

International Polymer Colloid Group
Newsletter

Volume 2, No. 2, February 1973

D.J. Williams, Editor

Well, we are a bit later than usual, but I have been receiving contributions from mid-January until virtually yesterday. John Ugelstad and Allan Robertson have excused themselves from this issue.

You can all relax until next September when contributions to the next issue are due. Our next number is to contain the agenda for our June meeting. It is my understanding that this matter is being handled by Irv. Krieger and Gary Poehlein.

The possibility of the group's publishing a textbook, as stated in my letter of November 10, 1972, has received unanimous endorsement. I'll put together a more detailed outline with tentative topic assignments so we'll have a focal point for discussion in June.

Dunn - Manchester

The 'HETTEROPHASE and EMULSION POLYMERS' Symposium organised by Dr Eric White of UMIST on behalf of the Plastics and Polymer Group of the Society of Chemical Industry held in London 24/25 January attracted a total attendance of 193 and seemed to be generally felt to be a very successful meeting scientifically and socially as well. I will be writing a report of the meeting for 'Polymer Age' and should be able to circulate a preprint of this report shortly.

I was glad to be able to make the acquaintance of two new entrants to this field of research - Dr J. M. Liegeois of the University of Liege and Dr N. Friis of the Danish Atomic Energy Commission Research Establishment at Risø. Liegeois presented a paper at the 1970 IUPAC Brussels-Louvain Macromolecules Symposium (*J. Polym. Sci. C* 33 (1971) 147) on the rate of initiation of the vinyl chloride emulsion polymerisation by persulphate in which he shows, from the effect of oxygen concentration, that the reversibility of the reactions involved in the oxidation of persulphate by water must be considered. He has recently published (in English) the detailed evidence for this (*Bull. Soc. chim. Belg.* 81 (1972) 393). Friis has had a paper entitled 'A Kinetic Study of the Emulsion Polymerization of Vinyl Acetate' accepted for publication in *J. Appl. Polym. Sci.* This is a study using persulphate initiation undertaken to support a study using radiation induced emulsion polymerisation which he reported at the 1972 IUPAC Macromolecules Symposium at Helsinki (Preprint 1 - 15): he finds that the Stage II polymerisation of vinyl acetate is characterised by the importance of transfer to monomer resulting in the escape of radical from the latex particles.

My own contribution to the Symposium was the European presentation of the paper I gave at the A.C.S. New York Meeting, of which a Preprint has already been circulated. However I included a rapid but extensive survey of the literature on enhanced initiator decomposition in emulsion systems which was not included in the preprint summarised below.

A. S. DUNN

PAPERS PROVIDING EVIDENCE FOR AN ENHANCED RATE OF PERSULPHATE DECOMPOSITION IN EMULSION SYSTEMS.

1. P.D.Bartlett & J.D.Cotman (J.A.C.S. 71 (1949) 1419) find the decomposition rate (iodometric) is $3/2$ order in persulphate and $1/2$ order in methanol using 0.015 M persulphate and 0.2 - 2 M methanol. These reaction orders were consistent with an Induced Chain decomposition of persulphate due to reaction with radicals derived from the methanol (similar to the reactions of organic peroxides studied earlier). Decomposition accelerated x 25.
2. A.I.Yurzenko & O.P.Brazhnikova (Zh. Obs. Khim. 26 (1956) 1311; J. Gen. Chem. USSR (English Translation) 26 (1956) 1481) find the decomposition rate (iodometric) accelerated by factor of approx. x 2.5 by dispersions of hydrocarbons. Sodium dibutyl naphthalene sulphonate emulsifier gives x 1.5 acceleration. Their activation energy for the decomposition of persulphate in the absence of additives (136 kJ mol^{-1}) agrees well with Kolthoff & Miller's value (140 kJ mol^{-1} ; J.A.C.S. 73 (1951) 3055) but extrapolating their results to 60°C gives a rate constant 6.6 times larger than Kolthoff & Miller's. (Probably their persulphate or water was impure. Even higher values were reported in earlier papers from the same laboratory: the authors themselves offer no comment on these discrepancies)
3. F. Stürzenhofecker (Angew. Chem. 71 (1959) 198. A report on the 1959 Freiburg Macromolecular Colloquium. No definitive publication has followed.) found that t-butanol did not increase rate of persulphate decomposition. Aromatic hydrocarbons retarded the oxidation of other alcohols and esters.
4. A.I.Yurzenko & T.S.Yurzenko (c.f. Chem. Abs. 51 (1957) 10117e) find $\text{AmOH} > \text{BuOH} > \text{EtOH} > \text{MeOH}$ in reducing rate of polymerisation and molecular weight of polymer produced from styrene emulsified with sodium dibutyl naphthalene sulphonate initiated by persulphate.
5. D.L.Ball & J.O.Edwards (J. Phys. Chem. 62 (1958) 343) find that the persulphate oxidation of isopropanol is catalysed by trace amounts of metal ions: lower rates are found when these are sequestered with E.D.T.A. Dissolved oxygen also affects the reaction.
6. L.S.Levitt, B.W.Levitt & E.R.Malinowski (J. Org. Chem. 27 (1962) 2917) propose the formation of a persulphate ester as an intermediate in the oxidation of alcohols. L.S.Levitt (c.f. J. Org. Chem. 20 (1955) 1297) advocates heterolytic mechanisms for oxidation reactions in general (excluding autoxidations). He claims oxygen does not affect the persulphate oxidation of alcohols. Contrary to the claim of K.B.Wiberg (J.A.C.S. 81 (1959) 252) 0.04 M allyl acetate does not reduce the rate constant for the decomposition of persulphate (0.02 M) at 60° in the presence of isopropanol (0.02 M) to the value (0.014 h^{-1}) observed in the absence of additives but only to the value (0.063 h^{-1}) observed in presence of the allyl acetate alone. Isobutanol has a similar effect. The effects could be explained by differences in the equilibrium constants for the formation of the postulated intermediate complexes.
7. J.O.Edwards, A.R.Gallopo, & J.E.McIsaac (J.A.C.S. 88 (1966) 3891). In absence of oxygen, decomposition rate constant in presence of alcohols is $3/2$ order in persulphate but zero order in alcohol. A spectroscopic method is used. The apparent dependence of the rate constant on alcohol concentration in earlier experiments at higher extents of reaction is now attributed to the competitive reaction of the intermediates product (aldehydes).

8. L.M.Bobinova & P.D.Elizarova (c.f. Chem. Abs. 66 (1967) 95431r).
3 % sodium C₁₅ alkyl sulphonates accelerated decomposition rate x2.

9. B.M.E. van der Hoff (reporting his own, earlier, previously unpublished work in Shinoda ed. 'Solvent Properties of Surfactant Solutions' Dekker, New York (1967) Vol.2 Ch.7 p. 298) found that dispersions of n-octane or benzene accelerated the decomposition of persulphate which was no longer first order in presence of the hydrocarbons. The decomposition was also accelerated by 0.01 M potassium laurate. Stirring enhanced the effect of the hydrocarbons.

10. C.E.M.Morris & A.G.Parts (Makromol. Chem. 119 (1968) 212) found that surfactants and monomers greatly increased the decomposition rate. Only a fluorinated soap had no effect. Vinyl acetate had a particularly large effect (x44 initially)

(Morris & Parts used Gleu's method to determine residual persulphate which is reacted with excess sodium arsenite which is then back-titrated with sodium bromate. We have been unable to confirm their results. Gleu's method is satisfactory in absence of additives but, although Morris & Parts say that they checked that the proposed additives did not interfere with the titration in blank experiments, we were unable to obtain an end-point while vinyl acetate was present. The bromate reagent oxidised vinyl acetate to acetic acid. Liegois has used Gleu's method to determine persulphate in vinyl chloride polymerisations but, in this case, volatilisation of residual vinyl chloride prevents interference.)

11. P.A.Winogradov, P.P.Odintsova, & A.A.Shitova (Vysokomol. soed. 4 (1962) 98: English translation in Polymer Sci. USSR 4 (1963) 33) studied the effect of potassium oleate, ammonium oleate, sodium dibutyl naphthalene sulphonate, and rosin soap on the solubilisation of styrene, the rate of the emulsion polymerisation of styrene, and the rate of decomposition (iodometric) of persulphate (and other initiators) in the presence of emulsified xylene. The emulsifiers accelerated the decomposition of persulphate to varying extents, but there was no correlation of the rate of polymerisation of styrene with the rate of initiator decomposition or with the amount of styrene solubilised. (The number and size of the latex particles formed was not studied, however).

12. I.M.Beileryan, A.L.Samvelyan, O.A.Chaltykyan, & L.A.Vardanyan (Arm. Khim. Zh. 20 (1967) 338: In Russian but we have translated this paper into English) find that polyvinyl alcohol (0.02 base mole dm⁻³) produced a marked acceleration in the rate of decomposition of persulphate (0.02 M) determined iodometrically. Reaction was first order in persulphate and 1/2 order in polyvinyl alcohol. To account for the course of the reaction, the effect of sulphate addition, and the effect of the acetyl content of the polyvinyl alcohol a mechanism involving the hydrogen bonding of sulphate ions to polyvinyl alcohol was proposed. (We have confirmed some of these results).

13. A.G.Khachatryan, N.M.Beileryan, & O.A.Chaltkyan (Arm. Khim. Zh. 23 (1970) 485, 575, c.f. Chem. Abs. 74 (1971) 6926f, 111350m). Persulphate oxidation of ethanol (< 0.2M) is strongly influenced by oxygen. Reaction is 3/2 order in persulphate in presence of traces of oxygen, and first order in persulphate and 1/2 order in ethanol in an inert atmosphere. Activation energy 74 kJ mol⁻¹. Ethanol does not participate in the initiation step which is first order in persulphate.

