

A.S.Dunn

Since the trickle of contributions from the New World now seems to have dried up entirely I am sending out this issue of the Newsletter without further delay. Unfortunately because of the summer vacation we were rather late in sending out the reminders on the arrival of which members seem to rely completely to stir themselves into activity, discover what their students have been doing, and compose a suitable contribution. I did get some reaction from Fitch and Stannett from which I gather that this cannot be done within a week. However Mrs Proctor has now got the dates for despatch of reminders into her 1977 diary and members should have a full month to complete this process for the next issues. I just hope that this will not be so long that members in other continents forget again within that time!

The target for the Spring issue will be to get contributions to Manchester by Monday 18th April 1977 which will allow me a week to get the issue out before the Summer Term begins. Members who have secretaries might ask them now to remind them to start writing their contributions on 30th March or thereby!

The Annual Meeting, held at Lehigh in June, decided to relax the rule requiring a contribution to each issue of the Newsletter for industrial members only since they cannot rely on having appropriate declassified results available at the required times. However they will be expected to contribute to the Newsletter when they can, attend the annual micro-symposium where their comments have been found most valuable, and circulate preprints or reprints of any relevant material published from their laboratories. The Annual Meeting decided to invite Andy Klein, Andy Homola, Tim Paxton, Per Stenius, Tim Paxton, and Prof. Watillon to join the Group. They have all accepted and we shall be expecting to hear from them in time for the Spring issue.

Bob Fitch reported that the proposal to hold a Gordon Research Conference on Polymer Colloids in the summer of 1977 had been favourably received when first put to the Director and Chairman of the Board verbally but he was still awaiting a reply to the formal proposal in early July. If the proposal is accepted he will presumably notify members of the dates selected as soon as the information is available since the intention would be to hold the Annual Meeting of the Group during the Conference similarly to the 1975 Meeting during the Advanced Study institute at Ironheim.

The success of the 'Control of Particle Size in Polymerisations' Symposium in London on 23rd November seems assured with a near capacity audience likely. The date for the 1977 'Emulsion Polymerisation' Symposium has now been fixed as **Tues. 27 Sept. in London** and it looks as though David Farmer will be able to get together an attractive programme for it. Any member who might be able to offer a contribution could write to Dr Farmer at Vinyl Products Ltd., Mill Lane, Carshalton, Surrey. The second circular for the IUPAC International Symposium on Macromolecules MACRO DUBLIN 1977, 17-22 July has been issued. There are four themes: anionic polymerisation, fine structure of polymers, polymer reagents and catalysts, and polymer engineering. Offers of Contributed Papers are asked for now: texts for preprinting are required by 28 February 1977. The A.C.S. Polymer Chemistry Division has announced a further Emulsion Polymerisation Symposium for the **SEPTEMBER 1979 Washington** Meeting but the Chairman for this Symposium has not yet been named.

A translation of the Table of Contents of Dr Yeliseyeva's new book on emulsion polymerisation is included in this Newsletter. An English translation would be useful. I have long thought that a thorough review of Russian work in this area was needed particularly as a considerable part of it appears in books and journals which are not translated routinely.

Polymer Colloid Group

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Translated Table of Contents of 'Emulsionnaya Polimerizatsiya i ee Primenenie v Promishlennosti (Emulsion Polymerisation and its Application in Industry)' by V.I.Yeliseyeva, S.S.Ivanchov, S.I.Kuchanov, and A.V.Lebedev (deceased) 'Chimia' Publishing House, Moscow, 1976. pp 240. R O.98.

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24 SEP 1976

INTRODUCTION

An interesting paper describing the effect of various liquid additives upon the emulsion polymerisation of styrene was presented by Seymour and his co-workers⁽¹⁾ at the American Chemical Society "Emulsion Polymers" Symposium held in Philadelphia in April 1974. The full text of this paper has subsequently been published⁽²⁾. It reports the results of a study of the effects of various good and poor viscous and non-viscous solvents upon the rate of emulsion polymerisation of styrene, and upon the molecular weight of the polymer produced.

The rate of polymerisation was found to be retarded by good non-viscous solvents such as benzene, cyclohexane and octane, whose solubility parameters are within 1.5 units of that of polystyrene. The addition of poorer non-viscous solvents such as heptane and hexane caused a slight increase in polymerisation rate. A marked increase in rate was observed when viscous non-solvents such as diisooctylphthalate and mineral oil (Mujol) were added. The addition of a viscous good solvent, dibutyl phthalate, was found to have very little effect upon the polymerisation rate. The effect upon polymer molecular weight was found to depend upon both the nature of the additive and the amount present. In general, those additives which reduced the polymerisation rate also reduced the molecular weight of the product, whereas mineral oil gave a higher molecular weight than the control if present at low level, but a lower molecular weight than the control if present in larger amounts.

These results are interpreted by the authors in terms of the effect of the additive upon the viscosity of the reaction loci and upon the conformation adopted by the polymer molecules which form in the loci. Any tendency for the viscosity of the locus to increase, or for the polymer molecules to adopt a contracted configuration due to the presence of a poor solvent, would be expected to lead to a higher polymerisation rate and a higher polymer molecular weight, due to the operation of the Trommsdorff "gel" effect. Likewise, for the same reason a reduced viscosity, or the presence of a good solvent which encourages the polymer to adopt an expanded configuration, should lead to a reduction in both polymerisation rate and polymer molecular weight.

The purpose of this note is to report and discuss certain results which have recently been obtained at this College concerning the effects of added hydrocarbon diluents upon the rate of the emulsion polymerisation of styrene. They are of interest because they may have implications for the mechanism of styrene emulsion polymerisation in the absence of added diluents.

EXPERIMENTAL

The reaction system used was as follows: styrene + diluent 100, water 200, sodium lauryl sulphate 2, borax 0.76, potassium persulphate 0.01. The grade of sodium lauryl sulphate used was BDH "Specially pure" (99.5) further purified by the method of Harrold⁽³⁾. The function of the borax was to buffer the aqueous phase to pH 9.2. It should be noted that our experimental design differed from that of Seymour et al in one important respect: they added organic liquids in varying amounts to a fixed recipe for the emulsion polymerisation of styrene; we have taken a reaction system for the emulsion polymerisation of styrene and replaced part of the styrene with a hydrocarbon diluent. Thus we have kept the level of styrene + diluent constant whilst varying the ratio styrene: diluent. The values we selected for this ratio were such that the diluent was respectively 10%, 25% and 50% of the total oil phase.

Polymerisations were carried out at 50° under nitrogen in a multi-neck glass reaction vessel fitted with stirrer, condenser, sampling tube and nitrogen inlet. A constant rate of stirring was maintained throughout the reaction. Samples of the latex produced were expelled from the reaction vessel periodically by increasing

determining the total solids contents of the samples so obtained.

RESULTS

Data are available for the rates of emulsion polymerisation of styrene in the presence of various amounts of four hydrocarbon diluents, namely, benzene, toluene, ethylbenzene and cyclohexane. In all four cases, retardation of the polymerisation rate was observed in the presence of the diluent, and, in the case of the aromatic diluents, the retardation was severe. For a reason which will be explained below, particular significance is attached to the results obtained with ethylbenzene. These are summarised in Figs. 1, 2, and 3. Fig. 1 shows the conversion-time curves. Fig. 2 shows a plot of rate of polymerisation vs. concentration of styrene in the oil phase as indicated by the overall polymerisation recipe. Fig. 3 shows the results of Fig. 2 plotted on log-log scales; it indicates that the rate of polymerisation is approximately proportional to the third power of the overall concentration of monomer in the oil phase. The results for polymerisation in the presence of the other two aromatic diluents are similar. The approximate slopes of the log-log plots of rate vs. overall concentration of monomer in the oil phase are as follows: benzene 2.8, toluene 2.7, ethylbenzene 2.7. By contrast, the slope for the same plot for reaction systems which contained cyclohexane was approximately 1.0, i.e., the rate of polymerisation in the presence of cyclohexane is approximately first order with respect to overall monomer concentration in the oil phase.

