

POLYMER COLLOID GROUP

NEWSLETTER

Vol. 3, No. 2

Spring Issue, 1974

We have long been interested in the effect of polyvinyl alcohols in the vinyl acetate polymerisation. Grades containing 12 mole per cent residual acetate groups are preferred for application in emulsion polymerisation: they are customarily characterised by the viscosity of their 4% solutions and their acetyl content but the variability of the effects of ostensibly similar grades from different sources is notorious. This is because the stage at which the product precipitates during hydrolysis determines the distribution of the residual acetate groups: the earlier precipitation occurs the more 'blocky' the distribution of the groups and the more surface-active the product. A good method of characterising block length distribution has hitherto been lacking, however K. Toyoshima (Kuraray Co. Osaka) in his Chapter on 'General Properties of Polyvinyl Alcohol in Relation to its Applications' in C.A. Finch ed. 'Polyvinyl Alcohol - Properties and Applications' Wiley, London (1973) p. 45-7 Fig.2.26 calculates acetate block length distributions from melting points determined by Tubbs's Differential Thermal Analysis method: unfortunately the calculation procedure is not described in detail.

Dr Tonge found that samples from different sources did have very different effects on the rates of polymerisation of vinyl acetate solutions, also their adsorption isotherms on polyvinyl acetate latex differed markedly although there was no clear correlation between these effects. We thought that the presence or absence of ionic end-groups depending on the method used to polymerise the original polyvinyl acetate might be a factor and used an Antweiler Microelectrophoresis apparatus to investigate this: all the samples had very similar rates of electrophoresis, however, so that they presumably do not differ in this respect.

Effect of Polyvinyl Alcohol Concentration

Earlier Dunn & Taylor (Makromol. Chem. 83 (1965) 207) found that increasing concentration of DuPont 'Elvanol' 52-22 (12 mole % acetate), decreased the rate of polymerisation (and the size of the latex particles formed) in vinyl acetate solutions whereas O'Donnell, Mesrobian, and Woodward found higher concentrations to increase the rate of polymerisation of vinyl acetate emulsions (J. Polym. Sci. 28 (1958) 171). This effect has now been confirmed using the same polyvinyl alcohol sample (Gohsenol GH-23 from Nippon Gohsei, Osaka: 13.0 mole % acetate: 4% solution viscosity 55.4 cp). The rate of polymerisation of vinyl acetate solutions decreases whereas the rate of polymerisation of vinyl acetate emulsions increases.

2.0 % (v/v) vinyl acetate solutions at 60°C using 7.4×10^{-4} M peroxodisulphate

| | | | | | | |
|--------------------------|------|------|------|------|------|------|
| PVOH/% | 0 | 0.40 | 0.80 | 1.20 | 2.00 | 4.00 |
| Rate/% min ⁻¹ | 5.81 | 5.77 | 5.85 | 5.65 | 5.07 | 4.70 |

8.0 % (v/v) vinyl acetate emulsions at 60°C with 7.4×10^{-4} M peroxodisulphate on total volume.

| | | | |
|--------------------------|------|------|------|
| PVOH/% | 0.32 | 0.64 | 1.60 |
| Rate/% min ⁻¹ | 3.75 | 4.31 | 6.44 |

Lower molecular weight grades are more effective in reducing the polymerisation rate at a given concentration e.g. Gohsenol GM-14L (12.3 mol % acetate: 4% solution viscosity 18.0 cp) with 2% vinyl acetate solution

| | | | | | | | |
|--------------------------|------|-------|------|------|------|------|------|
| PVOH/% | 0 | 0.135 | 0.34 | 0.68 | 1.02 | 1.70 | 3.40 |
| Rate/% min ⁻¹ | 5.81 | 5.57 | 5.50 | 5.47 | 4.94 | 4.76 | 4.10 |

cf. Dunn & Taylor (1965) with Elvanol 52-22 (12 mol % acetate: 4% solution viscosity 22 cp)

| | | | | | |
|--------------------------|------|-------|-------|-------|-------|
| PVOH/% | 0 | 0.120 | 0.240 | 0.288 | 0.360 |
| Rate/% min ⁻¹ | 5.15 | 4.60 | 3.54 | 3.27 | 2.54 |

These grades of polyvinyl alcohol are all well above their critical micelle concentrations at the lowest concentrations used. We hope to study the solubilisation of vinyl acetate in the polyvinyl alcohol solutions. Although the solubility of vinyl acetate in water is more than 2%, it might be that distribution of the monomer between the micellar phase and the aqueous phase reduces the monomer concentration at the main locus of polymerisation (the latex particles) so that lower rates are observed despite the effect of the polyvinyl alcohol in stabilising a larger number of smaller latex particles which would account for the increased rate observed with the emulsions. The 1965 hypothesis that the retardation was attributable to transfer to the polyvinyl alcohol now seems unlikely

Effect of acetyl content

A series of polyvinyl alcohols of similar molecular weight but differing acetyl content showed clearly that at the same concentration (0.10 % w/v) the reduction in the rate of polymerisation was most marked for the samples with the higher acetyl contents.

2.0 % v/v vinyl acetate solutions at 60°C with 7.4×10^{-4} M peroxodisulphate.

| Gohsenol grade | Specification 4% viscosity/cp | Acetyl/mol % | Rate/% min ⁻¹ |
|----------------|----------------------------------|--------------|--------------------------|
| NH-17 | 25-30 | 0-1 | 5.24 |
| AH-17 | 25-30 | 1.5 - 3 | 4.83 |
| GH-17 | 30.0* | 12.4* | 4.69 |
| KH-17 | 18.5 - 21.5 | 32-38 | 4.05 |

* Actual batch analysis

The grades with the higher acetyl contents are likely to be more effective in extracting monomer from the aqueous phase.

Effect of molecular weight

Samples of differing molecular weight (as indicated by the 4% solution viscosity) but similar acetyl contents (12 - 13 mol %: variation within this range would by itself account for only a 0.1 % min⁻¹ change in polymerisation rate) were tested at 0.36% w/v concentration with 2% v/v vinyl acetate solutions at 60°C with 7.4×10^{-4} M peroxodisulphate. The results were rather erratic although it may be that if the distribution of acetyl groups is the same in all samples then the reduction in rate increases with molecular weight. The 'Elvanol' sample and 'Polyviol' grades (Wacker Chemie) had a much larger effect at similar 4% solution viscosities than most of the 'Gohsenol' grades. An increase of polymerisation rate was observed with three 'Gohsenol' grades but this might possibly be attributable to the introduction of traces of heavy metal capable of catalysing initiator decomposition with the emulsifier. If the acetyl group distribution is constant, then the amount of monomer solubilised might be expected to increase with molecular weight

Characterisation of acetyl group distribution in polyvinyl alcohols

Clearly the commercial samples used in these studies are insufficiently characterised by the customary parameters (acetyl content and viscosity of a 4% aqueous solution). Tubbs (J. Polym. Sci. A-1, 4 (1966) 623) has shown that the 'blockiness' of polyvinyl alcohols is characterised by their melting points as determined by differential thermal analysis and Toyoshima (in C.A.Finch ed. 'Polyvinyl Alcohol' Wiley (London) 1973, p. 47) appears to have succeeded in calculating acetyl group distributions from such data although, unfortunately, he does not describe his procedure in detail. Moyles (quoted by Gulbekian & Reynolds in Finch p. 430) and Nagai & Sagane (Kobunshi Kagaku 12 (1955) 195) have shown that shifts in the carbonyl and hydroxyl peaks in the infra-red spectrum of polyvinyl alcohol indicate the 'blockiness' of the product. Hayashi, Nakano, & Motoyama (Kobunshi Kagaku 20 (1963) 303) find that the reaction of partially saponified polyvinyl acetates with iodine can also be used to characterise blockiness. Mr D.M.Patten is currently undertaking a project to characterise the samples used in the preceding studies by these methods.

Adsorption of polyvinyl alcohols on polyvinyl acetate latex

Dr Tonge also studied the adsorption of some of the samples on a polyvinyl acetate latex prepared by polymerising a 2.0% v/v vinyl acetate solution at 60°C with 7.40×10^{-4} M peroxodisulphate under nitrogen in absence of emulsifier to give a latex with 3000 Å diameter particles. Equilibrium was found to be attained within 15 min. at room temperature. The residual polyvinyl alcohol concentration was determined after Johnson & Lewis (Br. Polym. J. 1 (1969) 266) by reaction with iodine and boric acid after centrifugation of the latex. Although the calibration curves for the different samples were not identical they did not differ markedly (the reaction with iodine alone - which gives a less intense colour less suitable analytically - may be different, however). Marked differences in the adsorption isotherms were observed, however, although there was no correlation between these and the effects of the same grades on the rate of polymerisation which accordingly cannot be supposed to arise from differences in the effectiveness of the grades in stabilising the latex particles produced. GH-17, NH-17 and 'Polyviol' W25/140 were strongly adsorbed to a similar extent, whereas GM-14L and GH-23 were only weakly adsorbed. Yet NH-17 had a very low acetate content and did not reduce the polymerisation rate of vinyl acetate solutions: W25/140, on the other hand, had the largest effect of any sample tested, reducing the rate of polymerisation from $5.14 \% \text{ min}^{-1}$ to $2.69 \% \text{ min}^{-1}$ at a concentration of 0.36%!

The possible solubilisation of vinyl acetate in polyvinyl alcohol micelles thus currently seems to be the most viable hypothesis to account for the observed effects.

A.S.D.
6/2/74

D-1
HYDRODYNAMIC CHROMATOGRAPHY, A TECHNIQUE FOR SIZE ANALYSIS OF COLLOIDAL PARTICLES, Hamish Small, DIG Physical Research, The Dow Chemical Company, Midland, Michigan 48640.

