We define here that: $\bar{n}_a = N_a^*/N_T$, $\bar{n}_b = N_b^*/N_T$ and $\bar{n}_I = N_I^*/N_T$ and $\bar{n}_t = \bar{n}_a + \bar{n}_b + \bar{n}_I$

By adding Eqs. (2), (3) and (4) and inserting Eq. (1), we have:

$$(k_{fa} \bar{n}_a + k_{fb} \bar{n}_b + k_{fi} \bar{n}_I + r_i/N_T)(1 - 2\bar{n}_t) - (k_{fa} \bar{n}_a + k_{fb} \bar{n}_b + k_{fi} \bar{n}_I) = 0 \quad (6)$$

Since we assumed that $N_a^*, N_b^* \gg N_I^*$, therefore, $\bar{n}_a, \bar{n}_b \gg \bar{n}_I$ and $\bar{n}_t \approx \bar{n}_a + \bar{n}_b$

$$(k_{fa} \bar{n}_a + k_{fb} \bar{n}_b + r_i/N_T)(1 - 2\bar{n}_t) - (k_{fa} \bar{n}_a + k_{fb} \bar{n}_b) = 0 \quad (7)$$

By solving Eq. (7) for \bar{n}_t , we get:

$$\bar{n}_t = \frac{1}{2} [-(CD) + \{ (CD)^2 + 2(CD) \}^{1/2}] \quad (8)$$

where, $C = r_i/k_{fa} N_T$ ($k_{fa} \neq 0$) and $D = \frac{1+A}{1+AB}$ (9)

where, $B = k_{fb}/k_{fa}$ and $A = (\bar{n}_b/\bar{n}_a) (k_{paa}/k_{pbb}) (\gamma_a/\gamma_b) (M_{bp}/M_{ap})$ (10)

$$\bar{n}_a = \frac{1}{1+A} \bar{n}_t \quad (11), \quad \bar{n}_b = \frac{A}{1+A} \bar{n}_t \quad (12)$$

Fig. 1 shows the plot of the average number of radicals per particle against $C = r_i/k_{fa} N_T$ with varying the value of D.

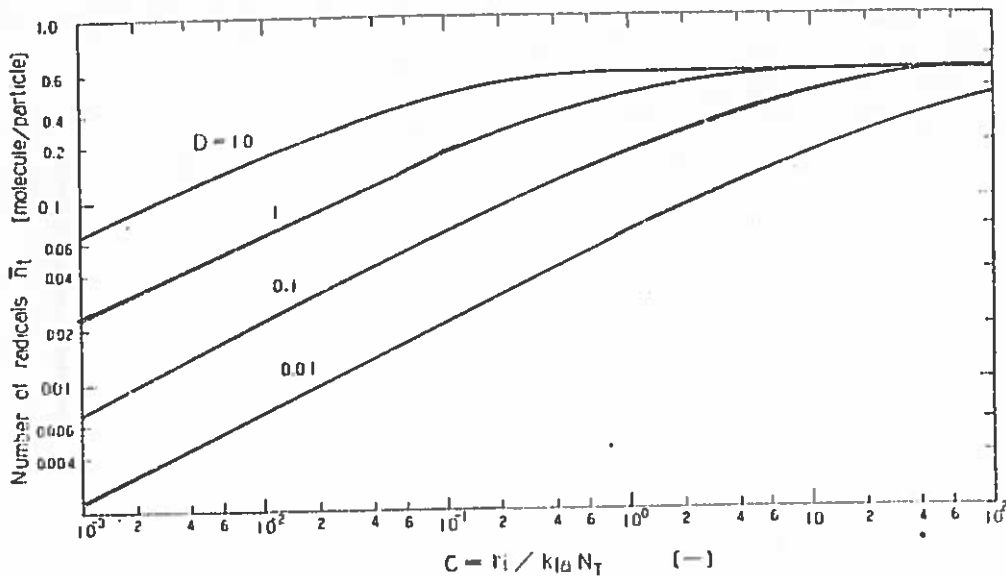


Fig. 1 Relationship between the average number of radicals per particle versus the value of $C = r_i/k_{fa} N_T$

Fig. 2 shows the effect of the values of A and B on the value of D.