DISCUSSION

The results we have obtained confirm the observation of Seymour et al that the emulsion polymerisation of styrene is retarded by the presence of non-viscous organic liquids which are good solvents for polystyrene. We have further shown that the polymerisation rate in the presence of aromatic solvents is approximately third order with respect to the overall concentration of styrene in the oil phase, when the reaction systems are such that the ratio styrene: diluent is varied keeping styrene + diluent constant. In the presence of cyclohexane, the reaction rate is approximately first order in monomer concentration.

Why should the rate of polymerisation be so sensitive to the replacement of monomer by an almost^{inert} aromatic diluent for the monomer? The results for ethylbenzene are especially interesting in that what we have done in our experiments is progressively to replace the styrene in the reaction system by its saturated analogue. Ethylbenzene and styrene are almost identical in all respects (including tendency to transfer with polystyryl radicals) except for the presence of the vinyl carbon-carbon double bond in the latter. We have therefore progressively replaced styrene with a non-polymerisable analogue.

But why should this replacement result in severe retardation? If one were to ignore the effect of viscosity upon the rate of polymerisation, then the rate of polymerisation would be expected to be first order with respect to monomer concentration at the reaction loci. Furthermore, since the monomer and diluent are so similar, one might expect that the monomer: diluent ratio at the reaction loci would be the same as that in the oil phase of the reaction system as a whole. Therefore, in the early stages of the reaction at least, the polymerisation rate would be expected to be approximately first order with respect to overall monomer concentration in the oil phase. This is what we have observed for reaction systems in which styrene has been replaced by cyclohexane, but not for systems in which styrene has been replaced by an aromatic diluent.

The most plausible explanation of the retardation in the presence of aromatic diluents is, of course, that put forward by Seymour et al, namely that the "Trommsdorff" gel effect is suppressed when an inert diluent is added. In the presence of the diluent the viscosity of the reaction loci is less than in the absence of the diluent. The retarding effect associated with the dilution of the monomer is therefore supplemented by the retarding effect which arises essentially from an enhancement of the rate of termination relative to that of propagation.

However, this explanation poses other problems. In the first place, the existence of a strong Trommsdorff "gel" effect in the normal emulsion polymerisation of styrene seems to suggest that, even in the early stages of the reaction, large numbers of reaction loci may contain more than one radical, contrary to the conventional hypothesis. But, secondly, why should the presence of diluent molecules which are almost identical with the monomer molecules bring about a reduction in the viscosity of the reaction loci, even at low conversions?

The results given in Fig.1 show that the retarding effect is present right from the earliest stages of the reaction, when a separate oil phase is still present in the reaction system. The phases which are present during that part of the reaction for which a separate oil phase exists are depicted schematically in Fig.4; I refers to a system which contains no diluent, whereas II refers to a system which contains diluent. The system I has a bulk oil phase which is exclusively monomer (M), and reaction loci which comprise monomer which is polymerising to polymer (P). If now some of the monomer is replaced by an analogous non-polymerisable diluent (D), as in system II, then it would be expected that the M + D of system II will behave exactly as the M of system I, except that no polymerisation of D occurs in the reaction loci. Thus if, as is commonly assumed, in both systems equilibrium exists between the bulk oil phase and the reaction loci, then it will be expected that the (M + D):P ratio of system II will equal the M:P ratio of system I. The reaction loci would therefore have similar viscosities in the two cases, and the only retardation to be expected in system II is that due to the reduction in monomer concentration. However, a different conclusion is reached if it is supposed that the reaction loci and bulk oil phases are not necessarily in equilibrium as polymerisation proceeds. Such an assumption was, of course, made by Grancio and Williams⁽⁴⁾ in advancing their "core-shell" model for the polymerising polystyrene/styrene particle. Suppose that the monomer in system I cannot diffuse sufficiently rapidly from the bulk oil phase to the reaction loci to maintain the M:P ratio at its equilibrium value as polymerisation proceeds. Replacement of part of the monomer by a non-polymerisable analogue, as in system II, will lead to a reduction in the rate of polymerisation. As a consequence the ratio (M + D):P will rise above the M:P ratio of system I. The viscosity of the reaction loci in system II will then be lower than that in system I, and this will in turn lead to a further reduction in rate of polymerisation by suppression of the Trommsdorff "gel" effect.

This view of the reaction mechanism gives a simple explanation for the pronounced retarding effect of inert monomer diluents at all stages of the polymerisation. It does, however, carry the implication that equilibrium certainly does not exist between the bulk oil phase and the reaction loci in systems for the normal emulsion polymerisation of styrene, and, indeed, may not exist even in systems which contain inert diluents.

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4. M. R. Grancio and D. J. Williams, *J. Polym. Sci.*, Pt. A-1, 1970, 8, 2617

ADDITIONAL NOTE

Sandy Dunn has kindly drawn my attention to an implicit assumption which has been made in the discussion section, namely, that the presence of the diluent does not greatly affect the particle concentration. I intended to mention this assumption, but unfortunately overlooked it. We are looking into the effect of diluent upon particle concentration at the present time. The preliminary indication is that the marked retardation cannot be explained in terms of a reduced concentration of reaction loci.