- 14. A.L.Samvelyan, N.M.Beileryan, & O.A.Chaltykyan (Dokl. Akad. Nauk. Arm. SSR, 50 (1970) 283, c.f. Chem. Abs. 74 (1971) 46035w). Oxidations of ethanol and glycerol are similar. Methanol is preferentially oxidised. Addition of sulphate retards the reaction. Results explicable with a mechanism involving two types of ethanol-persulphate complex.
- 15. H.A.Yablonsky (Ph.D. Thesis, Stevens Institute of Technology (1964). Supervisors: L.S.Levitt and E.R.Malinowski. No definitive publication). Parallel iodometric and manometric measurements show that no oxygen is formed by decomposition of persulphate in presence of low concentrations of alcohols. New maximae observed at 250 nm (MeOH) 275 nm (i-PrOH), 235 nm (t-BuOH) provides evidence for persulphate esters as an intermediate. Mechanism proposed involving transfer of tertiary H of isopropanol in rate determining step. Isotope effect $k_H/k_D = 1.6$ found with 2-propanol-2-D (but ~~= 7~~ expected if decomposition occurred exclusively by this mechanism). Mechanism leads to deduction of rate expression corresponding to empirical expression of Malinowski (1956) which reduces to first order in persulphate at higher alcohol concentrations. Activation energies 78 kJ mol^{-1} with 0.02M i-PrOH and 109 kJ mol^{-1} with 0.10 M t-BuOH compared with 140 kJ mol^{-1} in the absence of additives.
- 16. E.P.Crematy (Makromol. Chem. 143 (1971) 125) finds decomposition rate (iodometric) increased by cationic surfactants is first-order in persulphate.
- 17. M. Nomura, M. Harada, K. Nakagawara, W. Eguchi, and S. Nagata (J. Chem. Eng. Japan 4 (1971) 160) find a x5 increase in the rate of initiation (deduced from viscometric molecular weights adjusted to number averages) in the emulsion polymerisation of vinyl acetate with sodium dodecyl sulphate (but the same technique gave no evidence of acceleration with styrene as monomer: this could be connected with the possibility of vinyl acetate radicals escaping from latex particles).
- 18 B.M.E. van der Hoff (1972: private communication). A chain reaction occurs with fatty acid soaps which is 1.3 order in persulphate and 0.2 order in the alkyl carboxylate.
- 19. M.R.Grancio & D.J.Williams (J. Polym. Sci. A-1 8 (1970) 2733) find the decomposition rate (iodometric) in presence of octyl phenoxyethyl non-ionic and sodium dodecyl sulphate accelerated x 4.
- 20. M.R.Grancio & D.J.Williams (1973: Preprint circulated) find by an improved analysis of their Inhibitor Perturbation Technique an acceleration x 1.6 when styrene is also present.

PAPERS PROVIDING EVIDENCE THAT THE RATE OF RADICAL PRODUCTION FROM PERSULPHATE IN PRESENCE OF MONOMERS CAN BE CALCULATED FROM ITS DECOMPOSITION RATE CONSTANT DETERMINED IN ABSENCE OF ADDITIVES.

- 1. I.M.Kelthoff, E.J.Meehan, & E.M.Carr (J.A.C.S. 75 (1953) 1439). Alcohols (0.1 M) do not accelerate decomposition rate (Determined by reaction of residual persulphate with excess ferrous in presence of bromide and back titration with ceric) in presence of allyl acetate which is an efficient radical trap. The agreement between the experimental order and that required by the reaction schemes put forward by Bartlett & Cotman (1, above) is only moderate.

2. C.E.H.Bawn & D. Margerison (Trans. Faraday Soc. 51 (1955) 925) used diphenyl picryl hydrazyl as radical trap to determine rate of radical production in 50% ethanol solution. The rate was not affected by variation of the ethanol concentration. (We obtain good agreement for the rate constant at 50°C by this method, but the values are 2.5 times Kolthoff & Miller's value at this temperature, and the activation energy is significantly lower - 100 kJ mol⁻¹ compared with 140 kJ mol⁻¹. Our activation energy is rather lower than Bawn and Margerison's (118 kJ mol⁻¹) because, using a spectrophotometric method, we found it necessary to correct for the reaction of the DPPH with the solvent: using a filter photometer, they considered this correction negligible. The correction is, of course, temperature dependent. Though it thus appears that working in 50% ethanol - necessitated by the solubility of the DPPH - does not give the required information, the small effect of the large alcohol concentration is remarkable in view of the large effect of small variations of alcohol concentration at low concentrations in absence of a radical trap).
3. P.W.Allen (J.Polym. Sci. 31 (1958) 206) calculated the rate of initiation of 1% methyl methacrylate solutions from viscometric molecular weight determinations and found no effect of low concentrations (< 0.04%) of sodium dodecyl sulphate below its critical micelle concentration.
4. J. C. Hawke (unpublished work quoted by Morris, Alexander & Parts, J. Polym. Sci. A-1, 4 (1966) 985) found no rate enhancement using a radiochemical method (presumably at lower concentrations than those required by volumetric methods)
5. J. M. Ilegeois (J. Polym. Sci. C 33 (1971) 147) using Gleu's method found that the rate of decomposition was not affected by vinyl chloride. (The volatility of vinyl chloride prevented it interfering with the analytical method).
6. M. Harada, M. Nomura, H. Kojima, W. Eguchi, & S. Nagata (J. Polym. Sci. 16 (1972) 811), in contrast to the findings when the same method was applied to vinyl acetate, find no acceleration of the initiation rate for styrene with sodium dodecyl sulphate.

Appl.

The conclusion from our own experiments is that any acceleration of the decomposition rate of persulphate by vinyl acetate is certainly small (< x4, contrast Morris & Parts x 44) and probably nil so long as monomer is present and able to polymerise. An enhanced rate of decomposition probably occurs during any inhibition period when residual oxygen prevents polymerisation and after polymerisation is substantially complete when the sulphate radical will initiate alternative chemical oxidation reactions of the polymer and any other organic materials present. The use of initiation rates calculated from Kolthoff & Miller's rate constants in theoretical work would seem to be justified, but the realisation of these rates in practice requires careful attention to the purity of reagents and the assurance of the absence of contamination by low concentration of metal ions such as Cu²⁺, and Fe²⁺ which will catalyse the decomposition of persulphate.

February 12, 1973

TO: D. J. Williams
FROM: R. M. Fitch
FOR: Polymer Colloid Group Newsletter

The gang at UConn has increased in size:

Deborah Bakker is working on the details of oligomeric radical growth, and nucleation of the polymer phase by laser interferometry. Right now she's building apparatus and determining the kinetics of the photoinitiation using biacetyl.

Ron Mendoza will be seeing whether our ideas on particle nucleation can be applied to other types of colloids, specifically SiO_2 sols.

Chandu Gajria is looking at the surface chemistry of PMMA colloids and the introduction of surface groups via ionogenic chain transfer agents.

Will McCarvill will be studying chemically reactive interfacial systems. We're still thrashing around ideas!

In Kamath's work on non-aqueous dispersions, our analysis of the kinetics of growth at 30°C strongly leads us to believe that propagation is diffusion-controlled when the monomer concentration is below about 2M. Vivian Stannett has kindly consented to study the diffusion of MMA monomer into its polymer under such conditions, as a function of monomer concentration. He promises results soon. Initial data show diffusion to be "extremely slow".

Quotes from the ancient archives: "...it does not seem that the formation of polymer particles is a major factor [in the rate of polymerization],...because the rate constants are practically the same over as much as a 5-fold range of initial styrene [our emphasis] concentrations.This seems to us to indicate very strongly that the reaction may be properly treated as a homogeneous one [our emphasis]."

F. A. Bovey & J. M. Kolthoff, J. Polym. Sci. V, No. 4, p. 502 (1950).

POLYMER NEWSLETTER

CONTRIBUTION FROM CASE WESTERN RESERVE UNIVERSITY

Rheological Investigations: Attempts to obtain a rigid-sphere redispersion of crosslinked latex particles into m-cresol have been encountering difficulties. Successive dialyses, first against methanol and then against m-cresol, have produced stable, iridescent dispersions. The intrinsic viscosities, however, are in excess of 4.0, even when the latex is 15% crosslinked. This contrasts with preparations made several years ago, which gave intrinsic viscosities of about 2.7. Rigid-sphere redispersions in m-cresol are desired because dispersions in viscous media are expected to exhibit time-dependent thixotropy. If redispersion attempts continue to cause difficulty, two courses of action are open. One is to seek a different combination of viscous medium and polymer, which will not cause swelling of the particle. A second is to consider the swollen redispersion as a rigid-particle suspension whose effective volume fraction is augmented by the ratio of the intrinsic viscosity to 2.5.

Studies of the electroviscous effect are producing illuminating results. To date, a 40% dispersion of a 0.22μ latex has been studied as a function of electrolyte content and shear rate. The deionized material shows a pronounced yield stress, but at high shear rates its viscosity approaches that of the normal latex. Addition of electrolyte lowers the yield point and the viscosity, but does not change the high-shear limit. At a characteristic electrolyte concentration, the viscosity vs. electrolyte content passes through a minimum; the non-Newtonian viscosity of the latex at this electrolyte concentration agrees with that previously obtained in both aqueous and nonaqueous rigid-sphere dispersions. At

moderate electrolyte contents, the flow curve is well represented by the Casson equation.

Probably the most interesting observation in the studies of the electroviscous effect is the complete non-specificity of added electrolyte. The second electroviscous effect depends solely upon the normality of the added cations. HCl, NaCl, K_2SO_4 , $CaCl_2$, $MgSO_4$, $Al_2(SO_4)_3$, and $Th(NO_3)_4$ produced the same electroviscous effect at equivalent normalities.

Emulsion Polymerization Studies: Emulsifier-free emulsion polymerizations have been carried out with various concentrations of added electrolyte. As was reported previously, added electrolyte plays a similar role to that of added initiator in determining the ultimate particle size. Use of polyvalent cations permits achieving larger particle sizes, sometimes in excess of 1μ . Incorporation of sulfoethyl methacrylate comonomer produces smaller particles. Both sets of observations are consistent with the idea that the latex nuclei are produced by coalescence of oligomers or proto-particles, said coalescence being inhibited by Coulombic repulsions. Latexes with sulfo-ester comonomer have been produced at volume fractions up to 50%, in contrast with a ca. 15% upper limit for emulsifier-free recipes. The ionizable comonomer thus seems to behave as a surfactant emulsifier.

Monodisperse polyvinyltoluene latexes have been produced both using mixed emulsifiers (Dowfax and Triton types) and by emulsifier-free techniques. Seeded polymerizations in emulsifier-free systems have produced latexes in excess of 2μ without second generation, a result extremely difficult to obtain in conventional emulsifier-containing polymerizations.

POLYMER-COLLOIDS NEWSLETTER

D.H.NAPPER

UNIVERSITY OF SYDNEY

Van der Waals Attraction Between Latex Particles

There have been several theoretical estimates of the London-van der Waals attraction between latex particles. These have, without exception, all assumed that interatomic interactions exhibit pair-wise additivity. Moreover it is customary to suppose that only electronic correlations with frequencies in the ultra-violet region need be considered in calculating the attraction.

The major drawback with this approach, which was pioneered by London and Hamaker, is that it is wrong. At least the results are reliable only in order of magnitude at best. Ninham and Parsegian in a pioneering series of papers have shown that pair-wise additivity may well be appropriate for dilute gases but is scarcely reasonable in condensed systems where many body effects become significant. Moreover correlations involve more than just a pair of molecules. In addition correlations other than those propagated at ultra-violet frequencies can contribute significantly to the nett van der Waals attraction, especially if water is the dispersion medium.

Ninham and Mitchell have used the methods of quantum field theory to solve the problem for two dielectric spheres immersed in a uniform medium. This formalism, due originally to Lifshitz, enables the contributions of all spectral components to be included. It takes into account all the many-body interactions and properly accounts for the presence of the dispersion medium.

We have taken the formula of Ninham and Mitchell and calculated the van der Waals attraction between two spherical latex particles immersed in water or in hydrocarbons. Different polymers, e.g., polystyrene, poly(methyl methacrylate) and poly(vinyl acetate), were examined. These calculations permit for the first time a reasonably accurate estimate of the van der Waals attraction. What is perhaps most surprising is that what has always been referred to as the Hamaker constant is only a constant for some polymers in hydrocarbons. For polymers in water all so-called Hamaker constants are in fact Hamaker functions. For close approach in water the Hamaker function for latex particles decreases linearly with the ratio of the distance of separation between the particle surfaces and the particle radius. Both results can be derived analytically. The reason for the decrease in Hamaker constant with aqueous latices resides in the zero frequency contribution from the water.