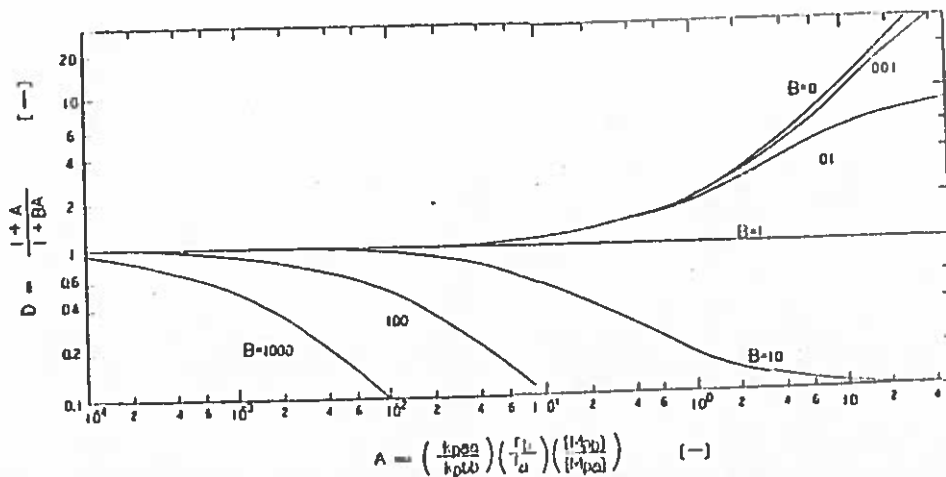


Fig. 2 Effect of the values of A and B on the value of D

We can calculate the rate of emulsion copolymerization from Eqs.(8),(11) and (12) as follows:

$$R_{pa} = - \frac{dM_a}{dt} = k_{paa} M_{ap} N_a^* + k_{pba} M_{ap} N_b^* = (k_{paa} M_{ap} + k_{pba} M_{ap}) \bar{n}_a N_a^* \quad (13)$$

$$R_{pb} = - \frac{dM_b}{dt} = k_{pbb} M_{bp} N_b^* + k_{pab} M_{bp} N_a^* = (k_{pbb} M_{bp} + k_{pab} M_{bp}) \bar{n}_b N_b^* \quad (14)$$

$$\text{and,} \quad R_{pt} = R_{pa} + R_{pb} \quad (15)$$

Copolymer composition

From Eqs.(13) and (14), we have:

$$\frac{dM_a}{dM_b} = \frac{k_{paa} M_{ap} N_a^* + k_{pba} M_{ap} N_b^*}{k_{pbb} M_{bp} N_b^* + k_{pab} M_{bp} N_a^*} \quad (16)$$

$$= \left(\frac{M_{ap}}{M_{bp}} \right) \left(\frac{\gamma_a M_{ap} + M_{bp}}{\gamma_b M_{bp} + M_{ap}} \right) \quad (17)$$

This equation is quite similar to so-called "Mayo-Lewis equation". It is found from this equation that the desorption of radicals from polymer particles does not affect the polymer composition. Therefore, the difference of copolymer composition between emulsion and bulk or solution copolymerizations must be attributed to other factors, for example, the solubility of monomers in the water phase.

Derivation of k_{fa} and k_{fb} , the rate coefficient of desorption of monomer radical

According to the definition of k_{fa} and k_{fb} , we have:

$$k_{fa} N_a^* = k_{oai} N_{ai}^* \quad (18), \quad k_{fb} N_b^* = k_{obi} N_{bi}^* \quad (19)$$

where, k_{oai} = desorption rate constant for A-polymer radical with i monomer units
and, N_{ai}^* = number of polymer particle containing A-polymer radical with i monomer units

As we suppose that only monomer radicals can escape from polymer particles, Eqs. (18) and (19) become:

$$k_{fa} N_a^* = k_{oa} N_{am}^* \quad (18') \quad k_{fb} N_b^* = k_{ob} N_{bm}^* \quad (19')$$

where, k_{oa} = desorption rate constant for A-monomer radical

N_{am}^* = number of polymer particle containing A-monomer radical

With the same procedure given in the paper of ACS Symposium Series No.24, p.102-p.121, we get the following approximate equations for N_{am}^* and N_{bm}^* .