Saunders

Introduction:

Chromatography has, until quite recently, been concerned exclusively with the separation of matter at the molecular level. One result of this restriction to the molecular domain is that from a practical point of view chromatographic methods invariably deal with species in solution in the chromatographically active phases. In fact, solubility in the eluting phase is often cited as a prerequisite for the practicability of any proposed liquid-chromatographic scheme. Recently however, chromatographic separations have been reported where the materials resolved can be more properly considered as being in suspension rather than in solution in the eluant phase. Krebs and Wunderlich (1) have reported on the separation of polymer latex particles by gel chromatography using porous silica gel as the stationary phase and Haller (2) has achieved fractionation of viruses on porous glass.

In this contribution I wish to report a new chromatographic technique which is capable of achieving size fractionation of colloidal particles in the range of a few hundred Å to a few microns in diameter. This technique, called "hydrodynamic chromatography (HDC)", is based on the discovery that the rate of transport of colloidal sized particles through a bed packed with solid, nonporous particles depends both on the size of the colloid and of the particles that constitute the packing. The utility of HDC as a size based chromatographic method is expected to be in the elucidation of areas of colloidal behavior where the particle size or size distribution of the colloid is, or is thought to be, of primary significance. Accordingly, as well as describing the phenomena underlying HDC, this contribution includes examples which demonstrate how the technique is employed in a relatively rapid and simple manner to provide size information in the polymer latex field.

Experimental:

A variety of experimental techniques have been used but all basically involve a typical chromatographic assembly consisting of an eluant reservoir, constant flow pump, sample injection device, column(s) filled with the appropriate packing, a detector and recorder. The most common experiment in this work involved injection at the head of the column(s) of a dilute suspension of a model colloid and measurement of the elution time of the colloid peak. A series of very uniform particle size polystyrene

latexes, which are manufactured by The Dow Chemical Company, proved very suitable as model colloids. Detection and measurement of the colloid in the effluent was effected by monitoring its turbidity in a flow through spectrophotometer which measures the optical density of the effluent at 254 m μ and expresses this as an output to a recorder.

The R_F number and its dependence on \bar{d} and \bar{D} .

The rate of elution of colloid particles through the bed is expressed by the quantity, R_F , which is defined as follows

$$R_F = \frac{\text{rate of transport of colloid through the bed}}{\text{rate of transport of the eluant}}$$

Eluants were exclusively aqueous solutions and their velocity through the interstitial volume of the columns was measured by observing the elution time of a suitable marker species such as the dichromate ion. The R_F values for a series of monodisperse polystyrene latex particles eluted through beds of ion exchange resin (Dowex[®] 50W x 16; Na⁺ form) of different mean spherical diameter \bar{D} , are plotted versus \bar{d} , the particle diameter of the latex (Figure 1). A number of important conclusions are evident from a study of this plot

1. R_F increases with increasing particle diameter (\bar{d}) of the latex, that is, large particles move more rapidly through the packed bed than smaller ones. This behavior alone provides the basis for a chromatographic size separation and Figures 2 illustrates such a separation. A mixture of 880 \AA and 5000 \AA polystyrene latexes was eluted through beds of 18 micron DOWEX[®] 50W (Na⁺) and Figure 2 shows a plot of the effluent turbidity (absorbance) as a function of time. Electron micrographs of fractions of the effluent, designated cuts 1 and 2, when compared with that of the feed mixture provided conclusive proof that a separation of large particles from smaller had indeed been achieved.
2. As the particle size of the packing is reduced the R_F increases. Furthermore the slope of the R_F versus diameter plot increases, which manifests itself in improved resolution of different particle sizes as the size of the packing is reduced. This type of behavior is distinctly different from conventional chromatography where the rate of elution of a solute peak is normally independent of the particle size of the stationary phase.

3. R_F is always greater than unity or in other words the latex particles move more rapidly through the bed than either the carrier fluid or low molecular weight soluble species, ionic or nonionic, which move with approximately the same velocity as the eluant. This is a very striking observation which is also in sharp contrast to normal chromatographic experience where for a variety of reasons, solutes are invariably detained in the column, $R_F < 1$, or in the limiting case appear immediately the void volume is displaced, $R_F = 1$.

Very similar behavior is observed when solid spherical particles of glass or styrene-divinylbenzene copolymer are used as packings. A point to be emphasized is that in all three cases the packings are impermeable to the species of interest, namely, the latex particles.

Mechanism of Hydrodynamic Chromatography

This new form of chromatography, called Hydrodynamic Chromatography for reasons which will appear later, bears some resemblance to gel permeation chromatography but also differs in important respects. Whereas gel permeation chromatography, or indeed any other form of chromatography, relies on some sort of chemical or physical interaction of solutes with the stationary phase, HDC is unusual in that the separation forces appear to be derived exclusively from factors operating in the interstitial volume of the packed bed. Separation appears therefore to be taking place under the influence of flow alone, a circumstance which was predicted independently by deMarzio and Guttman (3,4) and probably first observed by Pedersen (5) who obtained separation of proteins simply by pumping them through beds packed with glass spheres of suitably small diameter.

A qualitatively satisfying mechanism has been derived which is similar in many respects to one discussed by deMarzio and Guttman and is based on considering the interstitial space in the packed bed as a system of capillaries. It is well known that for a viscous fluid flowing in a capillary, a velocity profile exists such that the velocity of the fluid is maximum at the center and diminishes toward the wall. A colloidal particle injected into such a channel will by Brownian motion make radial excursions normal to the direction of flow thereby sampling and adopting velocities across the capillary. The mean velocity of the colloidal particle will therefore be a reflection of the velocity profile of the fluid in the capillary with the important qualification that the center of a particle, because of its size, will be excluded from the slowest streamlines closest to the capillary wall. Consequently, the particle will move through the capillary with a mean velocity which exceeds the mean velocity of the fluid by a factor which increases

with increasing ratio of particle size to capillary radius. Thus the wall effect would also explain the interesting dependence of R_F on the packing diameter.

It is notable that very similar behavior has been observed with glass packings so that the elution rate of colloidal particles of a particular size seems to depend mainly on the size and not on the chemical composition of the packing. Since this chromatographic separation appears therefore to be solely attributable to flow phenomena in the column void space, the name Hydrodynamic Chromatography is considered an apt name for the technique.

Dependence of R_F on ionic strength of the eluant

As well as being dependent on the diameters of both the colloid and the packing, R_F shows a considerable dependence on the ionic strength of the eluant, which manifests itself as a decrease in R_F with increasing ionic strength. Furthermore, at relatively high ionic strength the separation potential diminishes, which may be attributed to competition between two opposing effects namely (1) the HDC effect already discussed and (2) a weak interaction between the packing and the latex particles which on the basis of well known interpretations of colloid behavior might be expected to retard large particles with respect to smaller particles and therefore act in opposition to the HDC effect which advances large particles with respect to smaller ones.

Applications of HDC

Suitably calibrated HDC columns have been used to provide size information in several problems involving colloids - particularly polymer latexes. Space limitations permit only the following listing of the applications - more detailed descriptions are planned for a future publication.

1. Determination of latex particle size.
2. Assessment of particle size distribution.
3. Following the course of particle growth in emulsion polymerization.
4. Providing information on the state of aggregation of latex polymer particles.
5. Providing size information on colloids other than latexes, e.g., carbon black and silica sols.

Conclusions:

The phenomena associated with liquid flow through packed beds of non porous particles have been exploited in a useful way to obtain size separations and provide size information on colloidal particles in the range of 500Å to 1 micron. From a chromatographic point of view the separation is unusual in that it takes place solely within the interstitial volume of the column. Although satisfactory qualitative arguments have been evolved to account for this separation by flow alone, development of a successful quantitative description of the phenomena remains as one of the major challenges of hydrodynamic chromatography. In this regard the author believes that a successful solution of this complex problem could yield important side benefits in areas such as microrheology, biorheology, colloidal behavior and fluid flow in porous structures.

References:

1. KREBS, VON K. F. and WUNDERLICH, W., Die Angewandte Makromolekulare Chemie, 20, 203 (1971).
2. HALLER, W., Nature, 206, 693 (1965).
3. DIMARZIO, E. A. and GUTTMAN, C. M., Polymer Letters, 7, 267 (1969).
4. DIMARZIO, E. A. and GUTTMAN, C. M., Macromolecules, 3, 131 (1970).
5. PEDERSEN, K. O., Archives of Biochemistry and Biophysics, Supplement 1, 157 (1962).

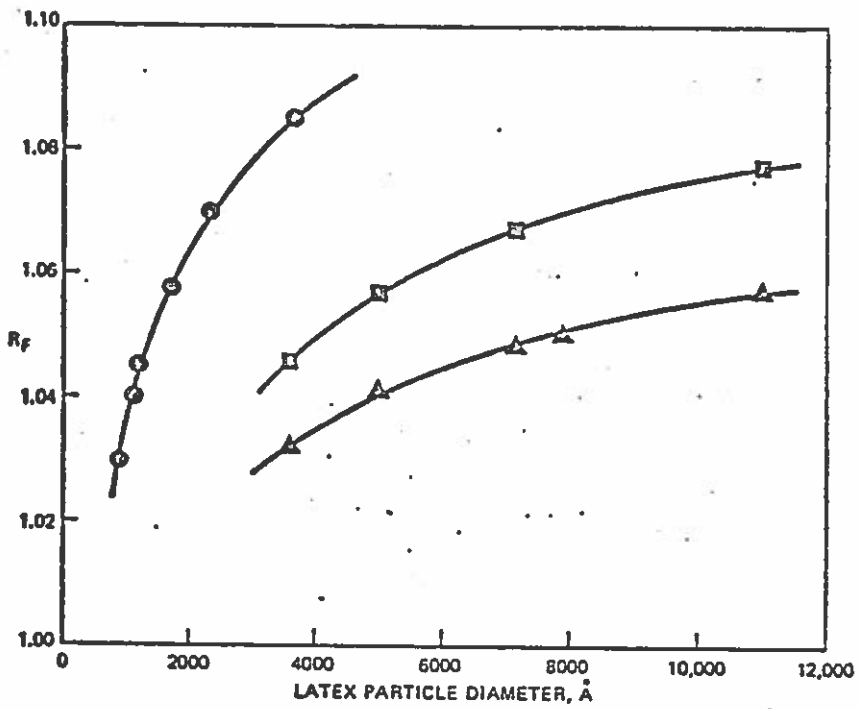


Fig. 1 The dependence of R_f on latex particle diameter and packing diameter (\bar{D}). \circ $\bar{D} \approx 18 \mu$; \square $\bar{D} \approx 40 \mu$; \triangle $\bar{D} \approx 58 \mu$.