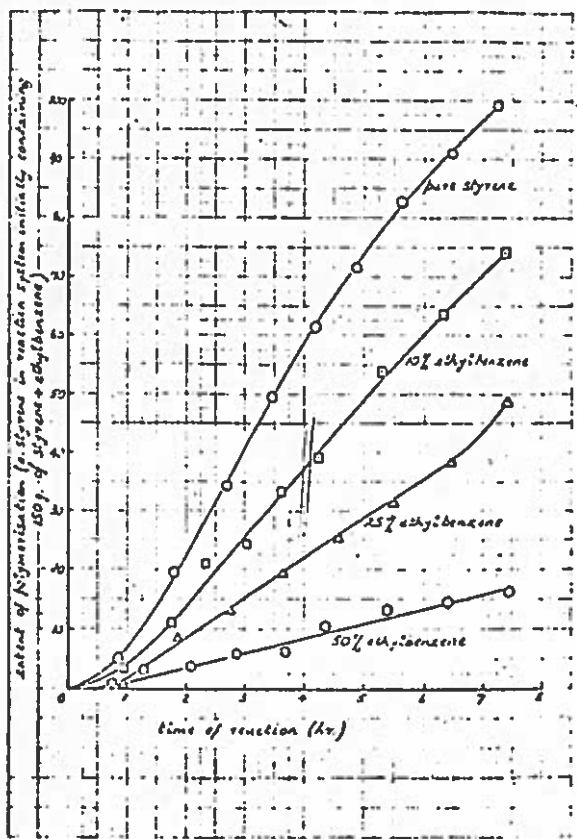


Fig. 1

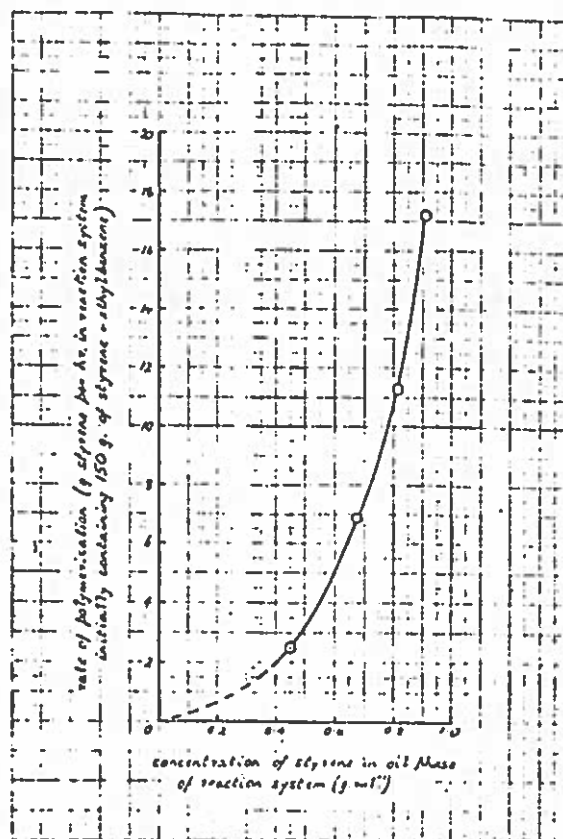


Fig. 2

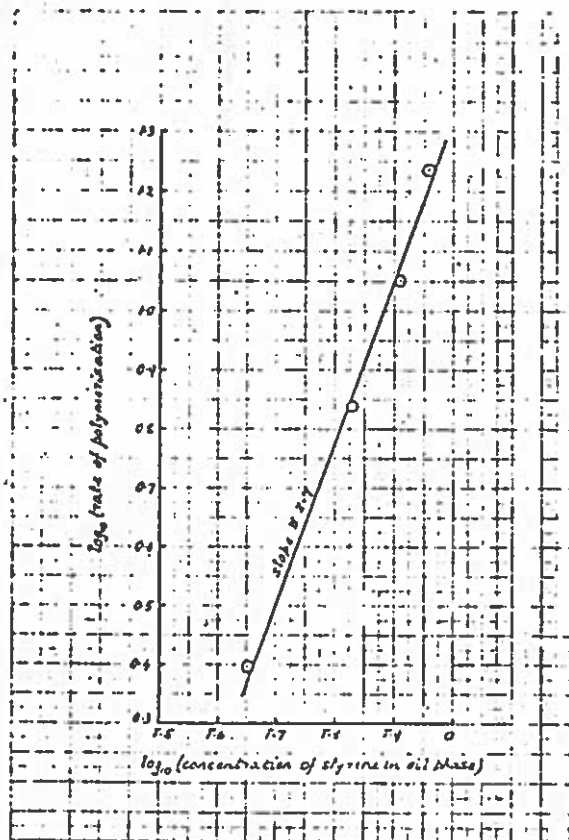


Fig. 3

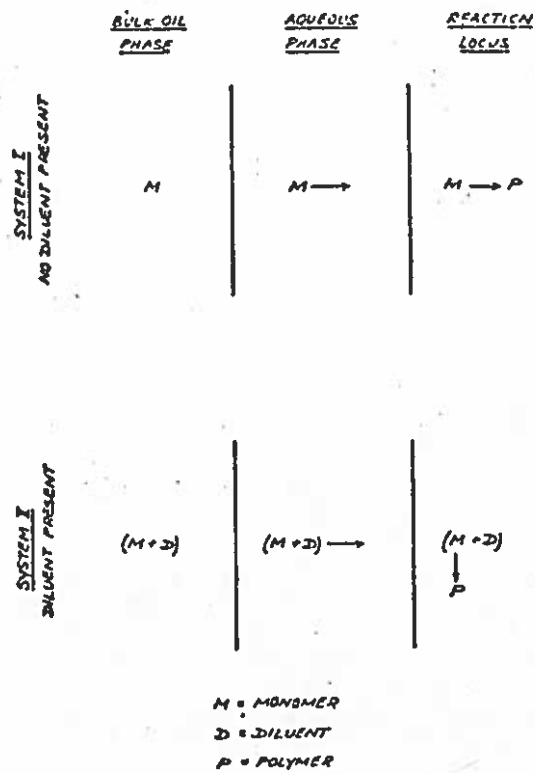


Fig. 4

Messrs. Al-Abbasi and Al-Naama have just finished writing their M.Sc. Dissertations. Al-Abbasi's project was initially to optimise the yield in the first stage of the preparation of the water soluble azo initiator azobis(sodium α -methylbutyronitrile sulphonate) involving the reaction of ethyl acetoacetate with potassium formaldehyde bisulphite in which the yield reported by Raschig & Frahl is only 20%. Unfortunately the lectures on optimisation procedures which I believed to be part of the M.Sc. course turned out not to have been given this year, I was under the illusion that sodium formaldehyde sulphonylate (which is commercially available) was an alternative name for sodium formaldehyde bisulphite. It isn't. In addition determination of the yield of sulphomethylated acetoacetic ester is difficult. Consequently some alternative routes to the desired product were considered. Starting from bromoacetone (rather than chloroacetone) and converting it to sodium bromomethane sulphonate seems promising an 80% yield of pure material being obtained. Unfortunately equal success in the Strecker reaction with sodium cyanide and hydrazine sulphate and subsequent oxidation to the azo compound was not attained, the final yield being 16%. However this is still much better than achieved here previously and should be capable of being much improved with some further work. Al-Abbasi is in the market for a research place for a Ph.D. in polymer chemistry although the result of his grant application to the Iraq government will not be known till the end of the year. Any potential supervisor could contact him at the Chemistry Department here.

Al-Naama has prepared a surfactant free polystyrene latex and determined adsorption isotherms of sodium dodecyl sulphate and sodium decyl sulphate on it in presence of enough sodium sulphate to maintain a constant ionic strength at room temperature using a colorimetric method for determining the equilibrium solution concentration of surfactant depending on the extraction of the complex formed with an excess of the cationic dye Methylene Blue into an organic solvent. This was eventually very successful, good Langmuir isotherms being obtained. However the 'surfactant-free' polystyrene latex gives a large blank when no anionic surfactant has been added although the Methylene Blue itself, after recrystallisation, gives only a small blank: this is attributed to the presence of water-soluble polystyrene sulphate oligomer in the surfactant-free latex. Al-Naama returns to Basra in November to take up a post with the Iraq National Oil Company.

Mr W. Al-Shahib has been determining adsorption isotherms too, but by using the de Nouy tensiometer to determine equilibrium surfactant concentrations at 60°C on latices prepared using the same surfactant at that temperature but without added salt apart from initiator residues. Under these conditions sodium dodecyl sulphate gives a Langmuir adsorption isotherm but sodium decyl sulphate does not appear to be adsorbed at all below a threshold concentration above which Langmuir type adsorption is observed. Although this result seems incredible at first sight, it is not, on reflection, implausible. The lowest alkyl sulphates (C_6 probably) are not adsorbed at all whilst, on the other hand, it is possible to use short alkyl chain length emulsifiers (e.g. C_8) if a high ionic strength is used. There was little added salt; the effect is probably attributable to ionic strength, the ionic strength due to the surfactant itself becoming high enough to produce adsorption as the concentration is increased. Of course some further work will be required to confirm this tentative conclusion.

Sodium tetradecyl sulphate also give a Langmuir isotherm and although the amount adsorbed in the saturated monolayer appears to be slightly less than for the other two alkyl sulphates this is probably because of competitive adsorption of teradecanol which may be present in the specimen in small amounts - the surface tension-concentration curve of this sample has a minimum which was absent for the other samples. The initial concentrations used to achieve equal concentrations of micellar surfactant would all be sufficient to produce a saturated close-packed monolayer on the latex particles initially formed. This has a surface concentration of 1.65×10^{-10} mole m^{-2} at $60^{\circ}C$ but falls to a much lower value as the latex particles grow. Although the Interval II rates and the final number of particles formed are equal for the homologous series of alkyl carboxylates and alkyl sulphates under conditions of equal micellar concentration, the Interval I rates are different being much lower for the lower members of the series. Estimates of micelle size from different laboratories using different techniques are not consistent but the size of the micelles, the number formed, and their surface area are unlikely to be precisely equal under conditions of equal micellar concentration, it seems probable that they will not differ by as much as a factor of two within a homologous series. Although we have not made any precise measurements of initial rates (for which the gravimetric technique we are using is not very suitable) these must differ by a much larger factor than this - a factor of 10 or more. It therefore looks as though the number of particles formed is not determined by the surface area of the micelles initially present but by the stability of the latex particles once they are formed which is determined (apart from a small contribution from charged polymer end-groups) by the surface concentration of adsorbed surfactant. Since a correlation between the solubilising power of a surfactant and the Interval I rate has been established (cf. Bovey, Kolthoff et al. 'Emulsion Polymerisation' Fig. V-10 and V-11) it looks as though this is what primarily determines the initial but not the ultimate (Interval II) rate. We should probably try to establish this correlation for the solubilisation of styrene in the homologous series of surfactants. It is possible, of course, that there may be a correlation between the surface area of the monomer-saturated micelles and the initial rate. This, too, is perhaps a point we should seek to establish. Although large numbers of latex particles can be formed below the c.m.c., the increase in the final particle number which occurs for a water insoluble monomer as its concentration is increased through the c.m.c. is so large that it appears that when a surfactant concentration above the c.m.c. is used 999 out of every 1000 particles must have originated from the micelles.