$$N_{am}^* = \frac{[(k_{mba}/k_{pba}) + (k_{paa}/k_{pab})(k_{maa}/k_{paa})(M_{ap}/M_{bp})] N_a^*}{(k_{paa}/k_{pab})(M_{ap}/M_{bp}) + (k_{paa}/k_{pab})(k_{oa} \bar{n}_t / k_{paa} M_{ap})(M_{ap}/M_{bp}) + 1} \quad (20)$$

By inserting Eq.(20) into Eq.(18'), we have:

$$k_{fa} = k_{oa} \left[\frac{C_{maa} \gamma_a + C_{mba} (M_{bp}/M_{ap})}{\gamma_a (1 + (k_{oa} \bar{n}_t / k_{paa} M_{ap})) + (M_{bp}/M_{ap})} \right] \quad (21)$$

With the same treatment,

$$k_{fb} = k_{ob} \left[\frac{C_{mbb} \gamma_b + C_{mab} (M_{ap}/M_{bp})}{\gamma_b (1 + (k_{ob} \bar{n}_t / k_{pbb} M_{bp})) + (M_{ap}/M_{bp})} \right] \quad (22)$$

where $C_{maa} = k_{maa}/k_{paa}$, $C_{mba} = k_{mba}/k_{pba}$, $C_{mbb} = k_{mbb}/k_{pbb}$ and $C_{mab} = k_{mab}/k_{pab}$.

In Eqs. (21) and (22), the terms $(k_{oa} \bar{n}_t / k_{paa} M_{ap})$ and $(k_{ob} \bar{n}_t / k_{pbb} M_{bp})$ are negligible. Otherwise, a large number of high molecular weight copolymers do not produced. This is the case in emulsion homopolymerization.

Derivation of k_{oa} and k_{ob} , the desorption rate constant for monomer radical.

According to the definition of k_{oa} and k_{ob} , we have:

$$k_{oa} = k_{sa} a_p / v_p = (d_p / 2D_{pa} + m_a d_p / 2D_{wa})^{-1} (\pi d_p^2) / (\frac{\pi}{6} d_p^3) = \frac{12D_{wa} \delta_a}{m_a \cdot d_p^2} \quad \text{----- (23)}$$

$$k_{ob} = k_{sb} a_p / v_p = (d_p / 2D_{pb} + m_b d_p / 2D_{wb})^{-1} (\pi d_p^2) / (\frac{\pi}{6} d_p^3) = \frac{12D_{wb} \delta_b}{m_b \cdot d_p^2} \quad \text{----- (24)}$$

$$\text{where } \delta_a = (1 + D_{wa} / m_a D_{pa})^{-1}, \delta_b = (1 + D_{wb} / m_b D_{pb})^{-1} \quad \text{----- (25)}$$

- D_{wa}, D_{wb} = diffusion coefficient of A,B-monomer radicals in water phase
- m_a, m_b = partition coefficient of A,B-monomer radicals between water and polymer particle phases
- D_{pa}, D_{pb} = diffusion coefficient of A,B-monomer radicals in particle phase
- a_p = surface area per particle, v_p = volume of a particle, d_p = diameter of particle, k_{sa}, k_{sb} = mass transfer coefficient around polymer particle.

In estimating k_{sa} and k_{sb} , the two-film theory is supposed and diffusion resistance for monomer radicals to go through the outer and inner diffusion films of polymer particle is supposed to be (particle diameter/diffusion coefficient).

Definition of m_a and m_b are:

$$M_{ap}^* = m_a M_{aw}^*, M_{bp}^* = m_b M_{bw}^* \quad \text{----- (26)}$$

Part II Comparison between experimental and theoretical results

To test the validity of the mathematical model of emulsion copolymerization given above, we have carried out seeded emulsion copolymerization of styrene and methyl methacrylate. Methyl methacrylate is denoted as A-monomer and styrene as B-monomer.

The copolymer composition of seed polymer particles used for this series of experiments is that A:B = 1:1 and average particle diameter is 0.07 μ m.