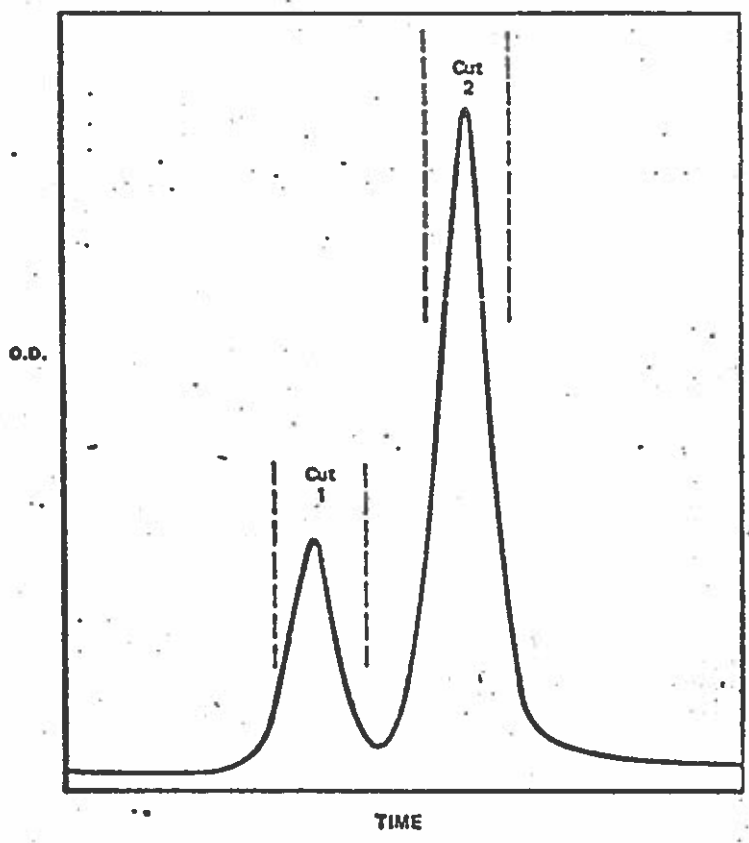


Fig. 2 The separation of 5000Å (1st peak) from 880Å (2nd peak) latex particles.

7-1

Polymer Colloid Group Newsletter

Fitch

1. A copy of my paper entitled, "The Homogeneous Nucleation of Polymer Colloids," which will appear in British Polymer Journal will be sent to all members as soon as reprints are available. It constitutes a review of the situation as it stood last summer.

2. Subsequently Miss Shih and I have submitted a long, pedantic manuscript to Kolloid Z. U. Z. Polymere on the topic of "Kinetics of Radical Capture by the Particles in Emulsion Polymerization." I haven't circulated this ms. to you because it is too long and pedantic, but herewith below are excerpts:

"The rate at which free radicals enter particles of the disperse phase from the continuous phase in emulsion polymerization depends upon the particle concentration and size, and the rate of radical generation. The kinetics of radical capture determine the rate of particle formation, relative growth rates of different sized particles in certain cases and the chemistry of the polymer/water interface. Smith and Ewart in their classic work (1,2) assumed, on the basis of a suggestion by P. Debye, that the process of radical capture by particles was diffusion-controlled to calculate the particle number concentration and one part of their "Case 1" polymerization kinetics. Under diffusion control, the radical absorption rate is proportional to the radius of the particles. There is good evidence to support this model: Ugelstad and coworkers applied it to calculate relative particle growth rates (3) and overall kinetics of vinyl chloride emulsion polymerization (4), and La Mer and Reiss found that the growth of aerosols and hydrosols could be ascribed to diffusion-controlled absorption of small molecules by particles (5,6). On the other hand Gardon proposed that the capture of radicals by monomer-swollen soap micelles should be described by a collision theory which gives a dependence of the capture rate on the square of the particle radius (7). Fitch and Tsai applied this theory to calculate particle nucleation kinetics(8). Alexander and Napper in an excellent review have recently stated that whether radical entry is diffusion- or collision-controlled is still an open, important question which needs to be resolved (9).

In this paper we investigate some of the assumptions of the original Gardon collision theory, and propose refinements to obviate them. Additionally we describe experiments using emulsion polymerizations of methyl methacrylate to test which theory is the more applicable.

Collision Theory

The rate at which radicals enter a given particle from the continuous medium, or the "capture rate" for a single particle, R_{C_1} , in terms of the number of radicals per second has been given as (7,8):

$$R_{C_1} = \pi R_i r_p^2 L. \quad (1)$$

This assumes that: (a) the polymer particle does not move, i.e. that its diffusion coefficient, D_p , need not be considered, (b) the size of the radicals is negligible compared to that of the particles, (c) the near presence of one particle does not interfere with the capture of radicals by others, i.e. there is no "crowding effect", (d) the system contains a uniform concentration of radicals throughout, and (e) there is no interaction between oligomers and particles. Each of these assumptions is discussed and the amended expression for the capture rate follows."

The subsequent examination of these assumptions leads to the conclusion that the overall calculated rate of radical capture by the particles would have a negligible correction if they were taken into account, fortunately for Mr. Gardon. This is so at least under the experimental conditions we chose for PMMA seeded latex polymerizations where the particles are of intermediate size (43-140 nm dia.) and of rather low surface potential. For very small particles, assumptions (a) and (b) cannot be made and for large particles assumption (e) is probably not valid.

In any case, if we find experimentally a functional dependence of R_c on Nr_p^2 , we may say that the system obeys the collision theory, where R_c is the rate of radical capture, N and r_p are the number concentration and radius of the particles, respectively.

Diffusion Theory

The discussion of this is given in the B.P.J. article. The prediction is that R_c should be proportional to N and to the first power of r_p , under certain favorable conditions. And certainly if we find experimentally that R_c is proportional to Nr_p , then we may conclude that radical capture is diffusion controlled:

$$R_c = 4\pi DC_s Nr_p,$$

where C_s is the steady state concentration of oligomeric radicals in the continuous phase.

Experimental

The MMA seeded polymerizations reported in both the B.P.J. and K.Z.Z.P. articles show that $R_c \propto Nr_p$, unfortunately for Mr. Gardon! The data are few and the errors potentially large in those experiments, although the agreement with theory is extremely good. Subsequently, upon looking at other data, the dependence is always on the first power of the radius. For example, Tsai's earlier results on PMMA latexes formed from homogeneous solution:

-3-

| $[M]_0$ mole l ⁻¹ | $N \times 10^{-16}$ l ⁻¹ | $r_p \times 10^9$ dm | Collision | Diffusion |
|---------------------------------|--|-------------------------|---|--|
| | | | Theory | Theory |
| | | | $\frac{Nr_p^2}{[M]_0^{1/2}} \times 10^{-4}$ | $\frac{Nr_p}{[M]_0^{1/2}} \times 10^{-11}$ |
| 0.380 | 48.8 | 55 | 2.39 | 4.35 |
| 1.90 | 56.0 | 90 | 3.29 | 3.65 |
| 3.50 | 63.8 | 104 | 3.69 | 3.55 |
| 5.71 | 75.0 | 116 | 4.22 | 3.64 |
| 7.61 | 80.0 | 126 | 4.60 | 3.65 |
| 9.51 | 90.5 | 131 | 5.04 | 3.84 |

Seeded latex polymerizations of vinyl chloride conducted by Gatta, Benetta, Talamini and Vianello (1968) also show dependence on Nr_p .

Absolute Rates

We liked the collision theory because we were able to easily calculate absolute values of R_c which agreed with experiment. Diffusion-dependent R_c , on the other hand, gives radical lifetimes on the order of 10^{-5} to 10^{-3} second, too short for any particle nucleation to occur in systems where we know it does occur. Thus John Ugelstad and I came to the conclusion that an electrostatic repulsion exists between the growing radicals in solution and the particles. Tsai's work with $\cdot OH$ and $\cdot SO_4^- / \cdot SO_3^-$ initiation gives some support of this, and C. C. Ho's work here in Bristol shows that it must be so in styrene-seeded polymerizations. We are now developing theory and experiments to obtain absolute values of R_c which will depend on R_i , surface potential, salt concentration, etc.

Please let me know if you want a copy of the K.Z.Z.P. manuscript now. Reprints will be sent whenever and if ever it is published.

Polymer Colloid Newsletter

I. M. Krieger

February, 1974

Emulsion Polymerization Studies (M. Juang, R. Seidewand)

Mr. Juang is directing his major energies toward preparation of monodisperse polystyrene latices incorporating ionogenic comonomer. Vinyl benzene sulfonic acid has been selected as a suitable comonomer; potassium persulfate is the initiator; particle size control is achieved through a combination of comonomer level and ionic strength. No conventional emulsifier is used. Particle sizes are typical of recipes using emulsifier, and are generally much smaller than those usually obtained with emulsifier-free recipes. Samples are withdrawn periodically to determine conversion and particle size (by electron microscopy). From these data the number of particles can be calculated. The particle number achieves steady state at 2 to 4% conversion, and remains constant to 100% conversion. In situ measurements show conductivity changes during polymerization at times corresponding to particle initiation and achievement of steady particle number.

Mr. Seidewand has initiated a study of overpolymerization of acrylic monomer onto a monodisperse polystyrene seed. Properties of films formed from this core-shell copolymer will be compared with those formed from latex blends and copolymers having the same overall composition.