One of the major difficulties encountered in

these calculations is to obtain information about the ionization potentials of the polymers and the liquid dispersion media. Gaseous ionization potentials for minimolecules abound but these cannot be used for condensed phases. (Unfortunately even Ninham and Parsegian have fallen into this trap.) Fortunately by allowing for polarization energy of the dielectric it is possible to calculate theoretically the ionization potentials of solids and liquids with some certainty.

We have now assembled the data obtained by J. Hearn and C.C. Ho during their thesis studies. Each thesis included a section on methods for the preparation of polymer latices in emulsifier-free systems.

Working on the hypothesis that flocculation in the early stages of growth controlled the ultimate size of the latex particles, a series of preparations were carried out over a range of ionic strengths. In addition, the influence of temperature, initiator concentration and monomer concentration were examined. A summary of the data is given in Table 1.

Results from the ionic strength experiments were found to give good linear plots of \log [final particle diameter] against \log [ionic strength] which could be represented by the equations :

at 70°

$$\log D = 0.261 \log [I] - 3.738$$

at 80°

$$\log D = 0.261 \log [I] - 3.870$$

at 95°

$$\log D = 0.261 \log [I] - 3.958$$

where D = particle diameter and I the total ionic strength based on the initiator concentration at the start of the reaction. After incorporating a correction for temperature, we found that these data were reasonably well given by the equation :

$$\log D = 0.261 \log [I] - \frac{T}{120} - 7.09.$$

The dependence of particle diameter on monomer concentration $[M]$, over the restricted range $10^{-2} - 1 \text{ mol dm}^{-3}$ at 70° , was fitted reasonably well by the equation,

$$\log D = 0.355 \log [M] - 4.287$$

and the dependence on persulphate concentration $[P]$ by the equation,

$$\log D = -0.239 \log [P] - 4.892.$$

We have then attempted to rationalise all the data by a plot using an empirical equation of the form,

$$\log D = k_1 \log \left[\frac{[I]^{0.261} [M]^{0.355}}{[P]^{0.239}} \right] + k_2 T - k_3$$

where k_1 , k_2 and k_3 are numerical constants. We are still working to obtain the best fit. An example of the type of fit obtained is shown in Figure 1. This shows that by suitable variation of temperature and ionic strength, using essentially constant monomer and initiator conditions, a range of monodisperse latices can be prepared under emulsifier-free conditions. The diameter range covered by this "single-shot" method is, so far, approximately 700 Å to 1 μ; we visualize possible methods to extend this range.

The majority of the latices prepared were analysed to obtain the molecular weight of the polystyrene and the type and number of end groups. Some of the data obtained are give in Table 2. The marked variation of molecular weight with initiator concentration and the effect on particle diameter are noteworthy. The more rapid rate of radical production seems to favour the formation of lower molecular weight polymer, produce more end groups on the surface and hence stabilize the particle, in the colloidal sense, at a smaller diameter.

Table 1

Latex No.	Monomer Conc. Mol dm ⁻³	K ₂ S ₂ O ₈ mol dm ⁻³ x 10 ³	NaCl mol dm ⁻³	Ionic Strength x 10 ³	Mean Diameter in Å	Coefficient of Variation	% Yield of Latex
A/55	0.57	2.76	14.0	22.3	9670	1.6	57
Temperature = 55°							
A/60	0.93	2.22	-	6.7	5510	3.0	69
B/60	0.93	2.22	13.3	20.0	6885	2.7	65
C/60	0.93	2.22	28.3	35.0	7710	2.1	61
D/60	0.93	2.22	43.3	50.0	8400	3.5	54
Temperature = 60°							
A/70	0.87	2.76	-	8.3	5363	1.9	66
B/70	0.87	2.76	3.0	11.3	5260	2.0	80
C/70	0.87	2.76	- †	11.3	5590	5.2	69
D/70	0.87	2.76	7.0 †	18.3	6520	4.5	75
E/70	0.87	2.76	10.0	18.3	6780	2.4	80
F/70	0.87	2.76	14.0	22.3	7130	2.9	81
G/70	0.87	2.76	11.0 †	22.3	7040	3.3	82
H/70	0.87	2.76	14.0 †	22.3	6600	4.0	74
I/70	0.87	2.76	14.0* †	22.3	7410	2.9	76
J/70	0.87	8.55	-	25.7	6920	2.0	89
Temperature = 80°							
A/80	0.87	2.76	2.2	10.5	4940	12.1	83
B/80	0.87	2.76	9.3	17.6	4490	17.4	50
C/80	0.87	2.76	16.3	24.6	5460	13.4	77
D/80	0.98	2.22	-	6.7	4100	2.5	83
E/80	0.98	2.22	13.3	20.0	5450	2.6	81
F/80	0.98	2.22	28.3	35.0	6450	4.9	80
G/80	0.98	2.22	48.3	35.0	6900	4.1	68
H/80	0.98	2.22	43.3	50.0	6880	2.5	76
Temperature = 95°							
A/95	0.58	0.29	-	0.88	2420	7.9	72
B/95	0.58	0.29	27.5	28.4	3080	1.5	88
C/95	0.87	2.76	2.2	10.5	3420	2.7	64
D/95	0.87	2.76	9.3	17.6	3060	2.7	73
E/95	0.87	2.76	16.3	24.6	3990	4.6	57

† Contained 3 x 10⁻³ M hydrochloric acid
 ‡ pH maintained constant at 10.0 ± 0.05
 * pH maintained constant at 7.0 ± 0.05

Degradation of Polystyrene Latexes - Effect of Temperature (D. G. G. & S. C. Ho)

Medium Concentration = 0.98 M; Solvent System = 300 v. 500 ml. 18 months reaction; Reaction time = 24 hrs.

Parameter	Temperature (°C)	Latex Conc. (% S ₂ O ₈)	Temperature (°C)	Diameter (μ)	Molecular Weight (Mn)
varied	70	2.76 x 10 ⁻³	70	0.586	1.41 x 10 ⁵
Ionic Strength	70	2.76 x 10 ⁻³	70	0.670	1.09 x 10 ⁵
	70	2.76 x 10 ⁻³	70	0.713	1.04 x 10 ⁵
	70	18.0 x 10 ⁻³	70	0.583	1.04 x 10 ⁵
Latex Concentration	70	7.0 x 10 ⁻⁴	70	0.731	2.77 x 10 ⁵
	70	3.4 x 10 ⁻³	70	0.864	5.46 x 10 ⁵
	55	2.76 x 10 ⁻³	55	0.667	2.89 x 10 ⁵
Temperature	70	2.76 x 10 ⁻³	70	0.7	1.04 x 10 ⁵
	85	2.76 x 10 ⁻³	85	0.667	1.03 x 10 ⁵

Table 2

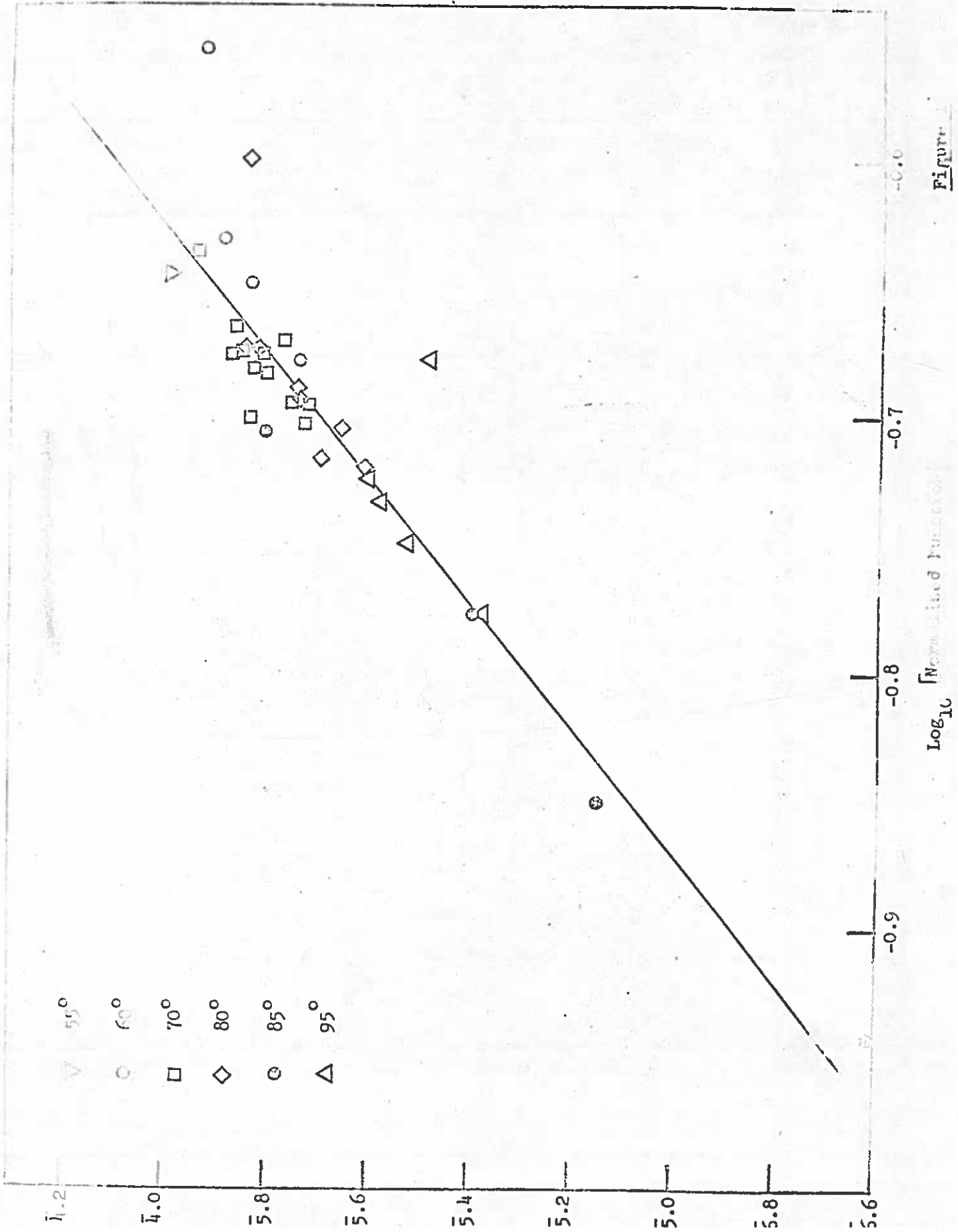


Figure 1

CONTINUOUS EMULSION POLYMERIZATION

Poehlein - Lehigh

This report will be short on explanations and a little longer than usual on data. Experimental results are presented for the polymerization of methyl methacrylate (MMA) and vinyl acetate (VA). We can't tie this data and a comprehensive theory into a nice neat package yet but hope springs eternal - - - - - . The following aspects of our work appear to be most significant at this point:

1. Reactor stability for both monomers is more of a problem than with styrene. Potential reasons for unstable behavior could be attributed to either or both the Tromsdorf effect and particle formation phenomena. These factors were discussed in an article distributed to you several months ago. We can now add the following qualitative observations:

- i. MMA recipes seem to be more unstable than VA emulsions
- ii. Stability seems to become more of a problem at high initiator concentrations and low emulsifier concentrations.
- iii. Careful start-up procedures to avoid the normal initial conversion overshoot help to avoid stability problems.