Fig. 1 is a typical example of the conversion of added monomer versus reaction time. It is seen that polymerization rate is linear at least up to 20% conversion. From the slope of a linear portion of conversion-time curve, total copolymerization rate can be calculated.

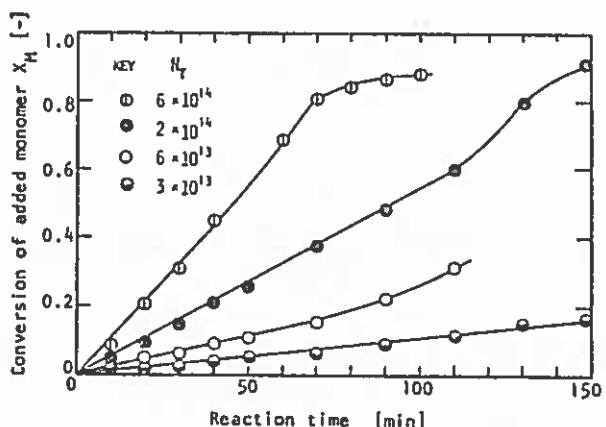


Fig.1 Effect of N_T on the course of copolymerization ($M_a/M_b=1$)

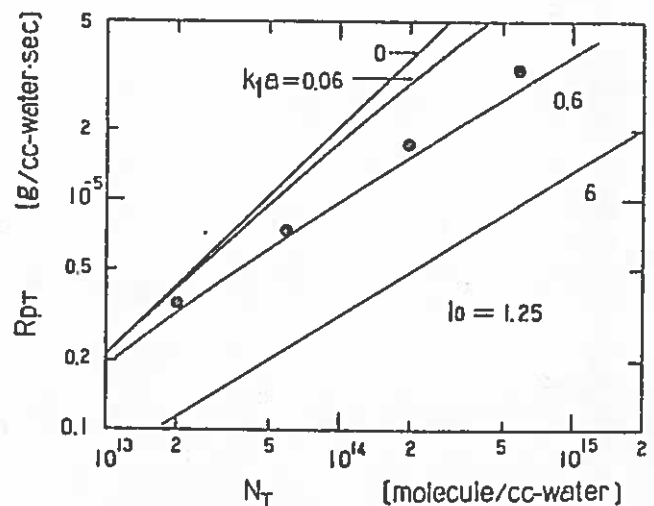


Fig.2 Effect of the number of polymer particle on R_{pt}

Fig. 2 shows the relationship between total copolymerization rate and the number of polymer particle. The solid lines represent the results of calculation where k_{fa} is a parameter. It is concluded from this figure that the rate of copolymerization of styrene and methyl methacrylate is not proportional to the number of polymer particle and the effect of desorption of radical should be taken into account.

Fig. 3 shows the effect of initiator concentration on the total copolymerization rate. If desorption of radical from polymer particles is negligible, initiator concentration would not affect the rate of polymerization. From this experiment, however, it is found that desorption of radicals from polymer particles is not negligible.

Fig. 4 shows the effect of initial monomer concentration on the total copolymerization rate. It is seen that monomer feed composition for methyl methacrylate does not affect the rate of polymerization over a wide range of monomer feed composition. The increase of the rate of polymerization at high methyl methacrylate composition is ascribable to gel-effect.