Polymer Colloids Newsletter Contribution, October 1, 1976

Case Western Reserve University

I. M. Krieger

6 OCT 1976

In the past, some attempts were made to polymerize vinyltoluene, using emulsifier-containing recipes suitable for production of monodisperse polystyrene latices. These were usually unsuccessful. Because polyvinyltoluene possesses certain advantages over polystyrene, due to its lower density and higher resistance to thermal decomposition, a reinvestigation was undertaken. This time, the starting point was emulsifier-free recipes using ionic comonomers.

Recipes used were adapted from those which had proved successful with styrene. Monodisperse latices with particle diameters in the range 0.1 to 0.3 μ were obtained. The effects of varying monomer content, initiator concentration, ionic comonomer content and ionic strength have been studied. From the results to date, it appears that the final particle diameter is less sensitive to these variables than in the corresponding recipes with styrene. This is especially true for monomer content; in one example, a four-fold increase in monomer content produced no change in particle diameter. In contrast with our experience with styrene, we have been experiencing considerable difficulty in scale-up from bottles to 2-liter resin kettle reactors.



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McGILL UNIVERSITY

21 OCT 1976

S.G. Mason and A.A. Robertson

Contribution to Polymer Colloid Group Newsletter September 1976

Studies of particle interactions in suspensions of latex spheres have been continuing. The work of van De Ven and Mason reported a year ago in the September 1975 Newsletter on stabilized and destabilized latex sphere suspensions in dilute electrolytes in shear flow has been extended to systems in which polymers are adsorbed on the particle surface. Detailed studies of the periods of rotation and trajectories of doublets of latex spheres have been made using freshly prepared surfactant-free polystyrene latexes of 2.6 to 4.0 μm diameter with and without polymer. In addition, models of polymer-bridged doublets of macroscopic polystyrene or polyethylene spheres linked by nylon or elastomer fibers were studied.

1. Latex sphere suspensions.

With surfactant-free suspensions of 2.6 μm dia. spheres in 10^{-3}M KCl, measurements of the period of rotation of doublets in Poiseuille flow appear to indicate the existence of three types of doublets:

(i) fused doublets (rigidly coupled) of touching spheres having an equivalent axis ratio $r_e = 2.0$, which correspond to van de Ven's "primary" doublets;

(ii) doublets having very small gap < 1 nm between spheres, presumably consisting of the so-called Stern or outer Helmholtz layer, in which the particles are in a deep primary energy minimum governed by Born repulsive and van der Waals attractive forces, with $r_e = 2.3$ and

(iii) doublets in which the particles are captured in a secondary energy minimum described by DLVO theory of colloid stability and with $r_e > 2.4$. In van de Ven's recent work no distinctions were made between (ii) and (iii), both of which he called "secondary" doublets; in both cases the spheres are not rigidly coupled so that relative rotation of each sphere is possible and the distribution of the dimensionless periods of rotation shows peaks corresponding to types (ii) and (iii). The existence of a type (ii) doublet in which the spheres are not locked together may explain some discrepancies between van de Ven's experimental results and theory, such as the short separation distance of his secondary doublets, the high concentration of electrolyte necessary to bring about the transition from secondary to primary minimum, and the existence of secondary doublets under conditions not predicted by theory.

The trajectories of separating doublets of latex spheres were studied in the presence of 1 to 2 p.p.m. cationic polymer (Cat-floc, Calgon Corp.) at which concentration the zeta-potential is close to zero. The existence of unexpectedly long range (2 to 5 μm) interactions between

the particles during the process of collision was demonstrated. Occasionally, these resulted in capture and the formation of a non-separating doublet in which the sphere centres were separated by as much as 2 to 3 particle diameters. From the observed dependence of the period of rotation and the shear rate, it is believed that the particles in these doublets were connected by a flexible bridge of the dissolved polymer.

2. Model doublet.

To gain further insight into the observations of the rotation of polymer-bridged doublets, some experiments on the rotation of model dumbbells in Couette flow were made.

The periods of rotation T of dumbbells of 1.1 and 2.4 mm dia. spheres joined by a nylon fiber and suspended in viscous oil were in excellent agreement with Wakiya's theory for rigid dumbbells over a range of shear rates G from 0.4 to 6 sec^{-1} and inter-particle distances from 3.5 to 13 sphere radii.

Flexible dumbbells of 3.0 mm dia. spheres joined by an elastomer filament fiber (Lycra, Du Pont) rotated in orbits in which the length of the particle axis varied periodically with the connecting fiber exhibiting appreciable bending, and the ends of the particle axis described an elliptical path. Surprisingly, however, at a given G the angular velocity of the doublet throughout complete rotations was in excellent agreement with Jeffery's theory for rigid spheroids using the value of r_e calculated from its measured period of rotation TG .

However, TG increased with increasing G by contrast to the rigid dumbbell where it was independent of G , and TG did not increase linearly with increasing the maximum interparticle distance. The investigation is continuing.

In the April 1976 Newsletter, we reported beginning rheological studies of dispersions of hydrolyzed polyacrylonitrile-grafted cellulose (150% graft level). These are dispersions of long rod-like cellulose protofibrils of about 35-45 Å wide and with very high axis ratio. The hydrolyzed PAN chains (polyacrylic acid (PAA) and polyacrylamide (PAAM copolymer) are believed to be grafted to these elements and act to stabilize the cellulose dispersion.

Using a cone-and-plate viscometer the apparent viscosity - from torque measurements - and the shear modulus G - from normal force measurements are obtained for suspensions at dilutions from 1.12% to 0.2% and at shear rates between 2.5 cm^{-1} and 250 cm^{-1} . At higher concentrations ($> 0.5\%$) the system is a gel. The concentration dependence at various shear rates and the shear dependence at various concentrations show a pattern that is consistent with hypotheses proposed for systems characterized by dynamic network formation-destruction equilibrium processes.

If the cone and plate geometry is replaced by eccentric co-rotating disks a reciprocating shearing motion is produced and the loss

and storage modulus can be determined. The dependence of these on frequency and on concentration can also be interpreted in terms of a network model.

Intrinsic viscosities at 5 different ionic strengths have been determined by capillary viscometry and introduced into the Simha equation to estimate the size (axis ratio r , specific volume V_{sp}) and the lateral expansion coefficient α of an equivalent hydrodynamic model of the rod-like particle. It was found that the intrinsic viscosity was linearly related to the reciprocal square root of the ionic strength in conformity with predictions. It has also been possible to show that the calculated values of V_{sp} in water and isoionic suspensions can be used to predict the experimental gel point. Apparent axis ratios range from 8.7 to 110 for intrinsic viscosities of 32.2 dl/g to 8.7 dl/g respectively.

27 AUG 1976

Polymer Colloids at the University of Sydney

Reporter: D. H. Napper

1. We have been interested for the past few years in obtaining analytical solutions for the Smith-Ewart equations, without adopting the steady-state approximation (SSA). The point of such studies can be seen most clearly if we take the (perhaps hypothetical) case of a seeded latex that obeys the Smith-Ewart case 2 kinetics ($\bar{n} \sim \frac{1}{2}$). The steady-state approximation is clearly quite unable to describe directly the approach to the steady-state condition. It merely tells you what happens when you get there. A complete solution is accordingly required as seeded polymerizations are easily performed.

The Smith-Ewart equations can be solved numerically, at least in principle, without adopting the SSA. John Gardon moved in this direction in his work, although he ignored free radical exit from the particles. In principle, it is also possible to use the O'Toole results for \bar{n} to calculate non-steady state kinetics. But the integrations required to calculate % conversion vs. time curves cannot be handled analytically. Resort to numerical computation is again mandatory.