2. Steady-state reactor performance does not follow the theoretical predictions of the model developed from Smith-Ewart concepts which were as follows:

$$R_p \propto R_i^{0.0} S^{1.0} \theta^{-2/3}$$

$$N \propto R_i^{0.0} S^{1.0} \theta^{-2/3}$$

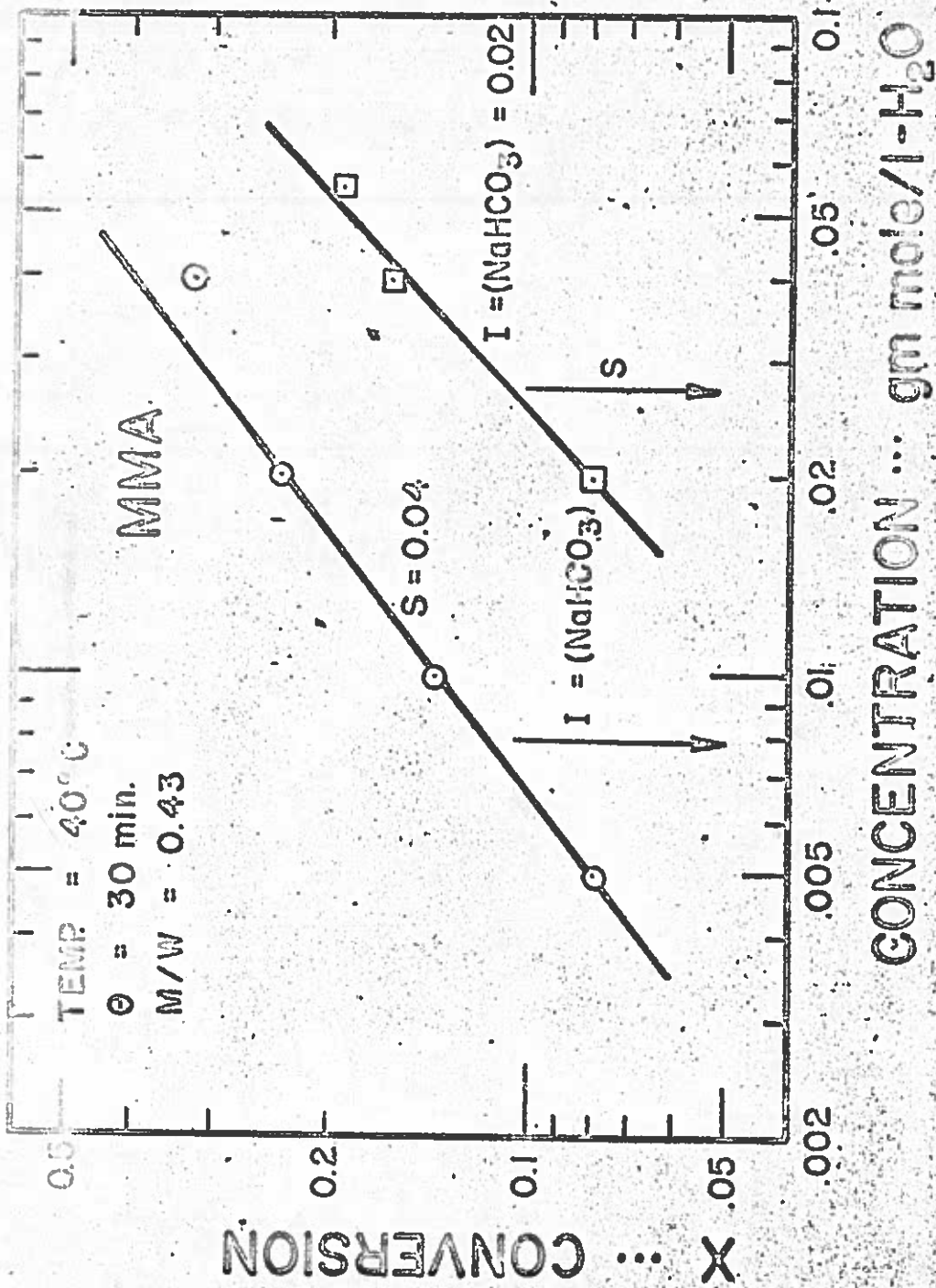
Figure 1 shows conversion data for MMA. Increases in surfactant concentration lead to higher conversions in qualitative agreement with the theory but the initiator rate also has a similar effect which is not predicted by the theory. Figure 2 shows a similar initiator dependence for VA. Figure 3, however, shows a peculiar surfactant behavior for VA. Any explanations for the relative maximum?

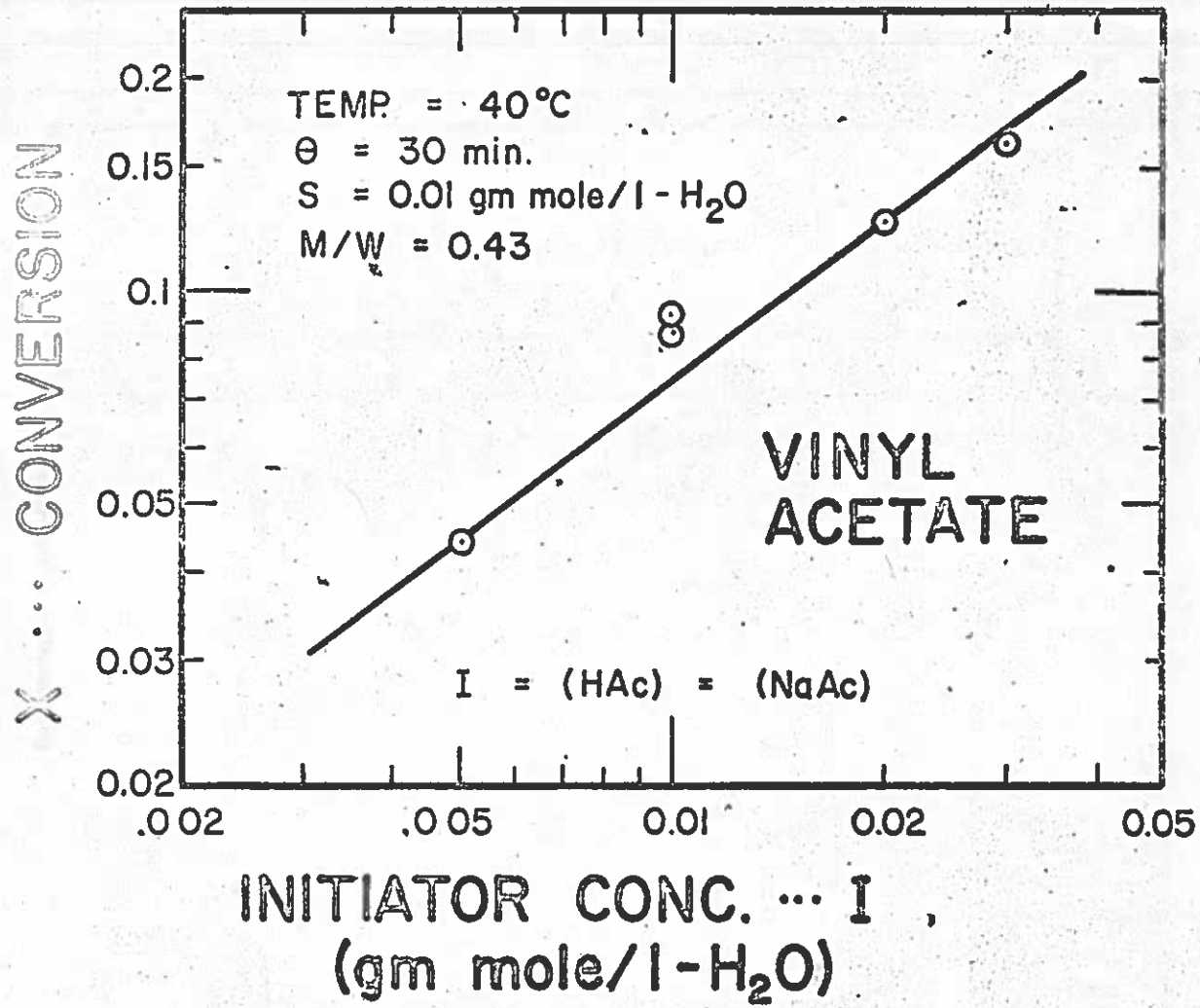
1.
P-2

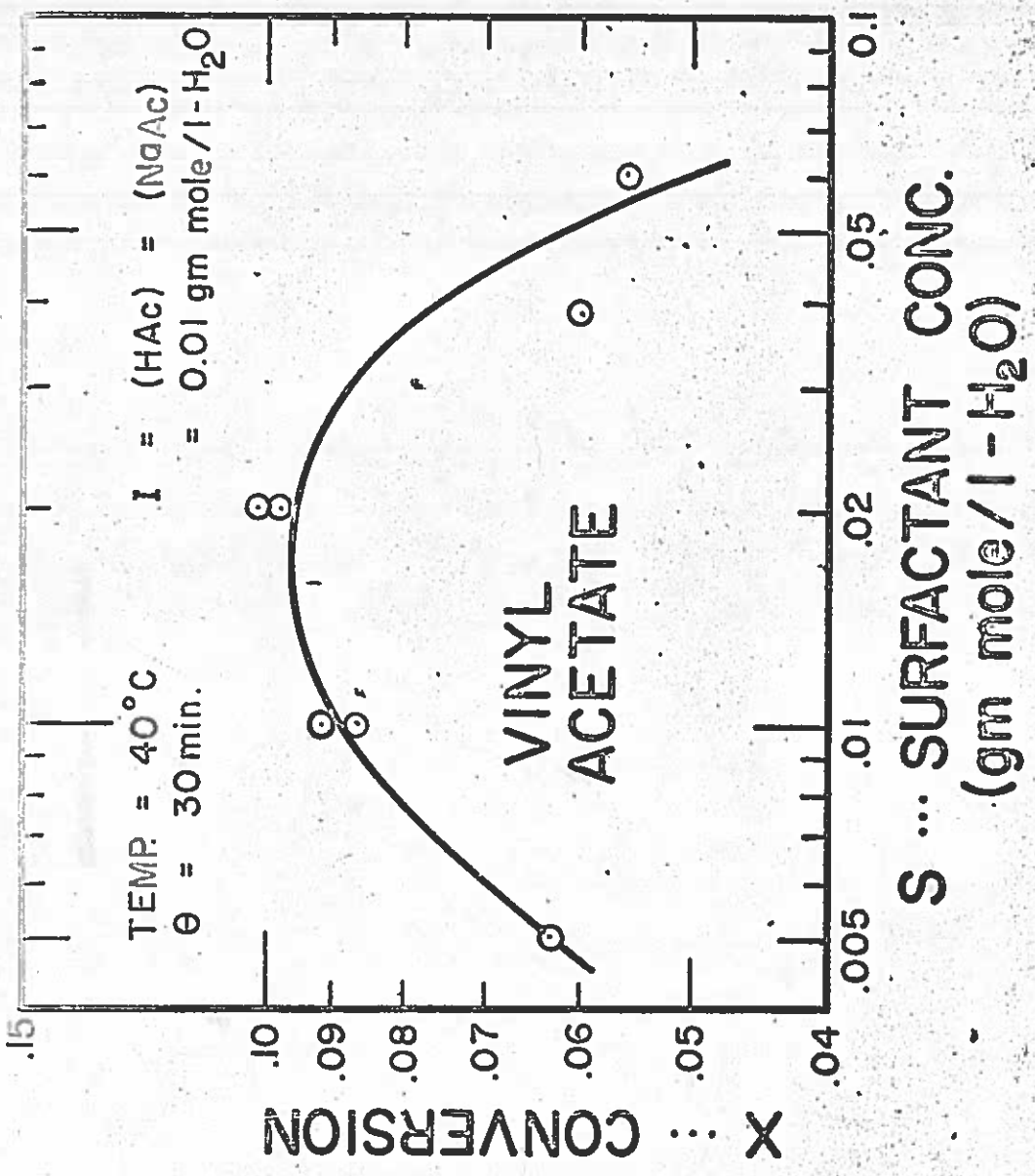
Figure 4 shows our only particle size distribution measurements to date. The large peak of small particles was not observed, nor were the bi-modal aspects in similar styrene experiments.