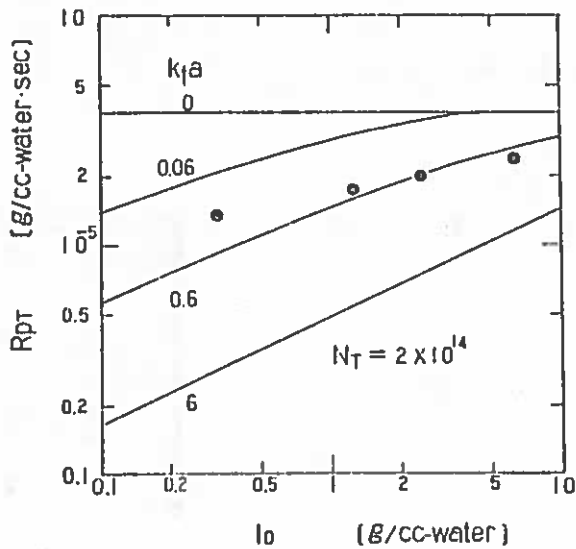


Fig.3 Effect of initiator concentration on R_{pt}

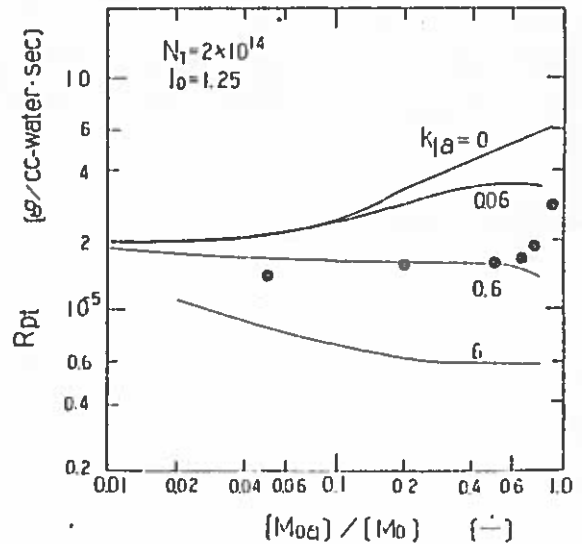


Fig.4 Effect of monomer feed composition on R_{pt}

Comparison of calculated and experimental value of k_{fa}

From Figures (2) and (3), it is found that the value of k_{fa} is about 0.6. The calculated value shown below is about 0.5. Therefore, the calculated value is in good agreement with the experimental value. This is one of good evidences which certify the validity of mathematical model of emulsion copolymerization given in this Newsletter.

This work will be submitted to J. of Applied Polymer Science in near future for publication.

Calculation of the value of k_{fa}

$$D_{wa} = 1 \times 10^{-5}, m_a = 50, d_p = 7 \times 10^{-6}, \delta_a = 1.0, \gamma_a = 0.5, C_{maa} = 1 \times 10^{-5}, M_{bp}/M_{ap} = 1.0$$

$$C_{mba} = 1 \times 10^{-5} \text{ (} C_{mba} \text{ value is unknown, however this value is assumed)}$$

$$k_{oa} = \frac{12 \times 1 \times 10^{-5} \times 1.0}{50 \times (7 \times 10^{-6})^2} = 5 \times 10^4, k_{fa} = 5 \times 10^4 \left[\frac{1 \times 10^{-5} \times 0.5 + 1 \times 10^{-5} \times 1.0}{0.5(1 + 0) + 1.0} \right] = 0.5$$

Contribution to Polymer Colloid Group Newsletter

From: D.W.J. Osmond,
ICI Paints Div.,
SLOUGH.

29 AUG 1978

This is a rather sad occasion for me; as some of you know, my health has not been good for several years and has further deteriorated of late. As a result, I am retiring on medical grounds very early next year. I feel that I must therefore offer my resignation to the Group and so this is probably my last contribution to the Newsletter.

I feel that I cannot go without saying that membership - both for the honour implied and the information made available - has been one of the better things to happen to me in my career, even though I may have seemed a rather passive member on occasions. I am glad to say that I am not in any sense "Dyingly ill" and I hope to maintain some kind of contact with both ICI and Bristol through which I hope to be kept abreast of the best of the news.

In view of the above, it is singularly maddening that the two areas which I had planned to discuss; stabilisation by poly-electrolyte chains and a novel kind of aqueous latex polymerisation yielding completely sterically stabilised particles, with no detectable charge and in ion-free water, are both under internal interdiction of one kind or another, so that I have no technical contribution for this final letter!

[^]Os Osmond

D.W.J. Osmond

I. Piirma

Sodium Borohydride in Emulsion Polymerization Redox Initiation System

The so-called redox initiation systems have been known and used for at least three decades. The name redox comes from the fact that the two or more chemicals involved in this system depend upon a reaction between a reducing and an oxidizing agent. The interest in our study was the use of the reducing agent sodium borohydride. The preliminary results of our study of the effectiveness of this compound is the subject of this report.