Order-Disorder Transition (B. Zysman, T. Yang)

Mr. Zysman's measurement of chloride ion concentration in the co-existing ordered and disordered phases, accomplished with silver-silver chloride electrodes in a concentration cell arrangement, yields contro-

versial results. The major question is whether the measured activity correlates with the concentration based upon the aqueous phase, or on the overall concentration in equivalents of chloride ion per liter of latex. Attempts will be made to refine the accuracy and reproducibility of the measurements in order to resolve this question. The same sort of improvement in accuracy is necessary in order to study any difference in chloride ion concentration between the ordered and disordered phase.

Mr. Yang has measured laser Doppler scattering from a 20% latex in both ordered and disordered condition, and observed a great difference between the autocorrelation function vs. time curves of the two systems. The disordered system, however, does not yield the exponentially decaying curve which would be expected at high dilution. Measurements of the disordered phase at lower concentration will be made, in order to obtain information on the effect of particle-particle interaction on the laser Doppler scattering.

The order-disorder equilibrium has been attributed by S. Hachisu et al. to the sort of phenomenon which Alder and coworkers observed in computer-dynamic studies of hard-sphere gases. An alternate explanation, based upon the existence of van der Waals forces of long range, has also been advanced. Our group was visited by V. A. Parsegian, who has done some of the pioneering work on applying the Lifschitz-Dzyaloshinski theory to the calculation of van der Waals forces. In his opinion, based in part on recent calculations of forces between spherical latex particles which appeared in the October 1973 issue of Journal of Colloid and Interface Science, the forces are too small to play an important role in the order-disorder equilibrium. This leaves the Kirkwood-Alder type of mechanism in command of the field!



DEPARTMENT OF CHEMISTRY
MCGILL UNIVERSITY P.O. BOX 6070, MONTREAL 101, QUE., CANADA

POLYMER COLLOID GROUP
CONTRIBUTION FROM S.G. MASON AND A.A. ROBERTSON,
DEPARTMENT OF CHEMISTRY, MCGILL UNIVERSITY.

FEBRUARY, 1974.

The following are reports of recent progress in those research projects that involve latexes or other polymer colloids.

Mr. A. Homola has completed his experimental work and is currently completing his thesis which will have an abstract similar to the following with the title "Studies of Particle Interactions in Latexes".

"A model colloidal suspension of polystyrene latex was prepared and characterised. The electrophoretic behavior of polystyrene latex in the presence and absence of surface active agents was studied. A technique based on the Hittorf mass transport method was applied to measure the electrophoretic mobility of latex particles in crowded dispersions and to determine the thickness of the adsorbed layer of surfactant on the latex surface.

The repulsive forces between colloidal particles as a function of separation distance has been estimated from measurement of the equilibrium pressure and volume of a model latex confined between a semipermeable membrane and an immiscible liquid. It was demonstrated that the forces, in aqueous and non-aqueous media, are smaller than calculated from the DLVO theory. Effects of steric repulsion in polystyrene latex system stabilized with non-ionic surfactants were investigated. The repulsive forces, in the absence of the electrostatic effects, were measured and found to be smaller than predicted by theory.

A technique based on the latex filtration was devised to study the effect of ionic strength, pH, and non-ionic emulsifier on the minimum pressure required to coagulate polystyrene latex particles. This study confirms that the stability of "soap-free" polystyrene latex is governed by electrostatic forces, whereas, in the presence of non-ionic surfactant, steric repulsion dominates."

A rather wide ranging program of studies of the behavior of suspensions comprises both theoretical and experimental approaches. The following are reported because they are based on the use of latexes as model dispersions.

Microrheology of colloidal dispersions (E.B. Vadas, H.L. Goldsmith and S.G. Mason)

Objectives: To study the influence of translational and rotational Brownian diffusion on the shear induced motion of colloidal particles in Poiseuille flow.

Recent Progress:

Experiments have been completed to record the rotary motions of doublets of 1μ diameter PS latex spheres in tube flow using the microtube apparatus. Film analysis has also been completed to determine the effect of Brownian diffusion on the flow behaviour of the particles at low rotational Péclet (Pe_r) numbers where rotary diffusion plays an increasingly important role. In this series of experiments Pe_r varied from 2 to 13, in contrast to previous experiments with doublets of 2μ diameter PVT latex where Pe_r varied from 25 to 120. The net angular displacement of particles vs time due to both shear and Brownian motion and shear are independent and additive the shear contribution to the motion of particles was computed using Jeffery's theory, and the values subtracted from the measured ones. The difference was considered to be the Brownian contribution to the motion of the particles. Subjecting the Brownian contribution values to a numerical analysis developed by R.G. Cox, the rotational Brownian diffusion coefficients of doublets of 1μ diameter spheres were calculated and found to be in good agreement with those predicted by theory, validating the above assumptions.

Lattice Structures in Colloidal Dispersions (T.G.M. van de Ven and S.G. Mason)

Objectives: To study the formation and properties of 1-dimensional (linear), 2-dimensional (planar) and 3-dimensional aggregates in monodisperse sols of various particle shapes.

Recent Progress:

1. The theoretical work on doublets and linear aggregates in shear flow has been completed. The theory describes the formation and behaviour in a shear flow of doublets consisting of equal sized non-conducting spheres having a homogeneous surface charge distribution of electric charge surrounded by an electrical double layer. The theory also applies if the net charges on the two spheres are not identical. The equations which describe the trajectories of two spheres in the limiting case that the distance between them approaches zero can also be used to describe the behaviour of a linear array of equal sized spheres with non-zero gapwidth.

2. The next logical step was to investigate the formation and behaviour of triplets in a shear flow. Observations were made of triplets in Poiseuille flow where it was seen that a sphere can interact permanently with a doublet at a surprisingly large distance of separation. These observations reveal that triplets are probably of much greater importance in suspension behaviour than hitherto believed. Because an exact theory for the behaviour of three spheres in a shear flow is not yet available, calculations are being made of the motion of an element of fluid in the neighbourhood of an ellipsoid rotating in a shear flow.

Lattice structures in colloidal dispersions (cont'd)

Another interesting case is the behaviour of non-linear triplets. Preliminary experiments seem to indicate that if the spheres, which make up the triplet, are touching (e.g. are captured in a primary energy minimum) the triplet behaves as a rigid body. If, on the other hand, the spheres are not touching (are captured in a secondary energy minimum) then the triplet bends periodically, the angle between the three spheres being maximum when the triplet is aligned with the flow and minimum when perpendicular to the flow.

Electrochemical filtration of dilute colloidal sols (S.L. Grassino and S.G. Mason)

Objectives: To explore and develop the use of bimetallic porous media for removal of dispersed particles from water.

Recent Progress:

A completion report on this project will be issued shortly. Following is the tentative abstract:

"The use of bimetallic coalescence filters consisting of granular beds of pairs of electrochemically dissimilar metals as a simple method of clarifying fine ultra-dilute emulsions was proposed by Fowkes, Anderson and Berger. They ascribed the filtering action (which we have confirmed with oil-in-water emulsions) to electrophoretic deposition of the electrically charged droplets in the self-generated electrical fields between each pair of dissimilar metal granules.

We have demonstrated that exposure of dilute hydrosols of solid particles to granulated metals can be used for removal of the particles and that the technique offers promise as a simple method of water clarification.

Using monodisperse cationic and anionic polystyrene latex hydrosols as model systems, we have studied particle removal by compacted granular beds and stirred suspensions of single metals or in pairs. Our measurements of the removal efficiency of particles in the presence of various electrolytes and metal combinations, coupled with our observation that the method can be made to work with single metals, cast doubt on the validity of the FAB mechanism; several alternatives are briefly discussed."

Studies of dynamic wetting (J.F. Oliver and S.G. Mason)

A novel application of monodisperse latexes has been demonstrated in this study wherein polystyrene and polyvinyltoluene latexes are deposited by careful drying, with or without partial fusion, to obtain model surfaces of controlled uniform roughness for investigation of the phenomenon of fluid wetting and spreading. The use of liquid polyphenylethers permits dynamic studies in the scanning electron microscope.

N-1

POLYMER-COLLOIDS NEWSLETTER
STUDIES AT THE UNIVERSITY OF SYDNEY

D.H.Napper

This contribution reviews two of our recent theoretical studies.

(i) Steric Stabilization

The aims of any theory of steric stabilization must be to predict correctly both the flocculation behaviour of sterically stabilized dispersions and the distance dependence of the repulsion of stable systems. We have found that the theories of Meier, of Hesselink, Vrij and Overbeek and of Clayfield and Lumb fail on both accounts. The reasons for this are two-fold: first, their method of attack contains a subtle thermodynamic standard state error; second, they use segment distribution functions relevant to isolated molecules, whereas experiments usually refer to macromolecules with strong lateral interactions with their neighbours. When these errors are removed it is possible to develop a quantitative theory of steric stabilization that is in good agreement with most aspects of experiment. The theory is sufficiently simple to be expressed analytically.

(ii) Emulsion Polymerization

The Smith-Ewart recursion formula is based upon the steady-state approximation. Their solution for $\bar{n} \ll 1$ is unsatisfactory in that it involves unknown and undeterminable parameters (like free radical adsorption coefficients). Ugelstad and co-workers have extended significantly both our theoretical and experimental understanding of this case, again using the steady state approximation. We have been interested in obtaining analytical solutions to this problem without invoking the steady-state approximation, the advantage being that fewer model-dependent assumptions are then necessary. Fortunately

there is a useful analogy between the occupancy of quantized energy states and the presence in latex particles of free radicals whose basic 'quantum' is just one free radical. It is thus possible with the collaboration of our theoretical colleague, Dr. R.G.Gilbert, to use the mathematical procedures developed for unimolecular gas decomposition reactions to solve analytically the differential equations describing a polymerizing latex for which $\bar{n} \ll 1$.

Large Particle Size Latices

A considerable amount of our work on the formation of monodisperse polystyrene latices, in the particle size range 0.1 to 1 μm , has now been completed and written up. Reprints of the recent paper in Br. Polymer J., 1973, 5, 347 will be sent to all members of the group.