5. Mixing effects were observed with MMA recipes as shown in Figure 5. Since coalescence should be increased by higher stirring rates one would expect fewer particles at higher agitator speeds. The data support this qualitative picture. (Any comments, Bob Fitch?) Stirring effects were not observed with styrene and they seem to be less important with VA.

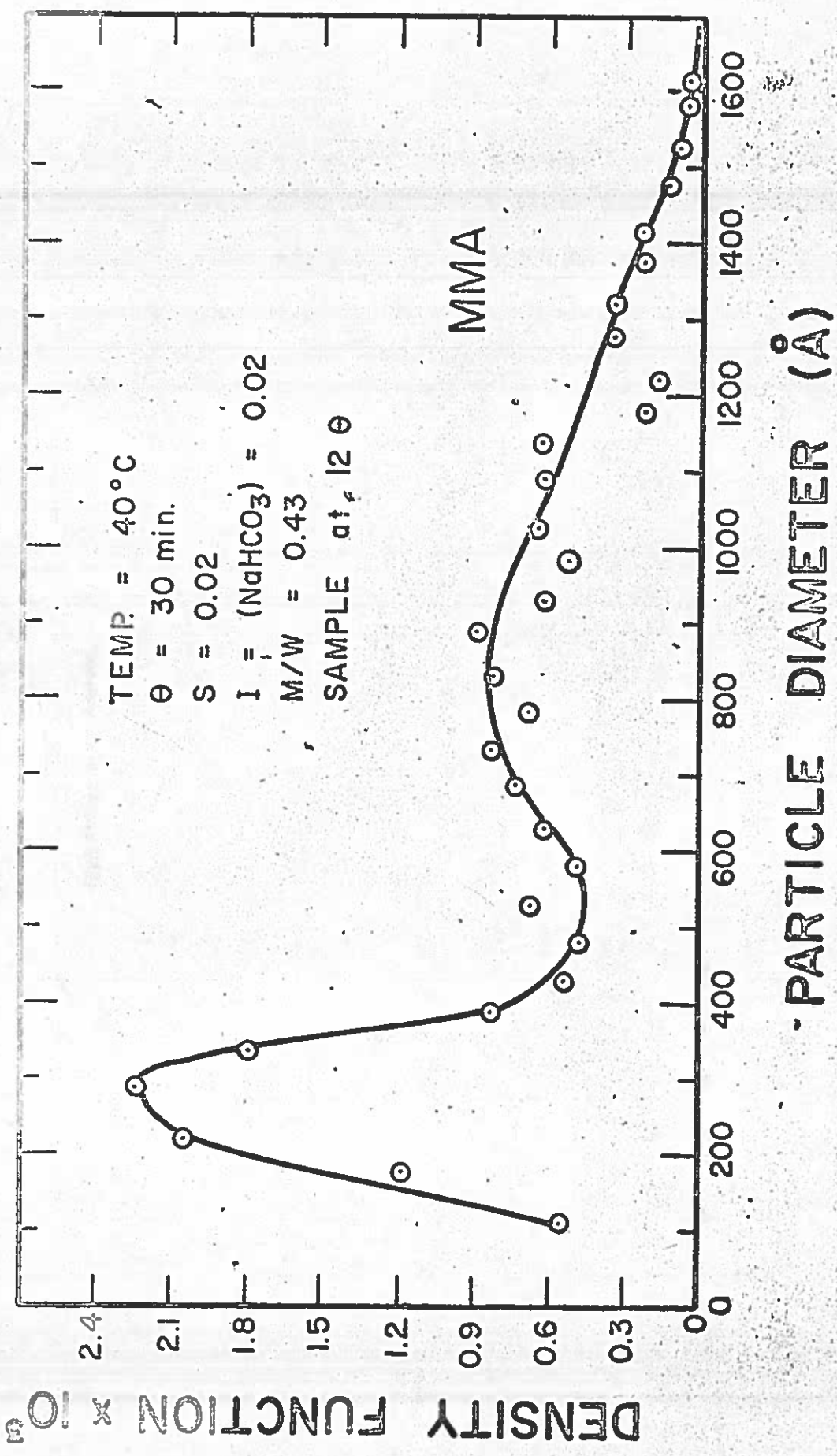
Gary Poehlein

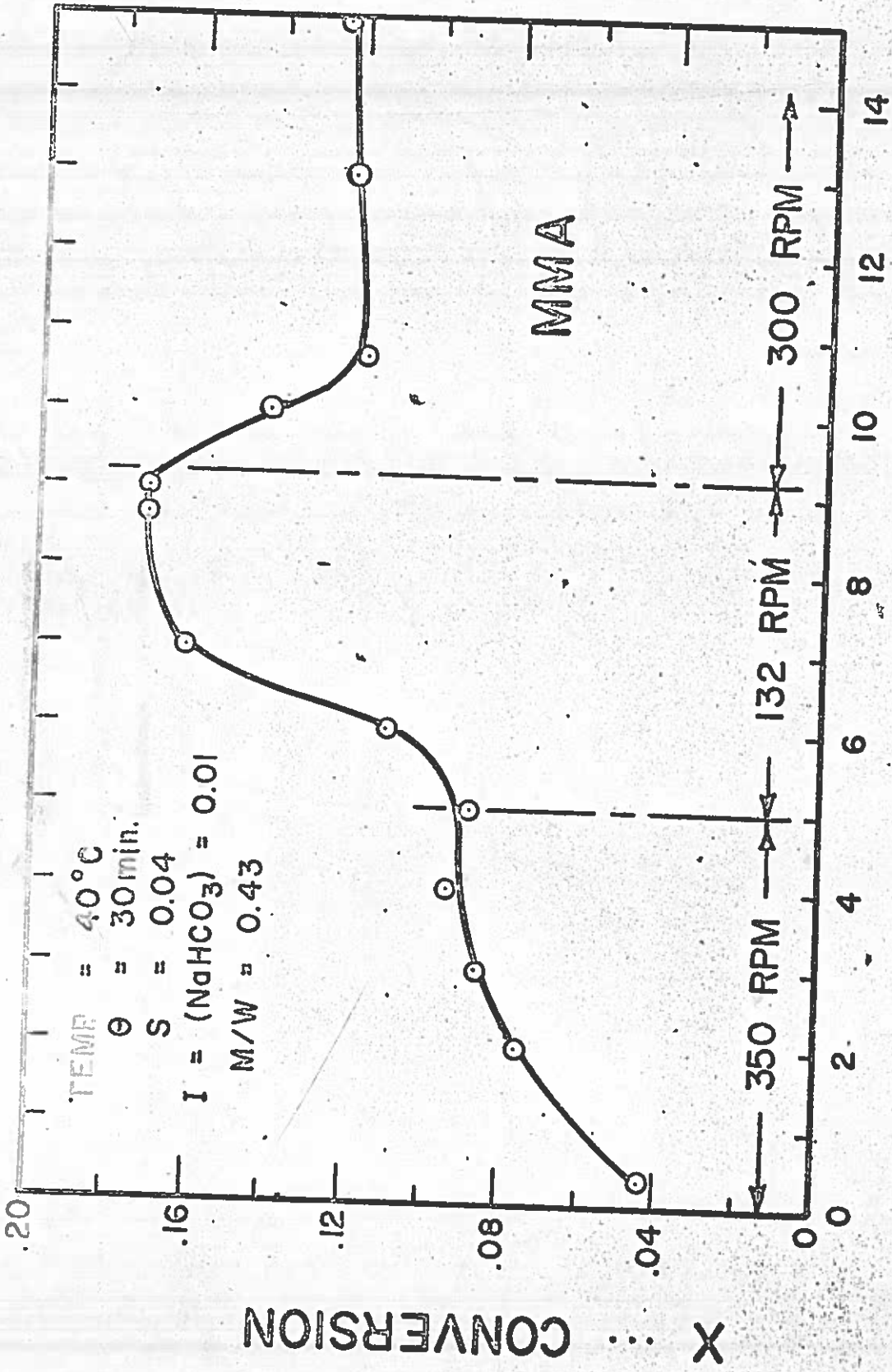






3





DIMENSIONLESS TIME ... 1/0

Summary Prepared for Newsletter

The Radiation Induced Polymerization of Styrene in Emulsion

H. Shiota and V. Stannett
Department of Chemical Engineering
North Carolina State University
Raleigh, North Carolina

The sodium lauryl sulfate emulsion system with styrene obeys the Smith-Ewart Case II theory very well with potassium persulfate.

In view of a number of reported discrepancies in the case of radiation initiation their same standard system has been carefully explored using radiation at 30°C. The following results were obtained:

1. Rate independent of water-monomer ratio
2. Molecular weights determined from intrinsic viscosities were independent of conversion from 15 - 80%.
3. Molecular weights proportional directly to the rate
4. Rate proportional to soap 0.6 - 0.7
Number of particles proportional to soap 0.6
5. Approximately the efficiency of initiation is about 0.4
6. The overall activation energy for both the rate and the degree of polymerization was 7.9 Kcals per mole in good agreement with Vanderhoff

In general an almost exact fit to Smith-Ewart Case II kinetics was found in close correspondence to a similar system using potassium persulfate initiation at 60°C.

The work is slowly being written up for publication and will be available in the future.