All the polymerizations were carried out at 20°C with sodium dodecyl sulfate as the emulsifier. The oxidizing agent was potassium persulfate, and the monomers were vinyl acetate, styrene, and copolymers of styrene with butadiene and acrylonitrile.

I. Vinyl Acetate

a) Using the common redox recipe $K_2S_2O_8 - NaHSO_3$ with vinyl acetate at 20°C we observed a polymerization rate of 14%/hour. The addition of $NaBH_4$ to this polymerization system increased the rate 20-fold i.e., to 5%/min (300%/hour). Since no metal ion addition was necessary, no discoloration of the precipitated polymer was observed at all. The emulsion was quite stable, although there was quite a change of pH during the reaction, namely from pH = 7 to a pH = 2 at the end. The molecular weight of this polymer was $M_n = 2.55 \times 10^5$.

As far as the mechanism of this initiation system is concerned, we believe that the enhancement of the rate is due to a reaction between $NaHSO_3$ and the $NaBH_4$ forming a sulfoxylate which then in turn reacts with the $K_2S_2O_8$ to form the sulfate radical ion. A more detailed study is under way.

II. Styrene and the Copolymers

A maximum conversion of 22% per hour was obtained (depending on the ratio of the $NaBH_4$ and $K_2S_2O_8$) with the styrene monomer. A 50-50 styrene-acrylonitrile copolymerization rate with the same initiating system yielded a much faster rate, namely 75%/hour. The results were not as great in the styrene-butadiene copolymerization. In the presence of a mercaptan the rates were promising, in the absence of mercaptan the polymerization rates were slow and decreased with increasing butadiene concentration in the copolymerization charge.

All these polymerizations are still under investigation.

PRESENTED AT

THE FIRST INTERNATIONAL SYMPOSIUM ON COAL-OIL MIXTURE TECHNOLOGY

St. Petersburg Beach, Florida

May, 1978

30 MAY 1978

INVESTIGATION AND MEASUREMENT OF STABILITY IN COAL-OIL MIXTURES

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New England Power Service Company

ABSTRACT

The general problem of the definition and measurement of stability in non-aqueous dispersions has been investigated in connection with research on the utilization of mixtures of ground coal in No. 6 oil as a power plant fuel. The theoretical problem is expressed in terms of electrostatic, steric and matrix stability while the practical problem is understood in terms of static, dynamic and reactive stability. The measurement of static stability has been achieved through development of a thermostatted sedimentation column. The sedimentation column yields data on the time-dependence of the density during COM sedimentation. It also yields data on the rheological properties of the COM sedimentation matrix. The coal particles are characterized by sieve analysis and by optical microscopy. The particles were polydisperse and irregular in shape but some of the samples were predominantly in the 5-10 μm range with a significant fraction below 5 μm . The macroscopic measurement of stability is compared with microscopic stability. The effects of stabilizing and destabilizing additives are discussed.

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WIDE ANGLE LIGHT SCATTERING INVESTIGATION OF THE INTERNAL STRUCTURE OF POLYMER LATEXES. R. L. Rowell, J. R. Ford and J. W. Parsons, Department of Chemistry, University of Massachusetts, Amherst, Massachusetts 01003 and David R. Bassett, Union Carbide Corporation, Chemicals and Plastics, P.O. Box 8361, South Charleston, W. Va. 25303. (Work done at the University of Massachusetts).

A new apparatus has been developed for the measurement of wide-angle and low-angle scattering from colloidal suspensions. The instrument employs an argon ion laser source, single photon counting detection, data acquisition by minicomputer and has an easily accessible angular resolution of 0.6° . The accuracy of the light scattering apparatus along with the reliability of the data-inversion procedure has been tested by critical comparison of measurements on a standard polystyrene latex by four independent methods on the same sample as well as comparison with numerous reports in the literature. In related work a computer study of the theoretical behavior of the light scattering functions has been carried out using computer graphics. An improvement of the inversion procedure of Rowell and Levit has been used in a double blind analysis of a control latex with minimal shell structure and the subject latex of pH-dependent shell structure. Both control and subject latex were analyzed using both homogeneous sphere theory and concentric sphere theory. The results conclusively established the existence of a concentric-shell structured latex and were in agreement with an independent study of the system by sedimentation methods, which is reported elsewhere.