We have obtained analytical solutions for the Smith-Ewart equations without adopting the SSA and with the inclusion of both the exit and bimolecular termination terms. These give the O'Toole results in the limit of the steady-state.

We have also extended the matrix approach to include initiation and particle growth. The general equation obtained is

$$\frac{\partial \underline{n}}{\partial t} = \underline{\Omega} \underline{n} - \frac{\partial}{\partial v} (\underline{K}^T \underline{n})$$

27 AUG 1978

Where \underline{n} = vector whose i -th component is the volume distribution of the i -th type of particle,

$\underline{\Omega}$ = matrix describing kinetic coupling between the particles,

\underline{K}^T = the transpose of the vector \underline{K} such that its i -th element describes the volume growth of the i -th species.

This differential equation reduces to the Smith-Ewart equation in the expected limit. It can be solved numerically in most cases and analytically in some particular cases. The equation includes elements of both the deterministic and stochastic approach.

2. We have now completed our studies on sterically stabilized emulsions and have shown that they exhibit the same general behaviour as latex particles. Of course, it is necessary to ensure that the anchoring of the stabilizing moieties is suitably strong but this is fairly easily achieved. The strong parallelism between the thermodynamic stability limit of latex particles and emulsion droplets is scarcely surprising but it has lacked experimental verification heretofore.

23 SEP 1976

Introduction

A combination of commercial pressures, the holiday season, & the 'York Symposium' has made it difficult to find items suitable for this note. Work continues on emulsions stabilised by polymeric surfactants, but there are no reportable results.

York Conference

Over the last two decades, I.C.I. has held every four or five years an internal symposium on Colloids & Associated subjects; the most recent, at York, has just ended. Clearly, most of the proceedings are confidential; however, certain general points may be worth reporting:

- 1) The range of attendance & contribution from Divisions, Overseas Associates & Senior Management far exceeded that at previous meetings. It seems that the broad underlying importance of the subject is finally becoming accepted!
- 2) The desirability of considering many biochemical processes, eg. Phagocytosis, as problems in physical chemistry without invoking 'vitalist' attitudes, is gaining ground.

In this context there is an interest in 'complicated' aqueous polymer colloids (eg. particles sterically-stabilised by polyelectrolyte soluble groups & dispersed in salt solutions) as possible models.

- 3) There is a growing interest in high phase volume dispersions, especially those in which very weak flocculation is suspected. The conventional methods of detection (light-scattering, sedimentation behavior etc.) are not applicable, but two sensitive rheometers capable of measuring yield stresses below 1 dyne/cm^2 were described; these should be able to detect flocs in which the individual association energies are of the order of kT .

The Trondheim Co-operative Research Project

contribution from D.E. Yates, R.H. Ottewill and J.W. Goodwin

27 SEP 1976

1. Latex prepared following the "Homola" recipe

1-1 Preparation

Homola's conditions were all followed.

final pH = 2.6
final volume fraction, ϕ = 7.00%
yield of latex = 81%

1-2 Particle Size Analysis

Method: Electron microscopy, magnification calibrated by 460 nm diffraction grating and 1000 particles sized with a Zeiss TG23 Particle Size Analyser.

Number average diameter 459 nm
Standard deviation 11 nm

1-3 Purification

Method: The latex was filtered through washed glass wool and then purified in the following manner.

1-3 Dialysis - carried out in well-boiled Visking tubing against distilled water. The ratio of dialysate to latex was 10 to 2. The dialysate was changed every day for 22 changes.

1-3 Ion exchange. Carried out with Dowex resins purified by the Van den Hull and Vanderhoff method. The batch procedure was used with about 2 g wet resin for 100 ml of latex. A total of 5 consecutive exchanges were made.

1-4 Surface Group Analysis

Method: Conductometric titration of 25 ml aliquots of 3-8% latex with NaOH. All titrations were carried out in 10^{-3} M NaCl.

Results

<u>Purification Method</u>	<u>1st Endpoint₁ /μ moles g₁</u>	<u>2nd Endpoint₁ /μ moles g₁</u>
Ion exchange	4.2 ± 0.8	none
Dialysis	2.57 ± 0.01	5.5 ± ? *
Dialysis then ion exchange	7.4 ± 0.8	none

* The second endpoint was difficult to locate and varied with titration rate and precondition conditions.

2. Characterization of Vanderhoff's Latex

2-1 Purification

The sample was diluted to 10% and dialysed in the manner described above for 32 changes of the dialysate. The ratio of dialysate to latex was 25 to 1.

2-2 Results of Conductometric Titration

conditions - 2.24 g in 25 ml (9.0%), 10^{-3} M NaCl titrated with 0.1 M NaOH.

1st Endpoint	1.21 μ mole g^{-1}
2nd Endpoint	4.29 μ mole g^{-1}

Final Note

The latex supplied by Professor Krieger has again grown a green mould, so we discontinued our purification of it.

20 SEP 1976

F. L. Saunders, The Dow Chemical Co., Midland, Mich.

The following papers have been published or will be published in the near future. Copies of these articles will be sent to Polymer Colloid Group Members by separate mailing.

1. "Hydrodynamic Chromatography. A New Approach to Particle Size Analysis", H. Small, F. L. Saunders, J. Solc.
To be published in Advances in Colloid and Interface Science.

The development and application of Hydrodynamic Chromatography as a new technique for the particle size analysis of various colloidal systems is described. The measurement is based on the observation that the rate of transport of colloidal particles through a packed bed of spherical particles depends on such factors as the particle size of the colloid, size of the packing and ionic strength of the aqueous phase. Thus, under appropriate conditions and suitably calibrated, HDC offers a relatively fast, precise means of particle size measurement in the sub micron range.

From a chromatographic point of view, the separation is unusual in that it takes place solely within the interstitial volume of the column. Another interesting feature of this separation is that the elution rate of the particles varies inversely with its particle diameter and always faster than the void volume. A mechanism has been developed where it is proposed that the separation is determined by hydrodynamic effects in the void volume of the packing and elution rate is affected by electrostatic and van der Waals interactions between the colloid and the packing. However, the mechanism is qualitative and due to the complex nature of the system a quantitative mechanism awaits considerably more experimental and theoretical work.

A number of applications of HDC in analyzing the particle size of colloidal systems include characterization of latexes for particle size, particle size distribution, agglomeration and particle growth in emulsion polymerization. The particle size of several inorganic colloids has also been measured.

Additional studies on latex systems described here indicate further applications of HDC in characterizing latex systems in terms of factors that affect its hydrodynamic particle size. It has been shown that the size of latex particles, susceptible to swelling by changes in the aqueous environment, can be measured by HDC. Thus, the effect of latex composition and its aqueous environment on the effective particle size of the latex can be investigated which is of significance in terms of colloidal properties of the latex. While the particle size measurements by HDC of polystyrene latexes equilibrated with a swelling solvent did not agree with independent swelling measurements, resolution of this discrepancy and further work in this general area should be of interest as a possible method of measuring the swelling index of cross-linked latex particles.

HDC also appears to offer a unique method of characterizing agglomeration in latex systems. The observations made on agglomeration of latex particles produced by polymeric thickening agents demonstrated this application. Limited agglomeration of particles is difficult to measure, and the ability of HDC to give a relative measure of agglomerate formation should be useful in future studies on latex stability and the effect of various additives on latex systems.

2. "Characterization of Carboxylated Latexes by Potentiometric Titration", D. A. Kangas. Presented at 172nd ACS Meeting, San Francisco, Calif. Aug. 1976, Div. Organic Coatings & Plastics Chem.

For some latexes, such as crosslinked carboxylated styrene-butadiene latexes, the slow rate of neutralization has made it difficult to obtain both the equilibrium titration curve and the total amount of carboxylic acid needed to calculate apparent ionization constants as a function of degree of neutralization. A technique has been devised for direct determination of total carboxylic acid by potentiometric titration in a mixture of water and organic solvent. Equilibrium curves in water were determined for styrene-butadiene latexes containing either copolymerized acrylic or methacrylic acids. All of the carboxylic acid in both latexes was neutralized after three days standing. The

potentiometric titration curves can be divided into two parts, a fraction which is immediately neutralized and a fraction which is slow to neutralize. The ionization characteristic of the immediately neutralized fraction is the same as counterpart soluble homopolymeric acid. The slowly neutralized fraction has low values of ionization constant indicating that additional energy is needed for ionization compared to soluble homopolymer acid.