V-1

Lehigh University Bethlehem, Pennsylvania 18015
CENTER FOR SURFACE AND COATINGS RESEARCH

JOHN W. VANDERHOFF, Associate Director-Coatings
Telephone (215) 691-7000, Ext. 220

February 14, 1973

Dr. David J. Williams
Department of Chemical Engineering
City College of New York
New York, New York 10031

Dear David:

As my contribution to the Quarterly Newsletter, I am sending under separate cover to the members of the Polymer Colloid Group:

1. a reprint, "Additional Studies of Morphological Changes in Latex Films," J. Macromol. Sci.-Phys. B6(4), 671 (1972);
2. a manuscript, "The Transport of Water Through Latex Films," presented at the New York ACS meeting in August 1972 and submitted for publication in the Journal of Polymer Science;
3. the manuscript, "Separation of Latex Particles According to Size by Continuous Electrophoresis," presented in part at the National Colloid Symposium in 1970 and the Washington ACS meeting in September 1971, and now submitted for publication in Separation and Purification Methods.

The reprint describes an extension of the concept that latex particles in films that are dry, transparent, and continuous undergo a further gradual coalescence upon ageing at room conditions. During this further gradual coalescence, the particle contours disappear and the film properties improve, and any incompatible substances (e.g., emulsifier) are exuded to the surface. This concept was demonstrated in an earlier work (J. Macromol. Chem. 1, 335 (1966)) using a 67:33 styrene-butadiene copolymer, and the effect of polymer structure on the rate of the process was determined. The present work shows that the further gradual coalescence of the 67:33 styrene-butadiene copolymer occurs in the interior of the film and at the film-substrate interface, as well as on the surface. It is not affected by such different substrates as Bakelite, Mylar, Teflon, rubber, or mercury, but is affected by the environment, being accelerated in oxygen and greatly slowed in nitrogen. It is shown to occur in films of other polymers --- vinylidene chloride copolymers, acrylate ester copolymer, natural rubber. However, it does not occur in polyvinyl acetate films, whether from a commercial latex or from model latexes prepared without emulsifier. An explanation is advanced for the failure of polyvinyl acetate to undergo further gradual coalescence, based on a proposed surface hydrolysis of the polyvinyl acetate to form a thin sheath of chemically-bound hydrophilic polyvinyl alcohol.

The manuscript, "The Transport of Water Through Latex Films," was included in shorter form in the last Quarterly Newsletter. The present manuscript is a more complete description of the work, with some additional material. Also, a more complete analysis of the data has given slightly different values for the rates of water transmission. The drying process is still considered as a three-stage process comprising: 1. an initial stage which persists to 60-80 volume percent polymer and in which the rate of water evaporation is the same as for pure water or dilute emulsifier solution ($2-3 \times 10^{-4}$ g/min/cm²); 2. an intermediate stage in which the rate drops off rapidly and which is correlated with the coalescence of the latex particles; 3. a final stage in which the particles have coalesced to form a continuous film and rate of water evaporation is initially $1-3 \times 10^{-5}$ g/min/cm² and slowly decreases, asymptotically approaching the value representative of the polymer itself as the further gradual coalescence proceeds (indicating that the major route for escape of water is by diffusion through capillary channels rather than through the polymer itself). Also, the values obtained for liquid-water and water-vapor transmission rates through polymer films aged sufficiently for the further gradual coalescence to be complete are in reasonable agreement with values reported in the literature for similar but not identical copolymers.

A note of warning on values for water transport through polymers: Barrie's chapter on water transport through polymer films in Crank and Park's "Diffusion Through Polymers" contains many errors, both in the values cited and the literature references, and any values used should be checked in the original articles.

The manuscript, "Separation of Latex Particles According to Size by Continuous Electrophoresis," describes the use of the Beckman CPE instrument to separate monodisperse polystyrene latex particles of similar surface characteristics but different particle size. This separation is in qualitative accord with the theory of electrophoresis advanced by Wiersema et al., which predicts that such separations should be observed, particularly for particles with a high zeta potential. The present work shows that such separations are observed experimentally and in principle should serve as a means for determining latex particle-size distribution. Polystyrene particles which differ in diameter by as little as 500 A. can be separated quantitatively. The second part of the manuscript describes attempts to correlate the relative electrophoretic mobilities obtained in the Beckman CPE with the surface charge densities of the particles measured by the ion-exchange-and-conductometric-titration technique. This correlation is not completely successful, mainly because the values of the "apparent degree of dissociation" α of the surface sulfate groups has thus far been measured only in the ion-exchanged latexes and not in the electrolyte medium used in the Beckman CPE. The present work was carried out while I was at Dow, but was not continued when I came to Lehigh, because we had no instrument. However, we have been working with other methods of measuring electrophoretic mobilities of latex particles and expect to have a Beckman CPE within a few months, so we will have the opportunity to investigate this subject further.

Best regards to you and the other members of the Polymer Colloid Group. We are looking forward to seeing you at the 2nd Annual Meeting.

Sincerely,



John W. Vanderhoff

JWV/rm

SIZE DISTRIBUTION ANALYSIS OF MULTI-MODAL AND
POLYDISPERSED POLYMER LATEX SYSTEMS VIA COMBINATION OF
LIGHT SCATTERING AND ULTRACENTRIFUGATION TECHNIQUES

WALLACE - Rochester

In the Vol. 1, No. 3 edition of the newsletter, we outlined a method of size distribution analysis of polymer latex systems which utilized light scattering and ultracentrifugation. Subsequently we reported¹ the results of analyses of a bimodal and a multimodal system (report attached).

The method involves mechanically fractionating the polydispersed system utilizing a density gradient in the rotor of the ultracentrifuge. After pumping out the rotor and collecting small quantities of the fractionated sample, a light scattering technique² is applied which enables a determination of the size distribution of the fraction. In this manner the original size distribution can be reconstructed.

We are presently devoting our attention to applying this technique to a continuous distribution of polystyrene latex particles having diameters from 200nm to 800nm. In addition, we are systematically varying the experimental conditions of the ultracentrifugation experiment in order to obtain maximum separation. Our ultimate test of the method lies in the degree of separation of a "monodisperse" Dow latex to obtain the "most monodisperse" sample. Another graduate student, Mr. Robert Cembrola, has joined our group and has carried out experiments which vary the density gradient in the rotor as well as the time and speed of centrifugation.

Wa-2

<u>Density Gradient</u> <u>(% sucrose)</u>	<u>Force x 10⁻⁷ (rad²/sec)</u>	<u>Separation</u>
11.0 - 13.2	940	Good
11.0 - 13.2	1500	Fair
8.0 - 10.0	520	Poor
11.3 - 13.2	980	Good
11.2	795	Poor

1. T.P. Wallace and A.J. Migliore, Polymer Preprints, 13, No. 2, 1244 (1972).
2. T.P. Wallace and W.B. Scott, J. Polymer Sci., A-2, 10, 527 (1972).

Thomas P. Wallace
Department of Chemistry
Rochester Institute of Technology
Rochester, New York 14623

TPW/jw
1/29/73

SIZE DISTRIBUTION ANALYSIS OF MULTI-MODAL AND POLYDISPERSE POLYMER LATEX SYSTEMS VIA COMBINATION OF LIGHT SCATTERING AND ULTRACENTRIFUGATION TECHNIQUES

by Thomas P. Wallace and Alfred J. Migliore Department of Chemistry Rochester Institute of Technology One Lomb Memorial Drive Rochester, New York 14623

Introduction

There has been great interest in the development of a precise method of size distribution analysis of colloidal systems which possess either extensive polydispersity for a monomodal distribution, or the more complicating factor of a multi-modal distribution. The use of angular light scattering techniques has proven to be of the highest precision for size distribution analysis but is inherently limited to quite narrow size distributions due to the loss of structure in the angular scattering pattern as the distribution broadens. In addition, application to multi-modal systems is not feasible even for the simple bimodal case involving two narrow size distributions. These difficulties can be overcome if (1) it is possible to qualitatively detect the presence of a wide monomodal distribution as well as the presence of any multi-modal character, and (2) the system can be mechanically fractionated into narrow size distributions. The results from (1) will dictate which fractions should be further analyzed by light scattering and will also form the basis for the plan of reconstructing the total distribution of particle sizes. The above analysis can be achieved by combination of ultracentrifugation and light scattering techniques which will be demonstrated using polystyrene latex samples.

Background and Experimental

The fractionation of the polydisperse latex system is achieved by use of the Beckman L2-65B Preparative Ultracentrifuge and the B-15 aluminium rotor. This rotor permits large scale fractionation (1665 ml) and offers sufficient stability to minimize mixing during the loading and unloading procedures. The rotor has a removable core with four vanes which divide the bowl into four sector shaped compartments thereby reducing convection disturbances. Each vane contains a channel to carry fluid from the center of the core to the outer edge of the rotor bowl. The central part of the core has flat surfaces tapered from bottom to top toward the axis of rotation. The slope of these surfaces directs sample upward and into the four channels located in the center of each of the four compartments.

A density gradient (sucrose solution) is used in the fractionation process and is generated by the Beckman Model 140 continuous flow gradient pump. The gradient pump accurately controls the flow rate, gradient, and volume of liquid delivered. The density of the resulting solution is varied to comply with a pre-selected program. This gradient is achieved by feeding the pump light (least dense) and heavy (most dense) sucrose solutions which are mixed in a precise and reproducible manner as programmed, and fed into the channels of the core expelling the solution at the outer edge of the spinning rotor bowl. The gradient must, due to gravitational force, be less dense near the central part of the core than at the outer edge. The density gradient has two main functions in the fractionation process. First, it lends stability to the system by allowing for the pumping out of the latex with a minimum of mixing by convective disturbances. Secondly, it achieves separation during the run and maintains the particles in place during the pump-out stage.

The gradient and sample solutions are introduced into the rotor through a removable seal assembly (center of rotor) while the rotor is spinning at a slow rate of rotation (below 5,000 rpm). After the rotor is loaded, the seal assembly is removed, a cap placed over the shaft, and the ultracentrifuge

Wa-4

taken to the desired speed for sedimentation.

The overlay solution, which is the least dense component in the rotor is introduced by syringe at the central part of the core after the sample has been placed in the rotor. The purpose is to push the sample away from the axis of rotation and into an area where the gravitational forces are greater. Overlays need not be used if large latex particle (about 0.5 μ dia.) or high speeds (> 10,000 rpm) are used. Overlay solution volumes of about 50 ml have been employed. Great care must be taken when introducing the overlay so as not to cause mixing that will broaden the initial sample band.

After sedimentation has occurred, the rotor is returned to an unloading speed of about 3,000 rpm, the seal assembly is attached to the spinning rotor head, and a more dense solution is pumped to the outer edge of the rotor, thereby displacing the solution already in the rotor. The displaced liquid is continuously channelled into a Beckman DB-G equipped with a flow-through-cell where % transmission is measured at a wavelength of 546 nm. The solution then flows into a fraction collector. A recorder is programmed to output a graph of %T versus fraction tube number. Pump-out continues until the entire gradient has been displaced in the above manner.