5 SEP 1978

ON THE MORPHOLOGY AND MECHANICAL BEHAVIOUR
OF COMPOSITION LATEX POLYMERS

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In the present paper, on the example of three acrylate latex polymers having the same integral composition, it is demonstrated that their film-forming and physico-mechanical properties can be regulated within a wide range by changing the physical ^{size} nature of the polymer through the use of various emulsion polymerization techniques

Latexes were prepared under the same conditions (temperature of 80°C, gradual ⁺introducing of components into the reaction system, high conversion, 34.5% concentration of final latexes). The polymers had the following monomeric composition: butyl acrylate - methyl methacrylate - methacrylic acid (39.3 : 57.4 : 3.3).

Latex I (AB). The latex was synthesized by gradually ^{ation} introducing into the reaction medium the mixture of monomers in the above-specified ratio. Chromatographic analysis of the monomeric mixture in the process of polymerization has shown that (1) the process takes place at high conversion, corresponding to 80-90% concentration of polymer in p/m particles; (2) the composition of residual monomers remains approximately constant, this being indicative of statistical average alternation of the monomeric units in the formed copolymer, taking into account favourable copolymerization constants.

Electron-microscopic investigation of particles of the final latex AB at various pH values (5.5 and 9.5) has not revealed any changes in the shape and size of the particles, resulting from the dissociation of carboxyl groups at pH=9.5; this also confirms average distribution of the monomeric units in the macromolecules and in the volume of the particles.

When latex AB was allowed to dry under room conditions in a teflon

cell (film thickness 0.3 mm), the film developed cracks due to the origination of high internal stresses.

Latex 2 (A+B). Polymethyl methacrylate latex B which is not film-forming was mixed with film-forming latex A (copolymer BA-MMA-MAA, 55:40:5 wt. pts) in the ratio of 28.7:71.3 corresponding to the monomeric composition of the latex AB. When latex A+B was allowed to dry under room conditions, a continuous film was formed, contrary to the case with latex AB. The elasticity of copolymer A is higher than that of AB, in view of greater content of the plasticizing monomer (butyl acrylate), which conditioned its film-forming capacity at room temperature. Evidently, deformation of the particles of this latex under the effect of capillary forces in the course of the latex drying, as well as diffusion and autohesion of the boundary sections of the polymer chains of adjacent globules were the factors which ensured the formation of continuous film.

Latex 3 (A-B). Latex B (PMMA) which is not film-forming served as a seeding in polymerization of monomeric mixture A. The ratio of latex B and monomeric mixture A was the same as in the preceding latex A+B.

Coefficients of butyl acrylate and methyl methacrylate diffusion into corresponding polymers, viz., their 80-90% solutions in monomer, were determined interferometrically at the same temperature as that used in the polymerization process (80°C); polymer concentrations in the monomer were selected in accordance with those really taking place under the above-specified latex synthesis conditions, when the monomer is gradually introduced into the reaction mixture. The obtained data are presented in the table below.

Estimation of the possible influence of the diffusion rate on polymerisation shows that with the diffusion coefficient exceeding 10^{-10} cm²/sec non-uniformity of concentration of monomers in the particles can be neglected, so that the polymerization rate was not

limited by the diffusion process in the particles. Within the framework of the classical concepts of the emulsion polymerization it could be supposed that monomeric mixture A polymerized in the volume of the particles of seeding latex and, as a result, polymer A must be uniformly distributed in polymer B.

Coefficients of BA and MMA diffusion into PBA and PMMA at the temperature of synthesis (80°C).