3. "Old, new, borrowed, blue" L. B. Bangs, M. T. Kenny.
Industrial Research 18 Aug. 1976, p. 46.

A non-technical description of the processing which yields uniform latex particles. Describes treatment of carboxylate-containing uniform latex particles and application of these particles in various immunological and biomedical uses and in industrial processing.

by M. Nomura

Dept. of Industrial Chemistry, Fukui University, Fukui, Japan

28 SEP 1976

1) Rate of Polymerization of VAC in Aqueous Media

We have finished preparing manuscript for publication and submitted it to the J. Appl. Polymer Sci. with a title "A Kinetic Study of Vinyl Acetate Polymerization in Aqueous Media in the Absence of Emulsifier". We can send a copy of the manuscript if requested.

2) Continuous Flow Emulsion Polymerization of VAC in a CSTR

3) Effect of Free Radical Desorption on the Nucleation of Polymer Particles in Emulsion Polymerization

The state of these studies were reported in the previous Newsletter. We have now finished these studies and are now preparing manuscripts for publication in the J. Appl. Polymer Sci.

4) Gel-Effect in the Emulsion Polymerization of Styrene

It is well known that polymerization rate is accelerated at advanced degree of polymerization in a bulk, solution and emulsion polymerization system. The increase in rate has been ascribed to the decrease in the value of the rate constant of termination, this decrease being due to the decrease in diffusion rate of polymer radicals owing to the increase in the viscosity of the environment where polymer radicals are located. The factors which increase the viscosity of the environment are supposed to be, for example, molecular weight of polymer in the environment, composition in the environment and so on. This study aims to make clear first experimentally the gel-effect in the emulsion polymerization of styrene. In Figs. 1 and 2 is illustrated the effect of the molecular weight of polymers in the environment on the degree of gel-effect. In this experiment, we adjusted the molecular weight of polymers formed by the use of transfer agent (n-dodecylmercaptan) denoted by T. It is seen from these figures that molecular weight of dead polymers and active polymer radicals in the environment gives little or no effect on the variation of \bar{n} in the particles with progress of polymerization. This result differs from that by Gerrens (Zeitschrift fur Electrochemie, 60, No.3 334 (1950)). He pointed out that $\bar{n} \approx 0.5$, the degree of polymerization of polymers in the particles. Our results suggest that the variation of the rate constant of termination with progress of polymerization will be correlated with polymer weight fraction in the particles, as was also the case in the emulsion polymerization of VAC.

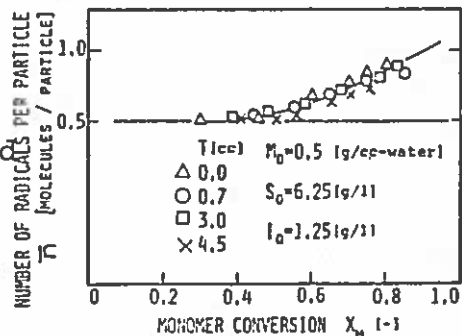


Fig.1 \bar{n} vs conversion

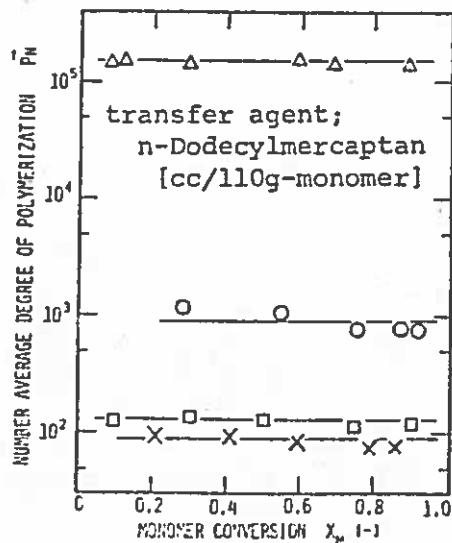


Fig.2 degree of polymerization vs conversion

30 SEP 1976

Report from the Institute of Industrial Chemistry.

It was decided that the activities as regards education and research in petrochemistry should to a great extent take place at our Institute.

In this connection we have just got two new members of the staff, one full professor Dr. David L. Trimm in heterogeneous catalysis, and an associated professor, Dr. Olav T. Onsager in metal organic chemistry.

As I have been the administrator of this, very much time has gone to get all these things settled.

However, we have continued our work in emulsion polymerization along two lines.

1. Theory and practice of particle formation.

This work has been led by F.K. Hansen. We send in our first paper in a series one of these days. It concerns the theory of particle formation where we consider in detail the following effects on formation of primary particles.

- a. Reversibility of oligomer capture. b. Electrostatic repulsion. Moreover limited flocculation of the primary particles is treated in detail.

As you perhaps will have seen we have published a relatively large review paper in Rubber Chemistry and Technology, August 1976, where we summarize some of the results. However, especially the electrostatic repulsion factor is much more thoroughly treated in our new paper.

The reversibility factor is expressed as

$$U_j = \frac{a_j D_{pj} (X_j \coth X_j - 1)}{D_{wj} + a_j D_{pj} (X_j \coth X_j - 1)} \quad (1)$$

where a_j is the distribution coefficient for the oligomer between particle and water.

$$X = r(k/D_{pj})^{1/2}$$

$$k = k_p [M]_p + nk_t/v$$

n being the number of radicals in the particle.

With a negligible electrostatic repulsion effect the capture constant for oligomer of chain length j is thus for one particle:

$$k_{cj} = 4\pi D_{wj} r U_j \quad (2)$$

I should like you to note an obvious error in the paper in the Rubber Chemistry and Technology. It is said in Equation (33) that if reversibility factor and electrostatic repulsion come into play we have:

$$k_{cj} = 4\pi D_{wj} r U_j / W_j \quad (3)$$

where W_j is the electrostatic repulsion factor. This is obviously misleading as U_j is a factor of W_j . To write it in this way, which would seem to indicate that U_j and W_j are mutually independent, is in fact inconsistent with the "first law" in kinetics, namely that of microscopic reversibility. The oligomer has to pass the same barrier forth and back. Equation (3), with independent U_j and W_j would mean that although the oligomer had to pass the energy barrier caused by W_j when it was captured, this was not necessary when it leaves.

Now it is easy to combine the effects of U_j and W_j , and this has been done in our new paper. The result is that the capture constant is given by:

$$k_{cj} = (4\pi D_{wj} r / W_j) \frac{a_j D_{pj} (X_j \coth X_j - 1)}{D_{wj} / W_j + a_j D_{pj} (X_j \coth X_j - 1)} \quad (4)$$

U_j in Equation (3) should be replaced by U_j' given by

$$U_j' = \frac{W_j a_j D_{wj} (X_j \coth X_j - 1)}{D_{wj} + W_j a_j D_{pj} (X_j \coth X_j - 1)}$$

Equation (4) does in our opinion give a good description of the capture rate. Note that in case that $D_{wj} / W_j \ll a_j D_{pj} (X_j \coth X_j - 1)$ we have an irreversible absorption with a value of k_{cj} :

$$k_{cj} = 4\pi D_{wj} r / W_j \quad (5)$$

If $D_{wj} / W_j \gg a_j D_{pj} (X_j \coth X_j - 1)$:

$$k_{cj} = 4\pi r a_j D_{pj} (X_j \coth X_j - 1)$$

It is one interesting aspect which is worth-while considering. Let us for simplicity assume $W_j = 1$, and that in Interval II we have:

$$D_{wj} \ll a_j D_{pj} (X_j \coth X_j - 1)$$

i.e. $k_{cj} = 4\pi D_{wj} r$.