For many studies on polymer colloids there are considerable advantages in being able to observe the particles directly by optical microscopy in a fluid medium. In order to do this particles in the size range 2-4 μm are convenient and give good resolution. The "universal plot" which we produced recently indicates that single-stage growth, in the absence of surface active agent, is not a convenient method to produce large particles in view of the risk of very extensive coagulation occurring.

We have therefore been using a seeded growth process. Starting with a seed of approximately 0.9 μm in diameter and using our previous preparation conditions (0.87 mol dm^{-3} styrene, 1.8×10^{-3} mol dm^{-3} potassium persulphate, total ionic strength 3×10^{-2} , temperature 60°C) we find the first growth stage produces particles of diameter 2.5 μm . A second growth stage under similar conditions produces particles of ca. 4 μm diameter with a very narrow spread of particle diameters. The method clearly works and produces good quality latices. It is, however, sensitive to the seed concentration used, too little seed producing extensive secondary growth and a polydisperse particle size distribution, too much seed producing coagulation (very dramatic!). Much of our experimental work on this project is now complete but we still have the task of completing the rather tedious particle size analysis required. We hope to report on this project more extensively in June.

Rheological Measurements

A preliminary investigation of the elastic properties of a polystyrene latex has been carried out. The apparatus that was used was identical to that used by van Olphen¹ in an investigation of the shear modulus of montmorillonite gels. It consists of two parallel discs which can be set at a known distance of separation up to 3 cm

1. H. van Olphen, Clays and Colloids

apart. A small transient deformation is applied to the sample in the form of a small shear pulse from one of the discs. The time taken for the shear wave to reach the second disc is measured so the propagation velocity of the shear wave is known and the shear modulus of the latex is related to the propagation velocity.

Experiments have been carried out with an emulsion polymerised polystyrene latex which had been extensively dialysed against distilled water. The particle size was 85.6 nm and the elastic modulus of this latex was determined as a function of volume concentration at electrolyte concentrations of 10^{-5} , 5×10^{-5} , 10^{-4} and 10^{-3} mol dm⁻³. It was found that, even at the highest electrolyte concentration, a measurable shear modulus (G) was observed at a volume fraction as low as 0.15. The order of G was 10^3 dyn cm⁻² and this is similar to that found with a fairly dilute gelatine solution. The results gave the lowest value of G at low volume fractions and at a fixed volume fraction there was a systematic variation with electrolyte concentration giving the lowest value of G at the highest ionic strength.

It is proposed that a shear modulus is found when there are appreciable interparticle forces produced by the overlap of the electrical double-layers of the particles in the suspension i.e. the same conditions that produce the ordered structures that are found in monodisperse lattices at low electrolyte concentrations. This kinetic method of the measurement of shear modulus produces a small deformation from the equilibrium position of an ordered latex structure. The restoring force may be calculated from the imbalance of interparticle forces and the shear modulus is a function of the slope of the force distance curve at the equilibrium position.

From:

Vivian T. Stannett
Dept. of Chemical Engineering
N. C. State University
Raleigh, N. C. 27607

During the last few months, work on emulsion polymerization has been very restricted, due to budget cuts. The only experimental work has been to carefully determine the intensity dependence of the rate of emulsion polymerization of styrene on the radiation intensity (cf. Feb. 1973 report S.1). A dependence of 0.36 was found, again confirming that styrene closely fits Smith Ewart case II with radiation initiation at room temperature.

I am taking advantage of this lull in experimental activity to write up some previous work and attach the abstract of three papers which are now being completed. I will try to get preprints or reprints of these to the members as soon as possible.

THE RADIATION-INDUCED POLYMERIZATION AND
COPOLYMERIZATION OF BUTADIENE IN EMULSION

by

K. Ishigure, T. O'Neill, E. P. Stahel, and V. Stannett
Chemical Engineering Department
North Carolina State University
Raleigh, North Carolina 27607

ABSTRACT

The polymerization of butadiene in emulsion initiated by Cobalt-60 gamma radiation has been studied in some detail. Similar studies with styrene and styrene-butadiene comonomer mixtures were also conducted. The rates of polymerization were found to be much lower than anticipated from the reported k_p values for butadiene and for the comonomer mixtures. Styrene, on the other hand, polymerizes at normal rates. A number of possible explanations for this behavior is discussed.

THE RADIATION-INDUCED COPOLYMERIZATION
OF
BUTADIENE WITH ACRYLONITRILE IN EMULSION SYSTEMS

by

K. Ishigure* and V. T. Stannett
Chemical Engineering Department
North Carolina State University
Raleigh, North Carolina 27607

Abstract

The copolymerization of butadiene and acrylonitrile in emulsion has been studied using gamma radiation for the initiation process. The polymerizations proceeded smoothly with good yields, G (monomer consumption) values ranging from 8,000 to 100,000. Some deviations from the standard Smith-Ewart Case II theory were observed particularly with respect to the dependence of the rate on the soap concentration. A strong post effect was observed showing a clear first order radical termination process. The copolymer reactivity ratios were found to be normal.

* present address: Nuclear Engineering Department, University of Tokyo, Japan

γ-RADIATION-INITIATED POLYMERIZATION OF
ACRYLONITRILE IN AQUEOUS SOLUTION AND IN EMULSION

Thomas O'Neill* and Vivian Stannett**

Department of Chemical Engineering,
North Carolina State University at Raleigh, 27607 N.C.,
USA

ABSTRACT The γ-radiation-initiated polymerization of acrylonitrile, (AN), at 25°C has been studied, both in aqueous solution and in emulsion, at dose-rates between 70 and 175 krad/h. The effect of added emulsifier sodium lauryl sulfate (SLS), on reaction rates, R_p , and on polymer molecular weight, M_n , has been investigated. G (monomer polymerized) values ranged from 7,500 in aqueous solution to 20,000 in bulk to 45,000 in emulsion, all based on the total energy absorbed.

In the aqueous solution polymerization, where R_p is approximately first order in initial monomer concentration over the range $0.15 \leq [AN]_0 \leq 1.06 \text{ ML}^{-1}$, addition of SLS increases R_p but does not influence the order of the reaction with respect to $[AN]_0$. In the emulsion system at 70 krad/h and at a phase volume ratio AN/H₂O of 1/2, (PR = 1/2), R_p varies as $[SLS]^{0.1}$ over the concentration range $0.01 \leq [SLS] \leq 2.5 \%$ wt/vol. of aqueous phase. At the same PR value, and at 80 krad/h, M_n of the polymer (measured by viscometry in dimethylformamide solution) is effectively independent of $[SLS]$ in the range of $0.01 \leq [SLS] \leq 10 \%$ wt/vol. of aqueous phase. Initial R_p values are either independent of PR in the range $1/3 \leq PR \leq 1/1$ or exhibit an insensitive and unsystematic dependence thereon. Based on measurements at 70 and at 175 krad/h, the intensity exponent of R_p at PR = 1/2 is approximately 0.4.

Investigation of Monomer Emulsion by Electron Microscopy.

John Uoelstad

Laboratory of Industrial Chemistry, The University of Trondheim, Norway.

As we have reported in some recent papers we found that a mixture of ionic emulsifiers and long chain fatty alcohols gave very fine dispersions of monomer droplets and we suggested that in this case the initiation of polymerization takes place in the monomer droplets. This conclusion was based upon the kinetics of polymerization¹⁾ and upon comparison of the monomer droplet size and latex particle size by optical microscope²⁾. The difficulty with optical microscopy lies in the fact that in some cases the size of droplets and latex particles are on the borderline of what may be clearly observed by optical microscopy, in some cases the electron microscopic pictures of the latex revealed a fraction of particles too small to be observed in the optical microscope.

During the last 4 months we have had the pleasure of having R. Fitch at our institute. One of the projects on which we have started a cooperation concerns emulsion polymerization of various monomers with different mixed emulsifier systems. In that connection we have been looking into different methods for determining size and size distribution of the monomer emulsions. It turned out to be difficult to obtain reliable results by light scattering because the size distribution is too broad. Quite lately we have, however, obtained very promising results with electron microscopy. This is obtained by treating the emulsion with OsO_4 which reacts with the double bonds. These investigations are being carried out by NORAD fellow A.R.M. Azad and civ.eng. Elizabeth Baumann Ofstad.

Schulman found that he could obtain rather good pictures of microemulsions of unsaturated oils or alkyd resins by exposure to OsO_3 vapour. In our case the technique described by Schulmann was not found to be satisfactory. The difficulty lies in obtaining a complete staining without destroying the emulsion. This could be achieved by application of a solution method where a water solution with the proper amount of OsO_4 was added to the emulsion. In Figures 1, 2 and 3 below are given some preliminary results of electron microscopy of monomer emulsion.

Fig. 1: Styrene-water 1:3 emulsified with Na cetylsulphate-cetyl alcohol.

Fig. 2: Styrene-water 1:3 emulsified with hexadecyl trimethyl ammoniumbromid + cetyl alcohol.

Fig. 3: is similar to Fig. 2: In this case, however, we have after the OsO_4 treatment shadowed with Pd/Pt at 30° angle. The figure shows that

we have obtained spheres by the OsO_4 treatment.

In Fig. 4 is for comparison given a picture of a latex prepared by polymerization of the emulsion shown in Fig. 1 with persulphate as initiator. As will be seen there is in the latex a broad distribution of particles in the range 0.4 to 1.5 μ very similar to the size and size distribution of monomer droplets. Also there is in addition a fraction of particles of about 0.2 μ with a rather narrow distribution. In previous papers we have suggested that the large particles with the broad distribution stem from initiation in the monomer droplets, the small ones from initiation in the water phase. A comparison of Fig. 4 with Fig. 1 seems to support this assumption.

Fig. 5 shows a latex prepared from a similar emulsion but with AIBN as initiator. Again this picture should be compared with Fig. 1 of the corresponding monomer emulsion. It is interesting to note that also in this case with an oil soluble initiator we have got a large fraction by number of small particles which seems to stem from initiation in the water phase. Possibly this may partly result from desorption of radicals from the droplets.