System	Polymer concentration, wt. %	Diffusion coefficients, cm^2/sec
PBA-BA	80	$3 \cdot 10^{-6}$
PBA-BA	90	$2.4 \cdot 10^{-6}$
PBA-MMA	80	$2.35 \cdot 10^{-6}$
PBA-MMA	90	$1.7 \cdot 10^{-6}$
PMMA-BA	80	$8.0 \cdot 10^{-8}$
PMMA-BA	90	$4.5 \cdot 10^{-8}$
PMMA-MMA	80	$2.6 \cdot 10^{-7}$
PMMA-MMA	90	$1.2 \cdot 10^{-7}$

However, from electron microphotographs of latex A-B it can be seen that when pH increases to 9.5 the external layer of the particles disintegrates into microglobules, whereas the core remains unchanged. This may be evidence either of polymerization of monomeric mixture A enriched with methacrylic acid in the surface zone of the particles, or of flocculation of the newly forming particles with the particles of the seeding latex. When pH increases, there takes place dissociation of the carboxyl groups of the macrochains, leading to changes in the external layer of the particles only. It may be therefore concluded that the particles of latex A-B have the structure of "core-shell" type.

When latex A-B dried in a teflon cell, a continuous elastic

film is formed; taking into account rigidity of the particle core, this fact once again confirms the structure of the "core-shell" type.

Studying the mechanical properties of films (stress-strain dependence, creep), we compared the behaviour of films resulting from drying of the latex with the behaviour of films obtained from solution of corresponding latex films in dioxane. In the latter case latex films were dissolved in dioxane to 3% concentration of the polymer, the solution was repeatedly applied to a teflon support and dried under room conditions to obtain a film of required thickness (0.3 mm); after that the film were kept in a vacuum cabinet for 14 days to remove residual solvent.

Investigation of cast films from latexes A+B and A-B has revealed incompatibility of their constituent polymers (PMMA and MMA-BA-MAA copolymer): films cast from solutions are turbid, whereas latex films are transparent; electron microphotographs from replicas of solution film of latex A-B distinctly demonstrate phase separation which has taken place in it. This testifies to the fact that the investigated film-formers were of composition type.

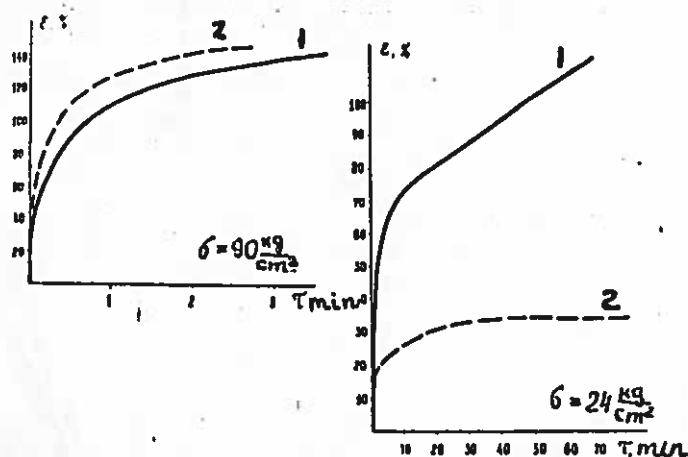
Tensile strength and elongation at break characteristics of the films are given in the table which follows.

Latex	Type of film	Tensile strength, kg/cm ²	Elongation at break, %
A-B	Latex	210	290
A-B	Cast	155	333
AB	Latex	Continuous film is not formed	
AB	Cast	130	415
A+B	Latex	135	250
A+B	Cast	160	283

As can be seen, the method of preparing latexes and films sub-

stantially influences the mechanical properties of the polymer having the same composition. Though films A+B, AB and A-B cast from solutions are close in their mechanical properties, latex films of these polymers sharply differ.

The identify of properties of cast films testifies to the identify of the structure of macromolecules. On the other hand, the same polymers in latex form give films with different properties, and this is definitely associated with the specific structure of the composition latex polymer. The "core-shell" (Williams and others) structure and the presence of a transition layer between the core and the shell are, evidently, responsible for the high strength and film-forming properties of latex polymer A-B. Such structure is confirmed by the investigation of creep of cast and latex films of this polymer under various stresses (Fig. 1). As can be seen, under high stresses the



film cast from solutions is deformed stronger than the latex one, whereas under small stresses creep curves, as it were, change their places: the latex film undergoes greater deformation. This can be explained by that under small stresses elastic shell of the

globules of the composition polymer deforms first of all, whereas under high stresses the entire system reacts to them.