Now as we pass into Interval III the value of D_{pj} decreases. The value of X_j increases, the value of $D_{pj} (X_j \coth X_j - 1)$ decreases and we reach as shown in the paper cited a limiting case (B I) where the value of k_{cj} is given by:

$$k_{cj} = 4\pi r^2 (D_{pj}k)^{1/2} a_j$$

Therefore we will expect that as we proceed in Interval III, the rate of capture will decrease and moreover the dependency on the particle will change from a rate of capture proportional to r to a proportionality with r^2 . We are for the moment checking this out. One thing which is clear from the above theory and observed in practice is that at a given value of N and r , new formation of primary particles is more pronounced as we proceed in Interval III.

b) We have continued our work with emulsions of monomer. We investigate a lot of additives. Our results show, we believe, that the effect of the additives, as discussed in the above cited paper, is chiefly due to a pure thermodynamic hindrance of degradation by diffusion. The theory of this is worked out and will be published soon. We have, however, also observed that with some additives we do in addition find indication of an interfacial effect of the additive which manifests itself by a hindrance of monomer diffusion across the interface. This is true for long chain fatty alcohols. We are working to reduce the requirements for homogenization of the mixture.

In our laboratory was found experimentally [1-3] that in the course of the emulsion polymerization (EP) of the monomers of the acrylic series in the presence of a persulphate the number of the particles at the steady-state stage varies significantly as a result of their flocculation; the steady-state stage continues for some time after disappearance of the monomer drops; the specific steady-state reaction rate V satisfies the following empirical equation: $V \sim C_i^{0.5} \cdot C_e^{k/S_e}$ (1), where C_i is the concentration of the initiator, C_e is the amount of the emulsifier in 1ml of the latex, S_e is the maximum area occupied by the molecule of the emulsifier in the saturated adsorption layer and k is a constant.

These results do not agree with any of the available theories. We have attempted to account for them taking into consideration some earlier suggested concepts, in particular, those developed by Ugelstad [4] and Lukhovitzkii [5].

The following assumptions have been made:

1. Polymerization occurs in the surface region of the latex particles^{x)}. One particle cannot contain more than one radical. The radicals are produced in the water phase. Only the oligomer (rather than primary) radicals enter the latex particles.

2. At the steady-state interval flocculation of the particles occurs in such a way that protection of their surface by the emulsifier remains constant (that is, the total surface area of the particles remains constant).

3. At the steady-state stage the rate of recombination of the radicals in the water phase and in the particles due to their flocculation is negligibly small compared with the recombination rate in the surface region of the latex particles when the oligomer radicals enter them.

4. The water phase contains oligomer radicals of two types which differ in the number of the monomer links (type 1 and type 2) and are actively involved in the EP process^{xx)}. The type 1 radicals diffuses from particle to particle during his lifetime t_{1w1} in the water phase. In the process it has the probability P of coming into contact with the particles (being adsorbed by their surface)^{xxx)}. If such radical comes into contact with a "dead" latex particle it will leave the particle after spending the time $\tau_1 \ll t_{cr}$ ^{xxxx)} in its surface region; if the radical comes into contact with a

x) The particle means here also an agglomerate of the primary particles.

xx) This concept is justified by the significant difference between the probabilities of radical capture by the particle according to the radical's size since the adsorption energy E_m per one monomer link is considerably higher than kT .

xxx) The radical comes into contact with N_1 particles during its lifetime.

xxxx) It is clear that $t_{cr} \sim \frac{1}{k_g^1 C_m^1}$, where k_g^1 and C_m^1 are the growth rate constant and the monomer concentration in the latex particle.

"live" latex particle it either leaves the particle after spending time \bar{z}_1 in its surface region or "kills" this particle with the probability P_r . If the type 1 radical does not disappear during its lifetime it converts into the type 2 radical (owing to addition of a monomer link). At its first contact with the "dead" latex particle the type 2 radical continues to grow in the surface region of this particle until the chain is transferred to the monomer^{x)} and the newly formed monomer radical leaves the particle since the lifetime of the type 2 radical in the surface region \bar{z}_2 is equal or higher than t_{cr} . When the type 2 radical comes into contact with a "live" latex particle it "disappears" owing to recombination with the macroradical in the particle.

5. The probability P that the oligomer radical in the water phase comes into contact with a latex particle when meeting it is determined by the degree of protection^θ of its interface by the emulsifier, for the type 1 oligomer radical: $P = P(\theta)$.

Compared with the concept of Ugelstad [4] and Lukhovitzkii [5] the assumptions Nos 4 and 5 in this model are new.

In the framework of this model we have estimated the specific rate of the EP when the monomer drops are present in the system (see Appendix 1). It has turned out that when we have $1/P_r \ll N_1 \ll 1/\bar{z}_1 k_g^1 c_m^1$

we obtain $V \sim \rho^{1/2} 1/P(\theta)^{1/2}$ (2) where ρ is the specific rate of initiation (per 1 ml of the latex)^{xx)}.

The above formulas describe, in our opinion, the experimental results reported in [1-3]. A comparison between (2) and (1) yields

$$P(\theta) \sim 1/c_e^{2k/S_e}$$

Evaluation of k/S_e (see Appendix 2) yields $x_{theor} \approx k/S_e \approx \sqrt[3]{\frac{9}{2}\pi \left[\frac{m}{\rho_m N_A}\right]^2 / 4S_e}$ where m is the molecular weight of the monomer, ρ_m is the density of the monomer and N_A is the Avogadro's number.

The good agreement between the predicted values of x_{theor} and the experimental results (see Table) testifies to the validity of such evaluation. The EP rate remains at the steady-state stage after disappearance of the monomer drops apparently due to the fact that the value of P_r decreases (owing to the decrease in the constant of the rupture rate k_{tr}^r for the type 1 radical with the macroradical in the latex particle) with decreasing monomer concentration in the particle.

The above discussion suggests that our EP model can account for some experimental results reported in [1-3]. In particular, it explains the origin of the link between the order of the reaction with respect to the emulsifier and the adsorption protection of the latex particles. However, the assumption that polymerization process occurs in the surface region of the latex particles has not been substantiated.

x)

Under the conditions of the EP process for which the above experimental results have been obtained it may be shown that the molecular weight of the polymer calculated from the constant of the chain transfer to the monomer [6] is $(3 - 30) \cdot 10^6$, that is, it is close to the experimental one and lower than the molecular weight $(50 - 100) \cdot 10^6$ calculated from the chain growth rate constant, the initiator decomposition constant [7, 8] and the experimental specific rate of the EP assuming the lack of chain transfer.

xx)

We believe that other cases are also of interest (see Appendix 1).

Table

The comparison of the experimental and predicted reaction orders with respect to the emulsifier (dodecylsulphate Na)

Monomer	S_e (\AA^2)	$x_{\text{theor.}}$	$x_{\text{exper.}}$
Methyl acrylate	176	0.095	0.13
Ethyl acrylate	86.2	0.22	0.2 - 0.25
Butyl acrylate	61.5	0.375	0.33

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Appendix 1

Before we attempt to estimate the mean number \bar{n} of the radicals per particle and the specific rate V of EP we note that thermodynamic equilibrium can be assumed to be established between the type 1 radicals which are on the surface of the latex particles and in the water phase (a radical appears many times in both phases during its lifetime t_{1w_1}) so that the number N_1 of the latex particles which come into contact with a type 1 radical during its lifetime t_{1w_1} is

$$N_1 = k_N 4 \pi R^2 N P(\Theta) t_{1w_1} \quad (1')$$

where R is the radius of the latex particle, N is the number of the latex particles in 1 ml of the latex and k_N is a constant. Let us assume also^{xx)} that $P_r \sim k_{tr} \bar{z}_1 / 4 \pi R^2 \Delta$ where Δ is the thickness of the surface region of the latex particles.

Denote now the mean lifetime of the radical by t_1 and the mean time spent by the radical in a particle from the moment of its capture till moment of chain transfer to the monomer by t_p / k_d ($t_p \gg t_{1w_1}$). Then the radical comes into contact with $N_1' + N_1 t_1 / t_p$ latex particles during its lifetime t_1 with the contact time \bar{z}_1 and it grows in $1 + t_1 / t_p$ particles during the time t_p .