It seems that this method of examination of monomer emulsions by electron microscopy may have many potential applications in several fields of emulsion problems beside emulsion polymerization.

We hope to publish a more extensive description of the method within soon.

References:

1. J. Ugelstad, F.K. Hansen and S. Lange: *Makromol.Chem.*, in press.
2. J. Ugelstad, M. El-Asser and J. Vanderhoff, *J.Polym.Sci. B 11*, 503 (1973)



Fig. 1. Styrene monomer emulsion
Styrene 300 g, H₂O 1000 g
Na cetylsulphate 2.15 g
Cetyl alcohol = 6 g.

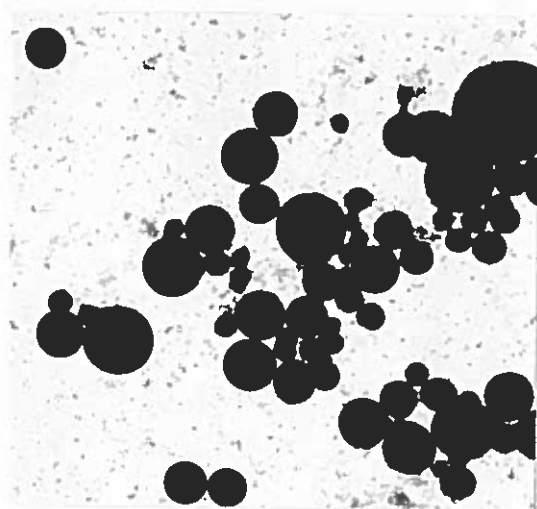


Fig. 2. Styrene monomer emulsion
Hexadecyl trimethylammonium
bromide = 3 g
Cetyl alcohol = 8 g

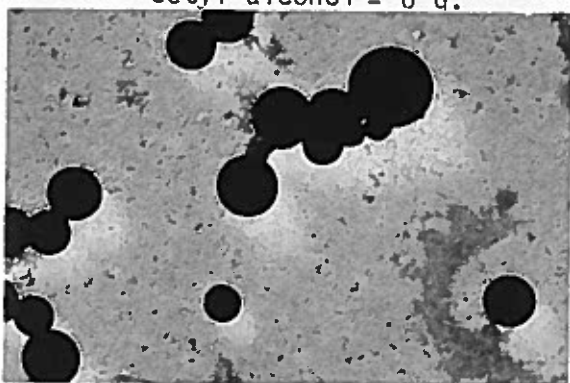


Fig 3. Styrene monomer emulsion as in Fig. 2.
Shadowed.



Fig. 4. Latex prepared by polymeri-
zation of monomer emulsion
shown in Fig. 1.
Initiator K₂S₂O₈.

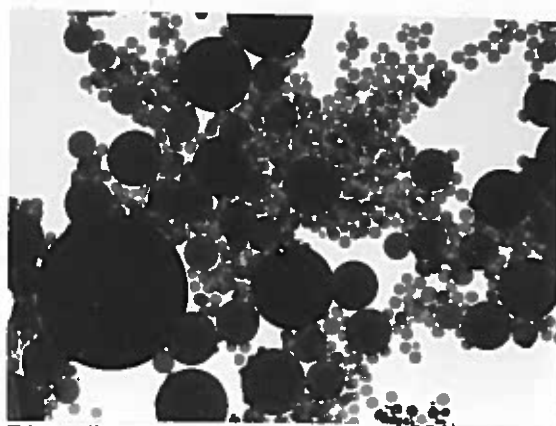


Fig. 5. As Fig. 4 with AIBN as
initiator.

MAGNIFIED 7800x

Polymer-Colloid Newsletter

T. P. Wallace

February, 1974

Core-Shell Morphology (O'Jea) - Work is proceeding with this project as outlined previously, and a satisfactory emulsion polymerization recipe for a heterogeneous copolymerization has been established. We are now examining the theoretical scattering from concentric spheres and hope to have some results by the summer meeting.

Size Distribution Analysis via Analytical Centrifuge (Loewenstein)

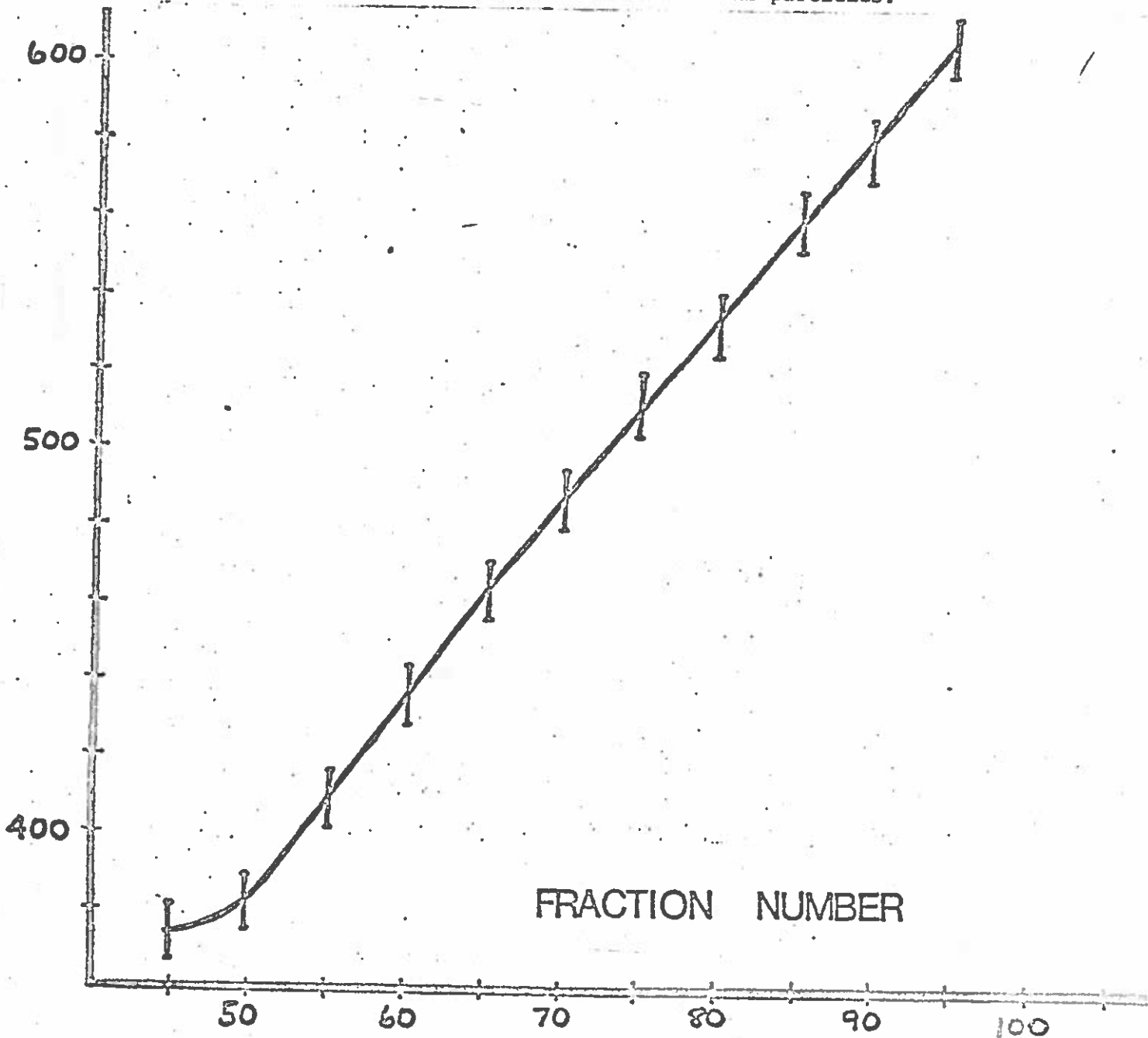
Particle size distribution of latexes are determined employing a sedimentation velocity ultracentrifugation and an absorption optical system in which the sedimentation of latex particles is initially recorded on photographic film. Results from the above technique will be compared to those of McCormick and Averink et. al. who did similar work using schlieren optics, and absorption optics (constructed with a direct-reading scanning absorption attachment in place of photographic film) respectively. Particle size distribution results are compared with light scattering distributions on the same samples.

Initial results show good agreement between modal diameters from the analytical ultracentrifuge with those of light scattering and electron microscope determinations. The distribution width from ultracentrifugation results appear to be smaller than those obtained from light scattering for the same "monodisperse" latex sample. An explanation for the deviation in distribution widths is being attempted by computer simulation of a velocity ultracentrifugation experiment.

Combined Preparative Centrifuge - Light Scattering Technique As Applied To Small Latex Particles (DeCann) - Based on our previous reports, the rotor

of a Beckman L 2-65 B Ultracentrifuge can be calibrated to yield a plot of Diameter vs. Fraction Number (i.e. distance from center of rotation, Fig. 1).

This technique is presently being extended to small particle sizes (i.e. $D < 0.2\mu$); the basis being the ability to calibrate the rotor with samples having $D > 0.2\mu$. We expect to be able to obtain a distribution width parameter from the angular light scattering pattern once the modal size is known. It should be noted that the usual size distribution analysis from angular scattering data is not possible for such small particles.



V.I.Yelisseyeva

ON THE EFFECTIVENESS OF NON-IONIC EMULSIFIER IN THE
EMULSION POLYMERIZATION OF ACRYLIC MONOMERS WITH
DIFFERENT POLARITIES

(A.V.Zuikov, N.G.Zharkova)

The effectiveness of an emulsifier in the emulsion polymerization is related to the HLB number and its monomer polarity. However no unequivocal relation was established. We studied an effectiveness of non-ionic emulsifier C-30 ($C_{16}H_{33}(CH_2CH_2O)_3H$) in the emulsion polymerization of acrylic monomers having different polarities and solubilities in water (MA, EA, BA, BMA). Earlier we have studied the emulsifiers of such type in the emulsion polymerization of styrene initiated by a less soluble substance /1/ and assumed a constant particle size in the course of latex formation within the "ultra-microemulsion" drops^x).