The size distribution analysis of fractions of narrow particle size is based on the use of the extrema⁴⁻⁶ in the angular light scattering pattern. In this study, the scattering function utilized was the polarization ratio which is defined as

$$\rho_{\theta} = \frac{(i_2)_{\theta}}{(i_1)_{\theta}} = \frac{H_{h,\theta}}{V_{v,\theta}} \quad (1)$$

where $V_{v,\theta}$ is the Rayleigh ratio for the vertically polarized component of the

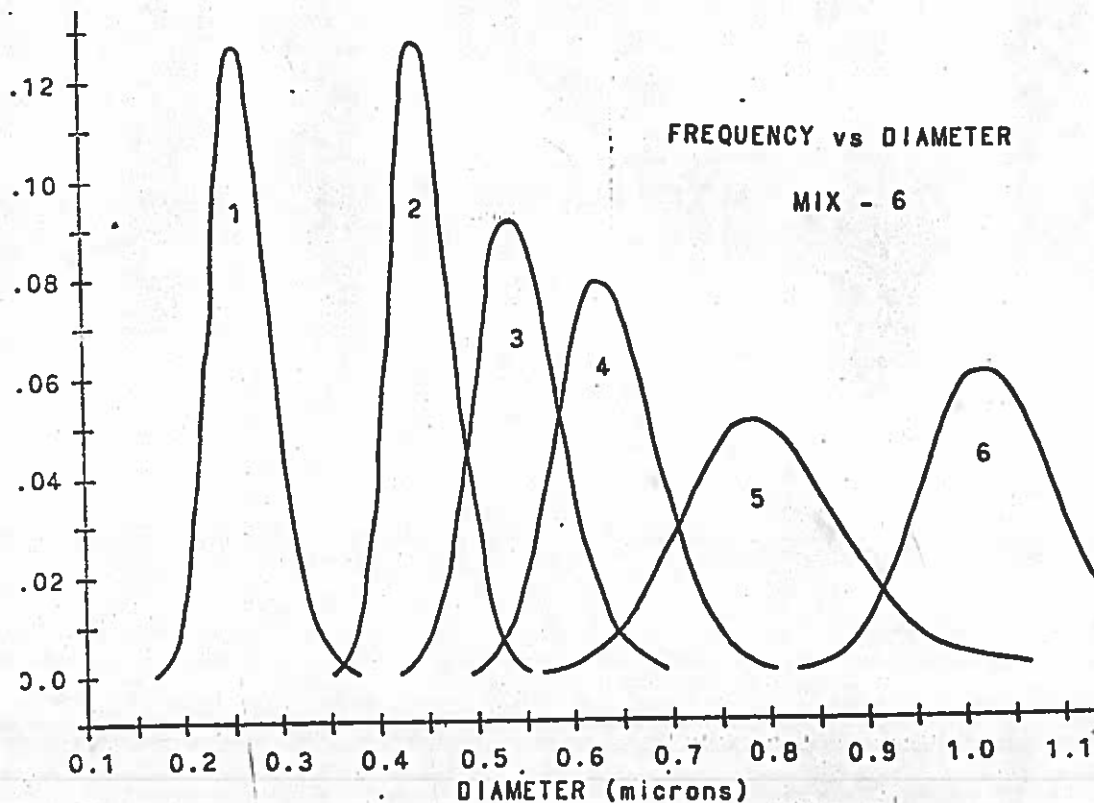


Figure 1

radiant scattered intensity per unit solid angle from an incident vertically (subscript v) polarized beam of unit irradiance; the definition of $I_{h,\theta}$ follows from that of $V_{v,\theta}$. The Mie angular intensity function $(i_1)_\theta$ for the vertically polarized component of scattered light from a scattering system of finite polydispersity is given by

$$(i_1)_\theta = \int_0^\infty (i_1)_\theta^0 p(\alpha) d\alpha \tag{2}$$

where $(i_1)_\theta^0$ is the intensity function at angle θ for a single sphere of optical size α , and $p(\alpha)$ is the frequency function for the zeroth-order logarithmic distribution⁹. The optical size α is $\pi D/\lambda$, where D is the particle diameter and λ is the wavelength of light in the medium. Therefore $p(\alpha)d\alpha$ gives the fraction of particles with sizes between α and $\alpha + d\alpha$. A similar expression exists for the horizontally polarized component of scattered light $(i_2)_\theta$. This distribution function has a slight positive skew and is expressed as

$$P(\alpha) = K \exp \left\{ -(\ln \alpha - \ln \alpha_m)^2 / (2\sigma_0^2) \right\} \tag{3}$$

where K is a normalization constant, α_m is the modal optical size, and σ_0 is a distribution breadth parameter which is related to the standard deviation by

$$\sigma = \alpha_m \sigma_0 \left\{ 1 + \frac{7\sigma_0^2}{21} + \frac{37\sigma_0^4}{31} + \dots \right\}^{1/2} \tag{4}$$

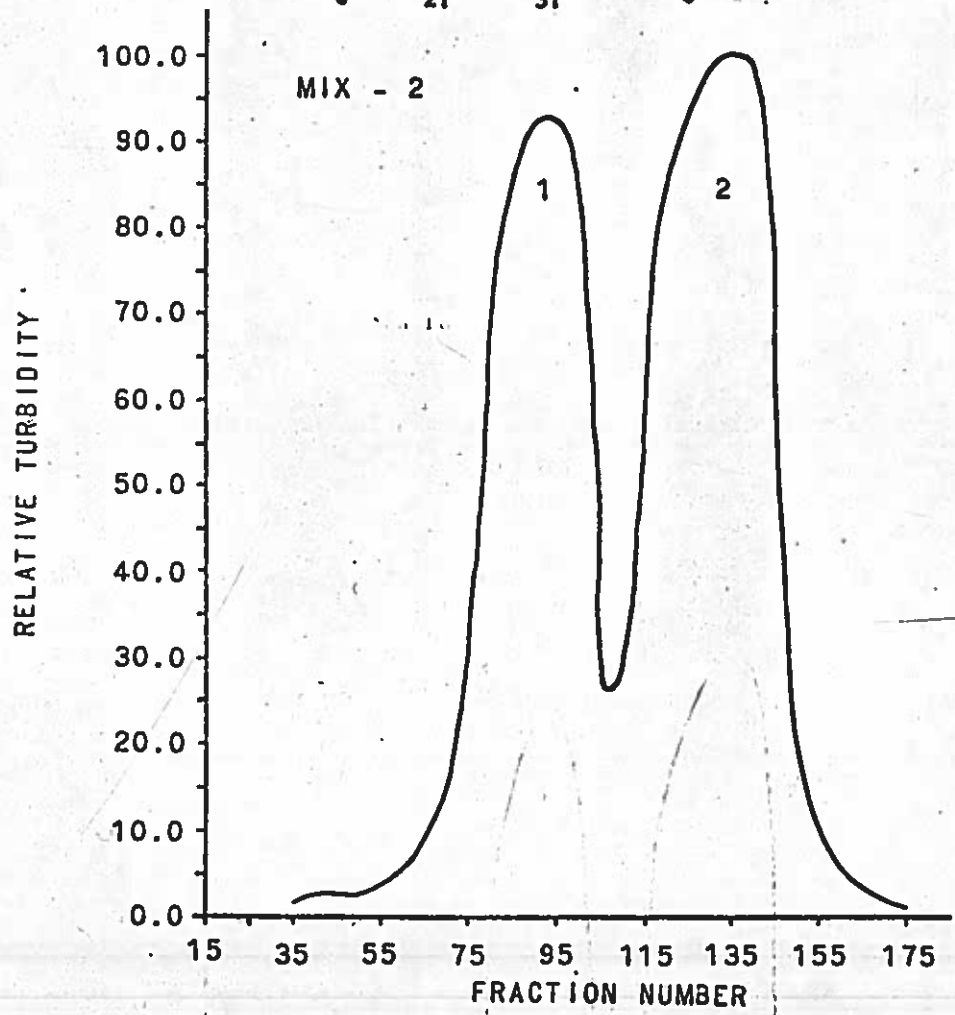


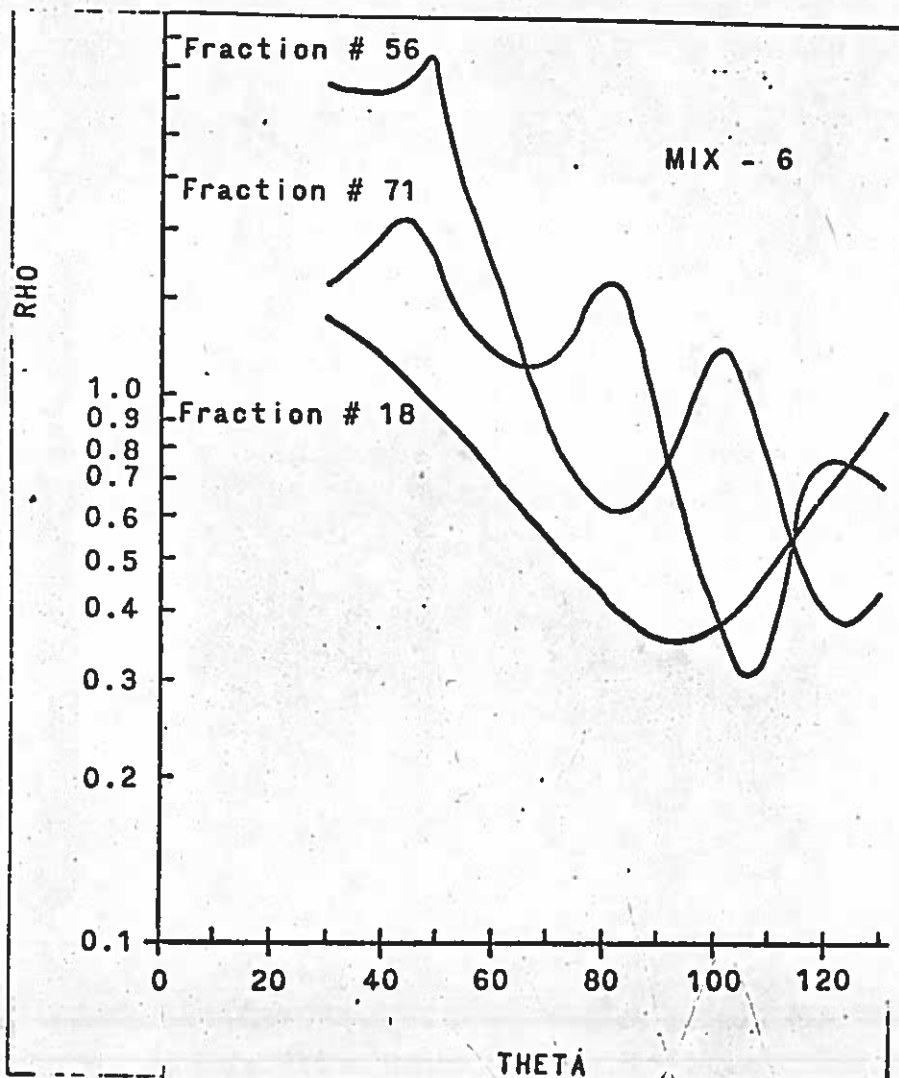
Figure 2

A number of other size distribution functions (e.g., Gaussian) would be equally suitable³. Therefore, ρ_0 is considered to be a function of m , θ , α_m , and σ_0 where m is the relative refractive index (i.e. ratio of refractive index of sphere to that of medium).