Thus we obtain $\bar{n}(k_1 + t_1 / t_p) N_1 P_r + \bar{n}(1 + t_1 / t_p) \sim 1$ (2') where $k_1 = N_1' / N_1$ and

$$t_{1w_1} k_g^w C_m^w + N_1 \cdot \bar{z}_1 k_g^l C_m^l \sim 1 \quad (3')$$

Here k_g^w and C_m^w are the growth rate constant of the radical and the monomer concentration in the water phase.

The following condition is satisfied when the rate of production of the radicals is equal to their decomposition rate:

Using the condition^{xxx)} $k_1 = 1$ we obtain^(4') from equations (1'-4') the following relation:

$$\bar{n}^2 + \bar{n} \frac{\rho / N}{k_d} - \frac{\rho / N}{k_d (N_1 P_r + 1)} = 0 \quad (5')$$

From equation (5') we obtain

$$\bar{n} \sim \sqrt{\frac{\rho^2 / N^2}{4k_d^2} + \frac{\rho / N}{k_d (N_1 P_r + 1)}} - \frac{\rho / N}{2k_d} \quad (6')$$

x) Note that in the case of an anion emulsifier and a persulphate initiator N_1' for the radicals of the type 1 with the group SO_4 at the end is lower than N_1 for a type 1 radical without this group owing to the electrostatic repulsion forces acting in the former case.

xx) We assume that the condition $k_{tr} \bar{z}_1 / 4 \pi R^2 \Delta \leq 1$ is satisfied for the experiments discussed in this paper. This can be seen from the appropriate estimates assuming $\Delta \sim 20 \text{ \AA}$ and $2R \geq (2 + 3) \cdot 10^6 \text{ cm}$.

xxx) If $k_1 \neq 1$ the following discussion shown that there is no significant change but equations (5) - (7) are more complicated.

and
$$V \sim k_g^1 C_m^1 \sqrt{\frac{\rho/N}{k_d}} \left[\frac{N/(N_1 P_r + 1)}{\sqrt{\frac{\rho/N}{4k_d} + \frac{1}{N_1 P_r + 1}} + \sqrt{\frac{\rho/N}{4k_d}}} \right] \quad (7')$$
 2.

We have also

$$N_1 P_r = \frac{k_N k_{tr} NP(\theta) \bar{Z}_1 / \Delta}{k_g^w C_m^w + k_N NR^2 P(\theta) k_g^1 C_m^1 \bar{Z}_1} \quad (8')$$

In particular, if we have $1/P_r \gg N_1$ and $\frac{\rho/N}{k_d} \gg 1$ then equations (6') - (8') yield the second case of the Smith-Ewart theory [9], that is,

$$V \sim k_g^1 C_m^1 N \quad \text{and} \quad \bar{n} \sim 1 \quad (9')$$

When we have $1/P_r \gg N_1$ and $\frac{\rho/N}{k_d} \ll 1$ we obtain the Ugelstad-Lukhovitzkii theory [3,4]^{x)}:

$$V \sim k_g^1 C_m^1 \sqrt{\frac{\rho \cdot N}{k_d}} \quad ; \quad \bar{n} \ll 1 \quad (10')$$

Here $k_d \sim k_g^1 C_m^1 C_m$ where C_m is the constant of the chain transfer to the monomer.

When $1/P_r \ll N_1$, $N_1 \gg 1/\bar{Z}_1 k_g^1 C_m^1$ and $k_1 \neq 1$ we obtain the following relations: $N_1 P_r \sim k_{tr}/R^2 k_g^1 C_m^1 \Delta$, $\bar{n} \ll 1$ and

$$V \sim k_g^1 C_m^1 \sqrt{\frac{\rho}{k_d}} \left[\frac{S_\Sigma k_g^1 C_m^1 \Delta / 4\pi k_{tr}}{\sqrt{k_1^2 \frac{\rho}{4k_d} + \frac{S_\Sigma k_g^1 C_m^1 \Delta}{4\pi k_{tr}}} + \sqrt{k_1^2 \frac{\rho}{4k_d}}} \right] \quad (11')^{xx)}$$

where $S_\Sigma = 4\pi R^2 N$ is the total surface area of the latex particles in 1 ml of the latex.

Or if we have $\rho/4k_d \gg S_\Sigma k_g^1 C_m^1 \Delta / 4\pi k_1^2 k_{tr}$

then we obtain

$$V \sim S_\Sigma \quad (12')$$

x) In the first two cases constant EP rate necessitates constant N but this does not affect the equations (in these cases).

xx) We do not rule out completely that this case can be used for describing the experiments described in [1-3], only if $S_\Sigma \sim C_m^\alpha$, where α depends on the interface and the emulsifier. Not also that equation (11) can be readily transformed into the following relation

$$V^2 \sim \frac{k_1' C_i}{k_2 C_i + k_3' + \sqrt{(k_2 C_i)^2 + 2k_2' k_3' C_i}}$$

which practically does not differ from the empirical relation

$V^2 = k_1 C_i / (k_2 C_i + k_3)$ derived in [11] (here k_1' , k_2' , k_3' , k_1 , k_2 , and k_3 are the constant for a given amount of emulsifier in the latex system).

when $\rho/4k_d \ll S_{\Sigma} k_g^1 C_m^1 \Delta / 4\pi k_1^2 k_{tr}$ we have $V \sim \rho^{1/2} S_{\Sigma}^{1/2}$.

The latter is similar to the Medvedev's formula [10].

When we have $1/P_r \ll N_1$, $N_1 \ll 1/\bar{z}_1 k_g^1 C_m^1$ and $k_1 \neq 1$ we obtain

$$N_1 P_r \sim \frac{k_N k_{tr} NP(\Theta) \bar{z}_1}{\Delta \cdot k_g^w C_m^w} \gg 1,$$

that is, the EP rate does not depend on either N or R (does not change in the process of flocculation of the latex particles). In particular,

when we have $\frac{\rho/N}{4k_d} \gg \frac{1}{k_1^2 N_1 P_r}$ we obtain $V \sim 1/P(\Theta)$, that is, saturation with the initiator.

When we have $\frac{\rho/N}{4k_d} \ll \frac{1}{k_1^2 N_1 P_r}$ we obtain

$$V \sim \rho^{1/2} \left[\frac{1}{P(\Theta)} \right]^{1/2}.$$

Appendix 2

The relationship

$$P(\Theta) \sim \left(\frac{1}{C_e} \right)^{2k/S_e} \quad (1'')$$

can be understood using the Langmuir concepts according to which the probability that a given site on the surface of a particle with the surface area S_e does not contain an emulsifier molecule is given by

$$P_1 = \frac{1}{1 + k_1 C_e^w} \quad (2'')$$

Here k_1 is the constant in the Langmuir equation and C_e^w is concentration of the emulsifier in the water phase at the steady-state stage of the EP. A type 1 oligomer radical can come into contact with a particle when meeting it if there is a free site of the area S_r on the surface of the particle where collision occurs. The probability of this is given by

$$P(\Theta) \sim \left[\frac{1}{1 + k_1 C_e^w} \right]^{S_r/S_e} \sim \left[\frac{1}{k_1 C_e^w} \right]^{S_r/S_e} \quad (3'')$$

assuming that $S_r/S_e \geq 1$ and that usually $k_1 C_e^w \gg 1$.

Further we assume that at the steady-state stage of the EP rate

$C_e^w = AC_e$ (where A is a constant; A does not change in the course of the process since the total surface area of the particles remain constant) and that S_r equals the effective cross-section of the monomer molecule (which is taken to be a sphere) Hence, we obtain

$$x_{theor} \frac{k}{S_e} \approx \frac{\sqrt[3]{-\frac{9}{2}\pi \left[\frac{m}{\rho_m N_A} \right]^2}}{4S_e} \quad (4'')$$

where m is the molecular weight of the monomer, ρ_m is a density of the monomer and N_A is the Avogadro number.

x)

S_r is the effective cross-section of the oligomer radical (viewed from the end).

xx)

Of course, this equation is valid when $AC_e = C_e^w \leq ccm$; when $AC_e > ccm$ the rate V does not depend on C_e according to the experimental results