The CMC of C-30 emulsifier is $5.22 \cdot 10^{-6}$ mole/l. When CMC is equal to 53 erg/sq.cm, the electrical conductivity of 1% solution at 25°C was $1.21 \cdot 10^{-5}$ ohm⁻¹cm⁻¹.

Table 1 lists the true and colloid solubilities of the monomers investigated in water and aqueous emulsifier and determined by refractometric method. It can be seen that these values depend essentially on the monomer polarity and they reverse for the given monomer series: for MA the true solubility exceeds the colloid one, while opposite dependence was observed for BA and BMA.

^x) Similar viewpoint has been advanced by Ugelstad et al. /2/ on the mechanism of polymerization of various monomers initiated by persulfate in the mixtures of emulsifiers: cetyl alcohol - Na lauryl sulfate.

Table 2 shows physical and chemical properties of the latexes obtained. The polymerization was performed in an ordinary laboratory reactor under argon at the monomer to water ratio 1:4.

Table 2 demonstrates that depending on the monomer employed the latexes obtained have different stabilities, particle size and surface tension. The lowest stability was observed with MA (the greatest quantity of coagulum). The highest colloid stabilities in both polymerization and storing were revealed for latexes of PBMA and PBA (prepared with ammonium persulfate). The PEA and PBA latex prepared with benzoyl peroxide separated into layers at storing (most rapidly in the case of PBA). A comparison of these results with the data of table 1 manifested no correlation between the latex stability and monomer solubility in the emulsifier solution. This could be expected because of different affinity of the hydrocarbon part of the given emulsifier towards the monomers investigated. Also this could be due to their different location in the micelles of emulsifier: it is assumed that hydrophobic monomer locates in a hydrocarbon core of the micelle, the portion of monomer in the polyoxiethylene chains increasing with polarity /3/.

Figures 1-5 present the electron micrographs of latex particles irradiated with Co^{60} (20 megarad) for solidifying the polymer. Fig.2a specifies the particles of sedimented PEA latex fraction (non-irradiated). Distribution of latex particles with the diameter (obtained by counting 300-500 particles) is shown in figure 6.

It can be seen from these data that the freshly prepared PMA and PEA latexes contain along with the finely dispersed fraction also a roughly dispersed particle fraction which could be due to a different generation mechanism (e.g. in the micelles, drops or aqueous solution). However specific viscosities of the polymer samples in acetone taken from the freshly prepared non-sedimented latex and its precipitate were equal to 22.43 and 22.2 respectively. Thus the mean molecular weight of the polymer in these samples is the same. Since the precipitate formation is a result of sedimentation of coarse particles (electron micrograph in fig. 2a) one may assume that all particles were generated by the same mechanism and their different size is explained by flocculation due to the low adsorption energy of emulsifier on the polar polymer surface.

The surface tension of PMA and PEA latexes is essentially lower than that corresponding to CMC of emulsifier (53 erg/sq.cm.). This may serve as an evidence that the polymerization starts in an aqueous phase with formation of the surface active oligomers which are known to be the source of particle generation during their growth and sedimentation. In this case the function of emulsifier introduced is consistent only with its adsorption on the generated nuclei and then on the polymer-monomer particles. (Apparently stabilization due to the low-molecular weight surface active oligomers generated in an aqueous phase is negligible: they formed in a great quantity in runs 1 and 2), but latexes formed are unstable. Such mechanism may take place as well at the persulfate initiated polymerization of the

less polar BA whose colloidal solubility in the emulsifier far exceeds its true solubility in water. This is confirmed by comparison of stability and distribution curves of PBMA latex particles obtained with persulfate (run 4) and oil-soluble initiator (run 3): when polymerization in an aqueous phase (at the beginning) is possible then a monodisperse stable latex is formed. On the other hand if polymerization in an aqueous phase is excluded and a micellar mechanism is prevailing (run 3) then the great number of particles is produced at ~~about~~ the same rate of radical formation and their surface is not stabilized by the given emulsifier quantity during the growth. It is quite probable that a decrease of stability (tendency to the flocculation of PBMA latex particles (figure 5)) may be due to the lower contribution of such less soluble monomer into polymerization in an aqueous phase.

The data obtained show that the emulsifier effectiveness in the persulfate initiated polymerization of the monomers investigated is not due to its solubilizing ability. It could be associated with its adsorption energy on the surface generated which for emulsifier investigated is decreasing with increasing monomer polarity and solubility in water.

REFERENCES

1. S.S.Medvedev, A.V.Zuikov, U.I.A.Gritskova, V.V.Dudukin, Vysokomolek.Soedin., 13A, No.6, 1397, 1971.
2. J.Ugelstad, H.Flogstad, F.K.Hansen, T.Ellingsen, IUPAC, Intern.Symp. on Macromol., Helsinki, Preprint, v.1, 273, 1972.

3. K.Sinoda, T.Nakagava, B.Tamamusi, T.Isemura, Moscow, 1966, p.163 (fig.54).

Table 1

| No. Monomer | | Limiting solubility, vol.%, at 25°C | |
|-------------|-----|-------------------------------------|-----------------------------------|
| | | in water | in 1% solution of emulsifier C-30 |
| 1 | MA | 5.24 | 4.29 |
| 2 | EA | 2.00 | 2.18 |
| 3 | BA | 0.18 | 1.22 |
| 4 | BMA | 0.003 | 0.85 |

Table 2

| No. | Mono-mer | Polymeri- zation temp. °C | Polymeri- zation time, hr | Emulsi- fier to monomer, % | Initia- tor to monomer, % | Mono- mer conver- sion, % | Latex con- cent- ration, % | Characte- ristics of latex, of stability | Latex sur- face ton- sion, γ erg/sq.cm | Size of latex particles, μ |
|-----|----------|---------------------------|---------------------------|----------------------------|--|---------------------------|----------------------------|---|---|--------------------------------|
| 1 | MA | 58-60 | 6 | 8 | (NH ₄) ₂ S ₂ O ₈ 0.025 | 97 | 16.60 | coagulum at the synthe- sis, 8% to monomer | 45.75 | 5000-70000 1800-2000 |
| 2 | EA | 63-65 | 5.5 | 8 | (NH ₄) ₂ S ₂ O ₈ 0.1 | 94 | 19.50 | coagulum is absent latex sedimented at storing | 46.70 | 5000-8000 500-1000 |
| 3 | BA | 50-55 | 16 | 8 | (C ₆ H ₅) ₂ O ₂ 0.1 | 80 | 16.00 | coagulum at the synthesis, 1.6% to mono- mer, latex sedimented on the next day. | 51.00 ^x | 1200-2000 300-800 |
| 4 | BA | 68-70 | 7 | 8 | (NH ₄) ₂ S ₂ O ₈ 0.1 | 93 | 19.60 | no coagulum, latex is stable at | 50.30 | 1000-2000 |

| | | | | | | | | | |
|-----|-------|---|----|---|----|-------|--------------|-------|------------|
| EMA | 80-85 | 8 | 10 | (NH ₄) ₂ S ₂ O ₈ | 91 | 19.60 | no coagulum, | 53.60 | 1600--1800 |
| | | | | 0.1 | | | latex is | | |
| | | | | | | | stable at | | |
| | | | | | | | storing | | |

The lower \bar{M}_v with respect to CMC may be explained by the presence of free monomer in the system (see conversion).

CAPTIONS

Fig. 6. Distribution curves of the latex particles obtained with the diameter:

- a - run 2,
- b - run 1,
- c - run 3.

Electron micrographs of the prepared latex particles, X 10000:

- Fig. 1. run 1,
- Fig. 2. run 2, Fig. 2a - run 2, latex precipitate,
- Fig. 3. run 3
- Fig. 4. run 4,
- Fig. 5. run 5

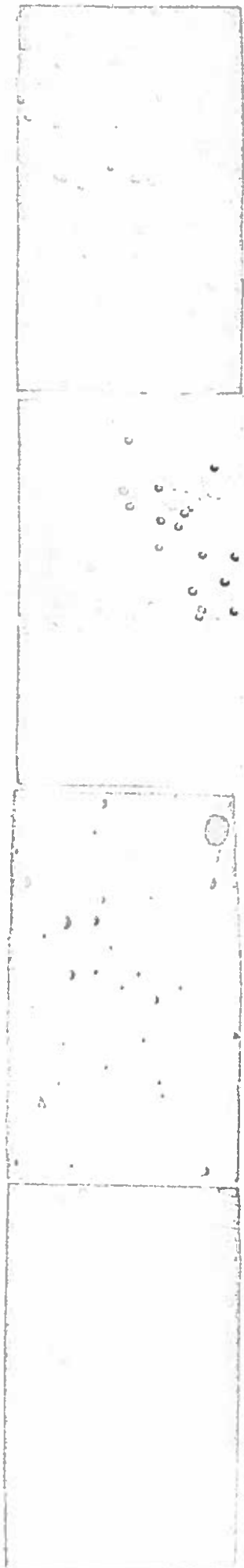


Fig.1. run 1

Fig.2. run 2

Fig.4. run 4

Fig.5. run 5.