From prepared diagrams⁴⁻⁶ α vs. position of minima, θ_i , one can evaluate the modal optical size and therefore the modal diameter D_i . In addition, from prepared diagrams of the extrema ratio for ρ_0 vs σ_0 ,^m the distribution width is evaluated. This technique is a quick, simple, yet precise method which is ideal when it is necessary to analyze a large number of samples.

The preparation of the light scattering samples, the procedure used to obtain data from the Sofica photometer and the theoretical details of the extrema method have been previously given⁴⁻⁶.

Based on the light scattering results which yields α_m and σ_0 and with Eq. 3, the frequency vs. diameter curves for the six latex systems utilized in this study are given in Figure 1. All six samples form MIX-6 while samples 2 and 4 were used for MIX-2. Samples were prepared either by Dow Chemical Company or in this laboratory and have been characterized by light scattering.



THETA
Figure 4

Results and Discussion

Figure 2 represents the relative turbidity vs. fraction number for MIX-2 obtained as the DB-G spectrophotometer output. Fractions 90 and 135 were selected for light scattering analysis and the results from the ρ_θ vs θ curves are given in Table 1. The size distribution analysis after separation agrees with the analysis performed on the individual samples prior to mixing which indicates that a clean separation was achieved. A mixture of six latex samples, MIX-6, was analyzed and Figure 3 illustrates the relative turbidity vs. fraction number demonstrating the presence of the six samples. The ρ_θ vs θ curves for three fractions are shown in Figure 4 and the results for all fractions are shown in Table 2. Again, light scattering analysis of samples before and after separation indicates a clean separation. In addition, electronmicroscopy verified that complete separation was achieved. A single Dow latex sample was fractionated and analyzed and the results are given in Table 3.

Table 1
MIX-2

<u>Fraction</u>	<u>θ_1</u>	<u>D_m (nm)</u>	<u>σ_0</u>
90	82°	445	0.06
135	52°	645	0.08
	85°	640	0.08

Table 2
MIX-6

<u>Fraction</u>	<u>θ_1</u>	<u>D_m (nm)</u>	<u>σ_0</u>
18	94°	259	0.12
56	82°	445	0.07
71	66°	543	0.08
90	54°	631	0.08
	88°	631	0.07
110	42°	776	—
	68°	776	—
	94°	786	0.10
127	52°	962	—
	70°	1070	—
	86°	1020	0.06

Table 3
Fractionation of Dow "Monodispersed" Latex

<u>Fraction</u>	<u>θ_1</u>	<u>D_m (nm)</u>	<u>σ_0</u>
136	34.0	457	0.07
132	35.0	449	0.07
129	35.5	442	0.07
126	36.0	440	0.08
121	36.5	435	0.08
114	37.0	433	0.08
105	37.5	430	0.08

References

1. T. P. Wallace and J. P. Kratochvil, in *The Computer in Polymer Science* (J. Polym. Sci. C 25), J. B. Kinsinger, Ed., Interscience, New York, 1968, p. 89.
2. T. P. Wallace and J. P. Kratochvil, J. Polym. Sci. B, 5, 1139 (1967).
3. T. P. Wallace and J. P. Kratochvil, J. Polym. Sci. A-2, 10, 631 (1972).
4. T. P. Wallace and J. P. Kratochvil, J. Polym. Sci. A-2, 8, 1425 (1970).
5. T. P. Wallace, J. Polym. Sci. A-2, 10, 193 (1972).
6. T. P. Wallace and W. B. Scott, J. Polym. Sci. A-2, 10, 527 (1972).
7. M. Kerker, *The Scattering of Light and Other Electromagnetic Radiation*, Academic Press, New York, 1969.
8. H. C. van de Hulst, *Light Scattering by Small Particles*, Wiley, New York, 1957.
9. W. F. Espenscheid, M. Kerker and E. Matijević, J. Phys. Chem., 68, 3093 (1964).

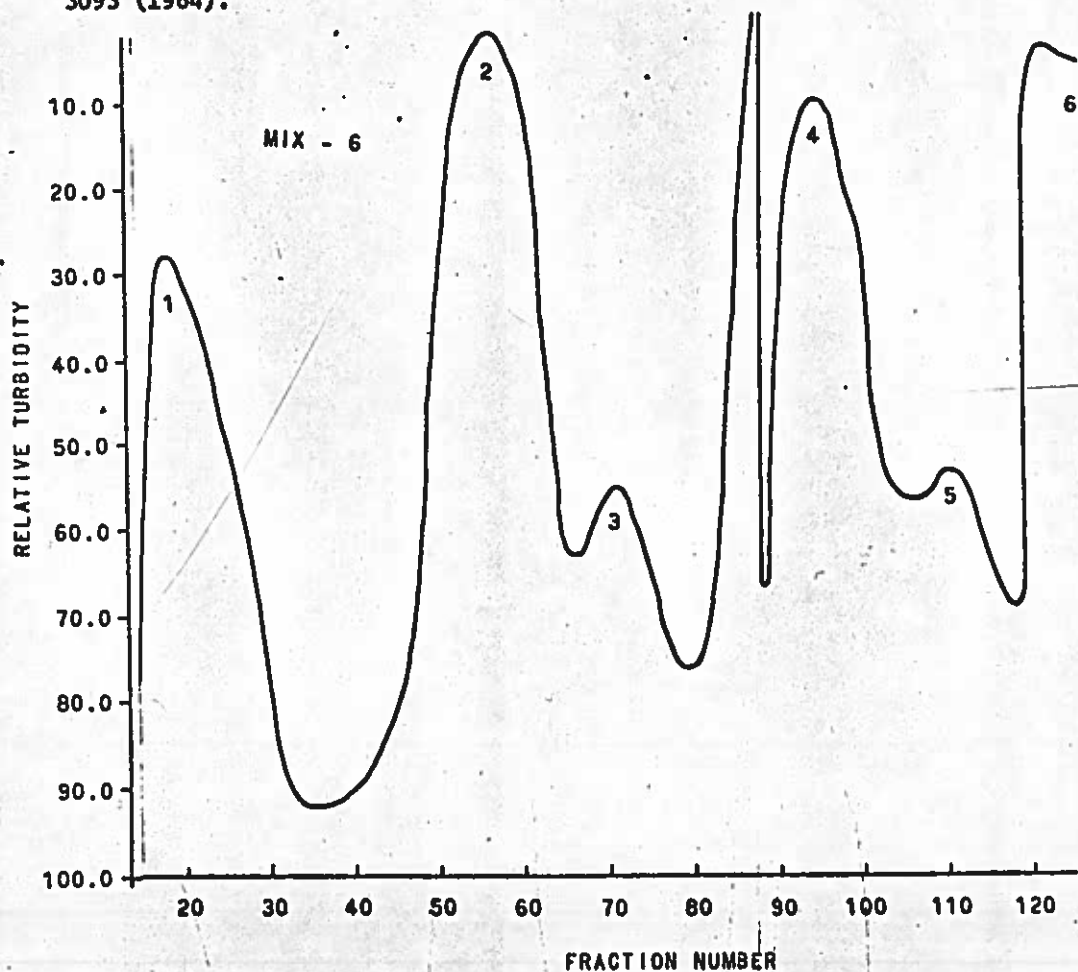


FIGURE 3

Wi-1

David J. Williams
The City College of New York
February 1972

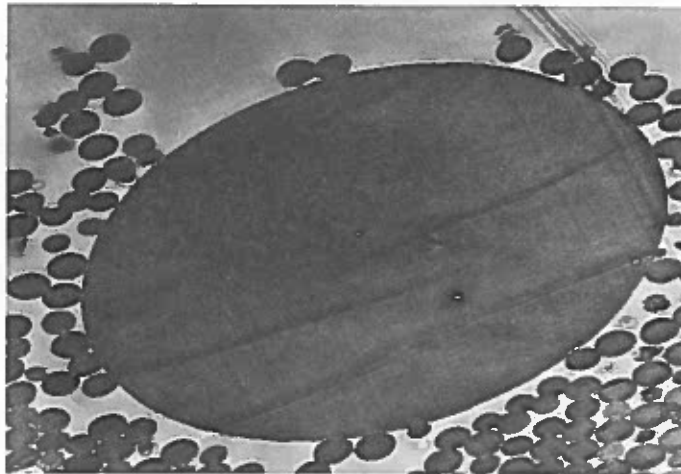
Fitch's gang has expanded but mine has shrunk by one to a group of one -- me. Preston Keusch defended his dissertation on January 29, 1973 with John Vanderhoff attending as an outside examiner. I have entered his thesis "Interfacial and Morphological Phenomena in Polystyrene Latex Systems" in the La Mer Award Competition sponsored by the A.C.S. Division of Colloid and Surface Chemistry. You will all receive copies of his thesis as soon as we have them assembled.

I am, of course, looking for students to continue this work, and I would be pleased to consider any nominations any of you might be able to make.

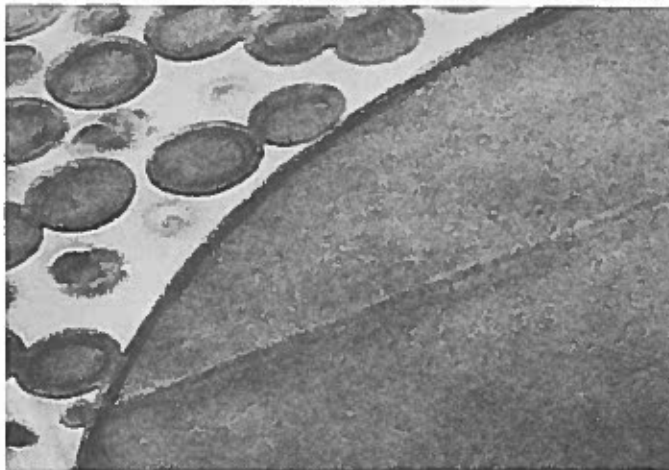
Preston made an interesting discovery in one of his last series of experiments. He was in the process of preparing some high molecular weight polystyrene seeds when he had the type of "accident" that befalls so many of us in preparing latexes. That is, along with the normal seed crop, small numbers of very large particles -- $>2\mu$ -- were produced. In this instance we attributed their generation to the agglomeration of the high molecular weight particles which tend to be unstable because of the reduced amounts of persulfate chain-ends on their surfaces. These large particles were included in a subsequent seeded polymerization experiment in which a trace of butadiene was added to the second generation charge. As shown in the accompanying figure, not only do the normal particles exhibit the core-shell morphology, but the large ones also display a peripheral region of high butadiene concentration. We have tentatively interpreted this observation to mean that even systems approaching the macroscopic in size may exhibit some form of the encapsulation phenomenon.



a. Micrograph of a whole particle (12,540X).



b. Ultra-thin section of large particle showing core-shell growth (28,215X).



c. Detail of the surface of the large particle (53,625X).

Figure 28. Electron micrograph of the largest particle exhibiting core-shell behavior.

78
E-2