Fig.2a - run 2, latex precipitate

Fig.3. run 3

Electron micrographs of the prepared latex particles, X 10000:

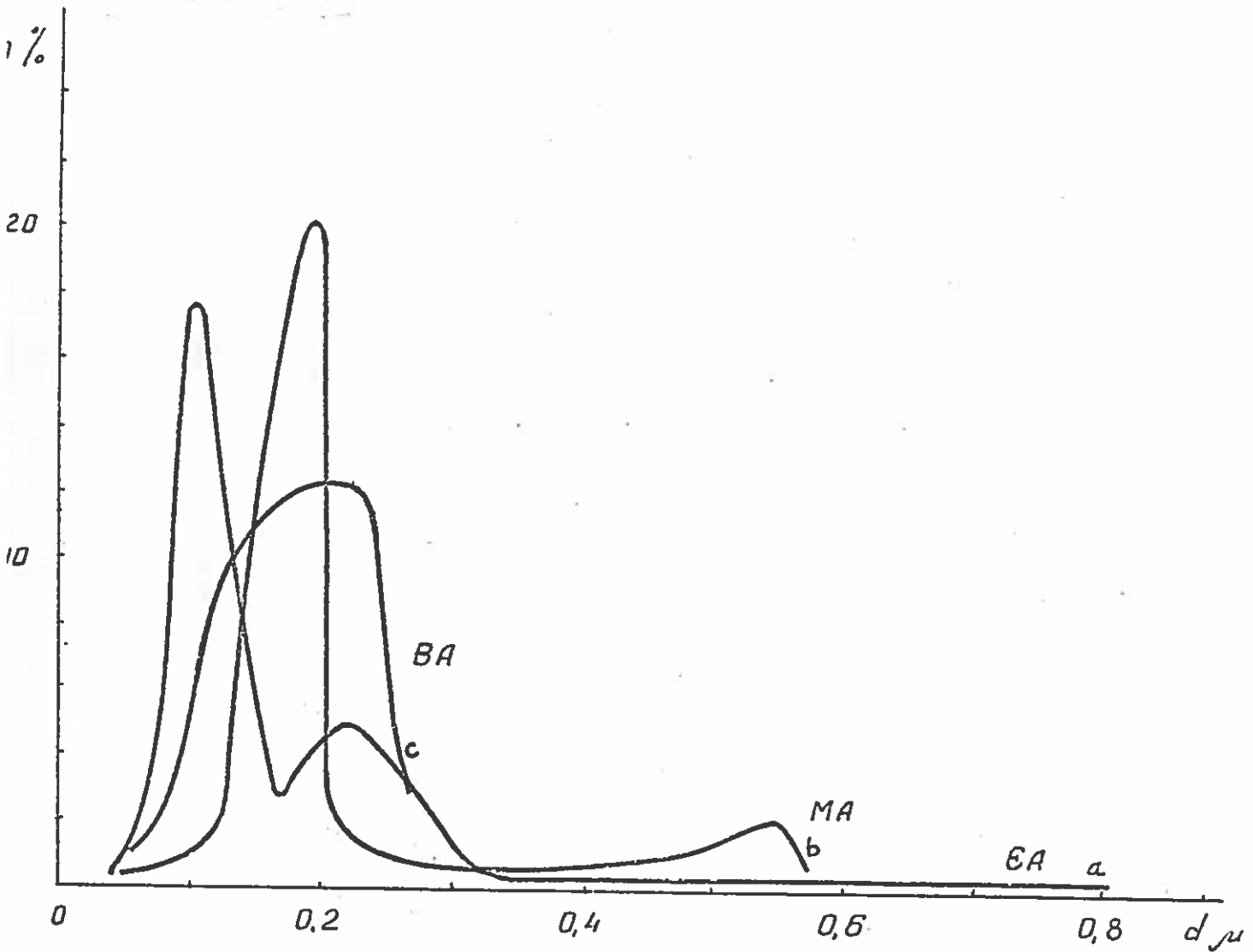


Fig 6

Distribution curves of the latex particles obtained with the diameter: a - run 2, b - run 1, c - run 3.

V.I.Yeliseyeva

A SUBMOLECULAR STRUCTURE IN THE LATEX POLYMER PARTICLES

(N.G.Zharkova)

Earlier we have shown that the mechanical, physical and chemical properties of the latex acrylic polymer films with the functional groups ($-\text{CONH}_2$, $-\text{COOH}$, $-\text{CONHCH}_2\text{OH}$) differ essentially from those of the polymer films prepared from their dioxan solution /1,2/. Thus we have first advanced an idea of specific submolecular structure of the polymer in its latex particles which may be destroyed upon dissolving in an organic solvent.

The reason to such a suggestion was an orienting effect of the aqueous phase upon the conformation of macromolecules with strong polar groups which may generate at an interface. To confirm this hypothesis we used the method of careful polymer pickling (degradation) in its latex particles and films with the active oxygen. The pickling procedure has been described in /3/.

Such method makes it possible to elucidate a polymer morphology by means of faster "pickling" its less dense areas. The polymer structure could be judged from the relief observed at considerably different densities.

The latexes were deposited on silicon monoxide film substrates, subjected to pickling and shadowed with platinum at an angle of 20° . After pickling with oxygen the films were studied by the method of one-step carbon replicas shadowed with platinum. An optimum pickling time of the particles and films was determined experimentally. Figures 1 and 2 show the electron micrographs of replicas from pickled surfaces of the

acrylic polymer films containing 4.3 % of methacryl amide and the same quantity of methacrylic acid respectively. Figures 1a and 2a present the data on latex films, figures 1b and 2b correspond to those obtained from solution.

In order to obtain an evidence of the specific submolecular structure in the latex polymers without the highly polar groups, we used the foregoing method for investigating the structure of the polystyrene latex particles as well as the particles and films of polyvinylacetate dispersions prepared with different emulsifiers. The respective electron micrographs are shown in figures 3, 4 and 5.

As it can be seen from the electron micrographs all investigated latex particles have complex structure depending on the chemical nature of monomers. Thus the polystyrene latex particles are the aggregates of smaller globules (figure 3). The structure of polyvinylacetate latex particles prepared in the presence of 10% polyvinyl alcohol (figure 4a) differs considerably from that of polystyrene and has a fibrillar polymer orientation (figure 4b) retaining in its film as well (figure 4c)

Polymerization of vinylacetate in the presence of other emulsifier, potassium hydrofluoropelargonate, produces the particles with sharply different packing density of the polymer in the bulk and periphery. This was evident from the electron micrographs of the same non-pickled latex particles shadowed with platinum (figure 5). Oxygen pickled the peripheral parts at first (figure 5a), with the polymer conformation (the presence of macromolecular blocks) in the bulk retaining after

pickling. Investigation of the structure of this latex films (figures 5c,d) may demonstrate that it is defined by the structure of latex particles, i.e. by the presence of parts with different densities.

The data obtained allows the assumption to be made that the polymerization takes place in the vicinity of interface with an aqueous phase. In this case the macromolecules of polar polyvinylacetate acquire an open conformation (figure 4) because of the minimum free energy at an interface. The adsorption of polymers with hydrophilic groups (proteins) has been studied in /4/. It has been shown that when macromolecules meet an interface they disclosed and increased the strength of the adsorption layers. By a similar reason at the polymerization of hydrophobic monomers the macromolecules generated in vicinity of an interface have twisted conformation (polystyrene) (figure 3). There is yet no explanation to a specific structure of PVA latex particles obtained in the presence of potassium hydrofluoropelargonate (figure 5) although it may resemble a "core-shell" morphology assumed by Williams et al.

REFERENCES

1. V.I.Eliseeva, N.G.Zharkova, E.I.Evko, V.M.Luk'yanovich, *Vysokomolek.Soedin.*, 9(A), No.11, 2478, 1967.
2. V.I.Eliseeva, N.G.Zharkova, T.N.Pavlinova, V.M.Luk'yanovich, *Vysokomolek.Soedin.*, 9(A), No.12, 2534, 1967.
3. M.R.Kiselev, E.I.Evko, V.M.Luk'yanovich, *Zavodskaya Laboratoriya*, 2, 201, 1966.
4. V.M.Izmailova, Autoreferate of doctoral thesis, Moscow State University, Moscow, 1971.

4. 13

CAPTIONS

- Fig. 1. Electron micrographs of replicas from the surface of pickled acrylate polymer films containing 4.3 mol.% of methacryl amide, X 40000:
- a - film obtained from the latex,
 - b - film obtained from polymer solution in dioxan.
- Fig. 2. Electron micrographs of replicas from the surface of pickled acrylate polymer films containing 4.3 mol.% of methacrylic acid, X 40000:
- a - film obtained from the latex,
 - b - film obtained from polymer solution in dioxan.
- Fig. 3. Electron micrographs of polystyrene latex particles X 80000:
- a - initial particles (sample without shadowing)
 - b - particles after oxygen pickling for 16 min.
- Fig. 4. Electron micrographs of the particles and replicas from the surfaces of polyvinylacetate latex film prepared with polyvinyl alcohol, X 10000:
- a - initial particles (sample without shadowing),
 - b - particles after oxygen pickling for 12 min (sample without shadowing),
 - c - film after oxygen pickling for 15 min.
- Fig. 5. Electron micrographs of the particles and replicas from the surfaces of polyvinylacetate latex films prepared with potassium hydrofluoropelargonate, X 40000:
- a - initial particles,
 - b - particles after oxygen pickling for 10 min.,
 - c - a non-pickled film,
 - d - film after oxygen pickling for 15 min.

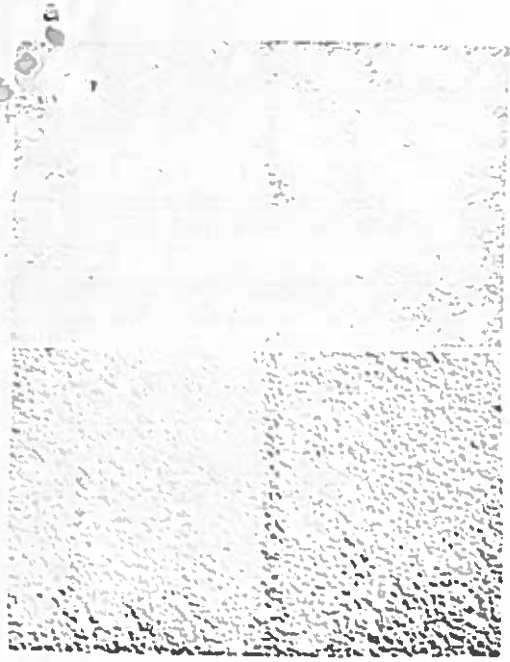


Fig.1.



Fig.2.



Fig.3.



Fig.4.

