

This issue of the Newsletter is being distributed a month earlier than usual because of the imminence of the 'Polymer Colloids' Symposium in Canada which Theo van de Ven was asked to arrange as the 1984 meeting for the Group although the dates of the Chemical Institute of Canada Conference in Montreal (of which the Symposium forms a part) have turned out to be awkward for many members of the Group. Nevertheless a full programme has been arranged and it has been decided that the Annual Business Meeting will be held during the Montreal meeting but that a meeting will also be held in Pittsburgh in the evening of Sunday 10 June prior to the 58th Colloid and Surface Science Symposium to brief those members who will be in Pittsburg but who were unable to be in Montreal.

The 'Polymer Colloids' Gordon Research Conference has now been accepted as a permanent biennial conference. The site will once again be Tilton School in 1985 and this is expected to be the venue of the 1985 Annual Meeting.

The 15th Lehigh Short Course is scheduled for 4-8 June which unfortunately clashes with the Montreal meeting: the dates for the 7th European version are August 20-24 in Davos, Switzerland.

Mohamed El-Aasser has been on a six month secondment to the C.N.R.S. Laboratory in Lyon, but will be back in the U.S. in June.

The Lyon on 'Emulsion Copolymerisation and Copolymers' was a great success with 250 participants impeccably organised by Drs. Guillot and Pichot: the papers are to be published in a two part Supplement to 'Die Makromolekulare Chemie' although it may be early 1985 before this can appear. A partial report follows.

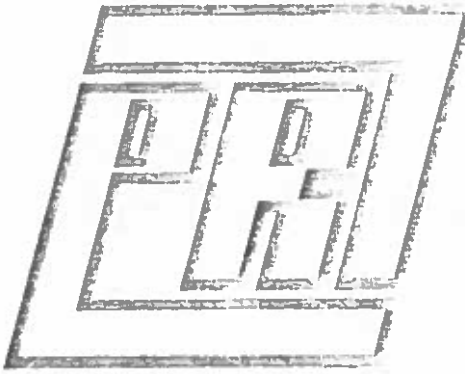
The tentative dates for the 1985 'Polymer Colloids' Gordon Research Conference are July 8 - 12. The Chairman is Dr R.A. Wessling (Dow Chemical Co. Central Research, Midland, Michigan 48640); Vice-Chairman Professor R.H. Otteill (School of Chemistry, University of Bristol, Bristol BS8 1TS, U.K.); they would welcome suggestions for topics and/or speakers which should however reach them in time for action to be taken before 1st January 1985 which is the deadline by which the Chairmen have to submit a complete programme to the Director of the Gordon Research Conferences.

Theo. van de Ven is sending the details of the Montreal meeting to all members directly by Air Mail. Members should therefore receive these long before this issue of the Newsletter can reach them: anyone who has not had this information but needs it should contact Theo directly

Elsevier Applied Science Publishers Ltd are considering a proposal to publish an 'international Journal of Latex Technology'. They point out that no existing journal devote much space to latex although academic aspects are thought to be adequately accommodated so that the new journal should cater for other facets of latex technology, commercial applications and latex products. The term 'latex' would be interpreted to comprehend non-aqueous colloidal dispersions of polymers. Personally I am inclined to counsel caution but other members of the Group might like to give Mr G.B. Olley, Elsevier Applied Science Publishers Ltd., 19 Albemarle St., London, W1X 4BS, U.K. Telephone: 01-493 2618, the benefit of their opinion.

Dr Muroi has had a book (in Japanese) on polymer lattices published (cf. Chem. Abstr. 100 [10]) 'Kobunshi Ratekkusu' 191 pp. (1983) Kobunsha, Tokyo ¥ 2500.

A.S.D.



Press Notice 2

The Plastics and Rubber Institute

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Sent by
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MDS/IT

Date
February 1984

CALL FOR PAPERS - POLYMER LATEX II - LONDON: MAY 1985
May 21-22

The second international conference on polymer latices organized by the Plastics and Rubber Institute will take place in London, UK, during May 1985. Offers of papers are now invited.

All areas of the properties, processing and applications of latices - both plastics and rubber - are of interest.

Topics of particular interest are:

the chemistry and chemical engineering of latex
preparation

and

health and safety.

Intending authors should contact without delay:

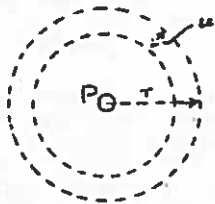
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As a consequence of lecturing commitments this academic session, I became interested in the derivation of the expression for the Fuchs stability factor for a lyophobic colloid. Having consulted various textbooks and finding myself dissatisfied with what they had to say on this matter, I then turned to the original Fuchs paper(1). This is, of course, written in German, and in such a way that, for a person such as myself whose knowledge of the German language is very limited, it is difficult even to guess at the underlying argument. However, I was fortunate in that a colleague whose native language is German was willing to provide me with a translation of the relevant part of the paper. This translation, which I presume is accurate, can be made available to any member of the Group who would like to have a copy. Having obtained an accurate translation of Fuchs' argument, it was then a relatively straightforward matter to devise a simplified derivation of the Fuchs result which would be appropriate for presentation to, say, postgraduate groups of students who were being taught the elements of the theory of the stability of lyophobic colloids. It seemed to me that, in view of the importance of the Fuchs result for the theory of the stability of lyophobic colloids, other members of the Group (especially the academic members) might find the simplified derivation useful. I discussed the matter with Sandy Dunn, who agreed that this might well be the case, and that therefore a summary of the simplified derivation would be a suitable subject for this contribution to the Newsletter.

The argument as given in the original Fuchs paper is rather terse and generalised, and requires a knowledge of vector calculus for its appreciation. The argument assumes that the lyophobic colloid is a dispersion of uniform spherical particles. The radius of the particles is denoted by a . The argument is greatly simplified if, as is usual in elementary treatments of the kinetics of flocculation of lyophobic colloids, we focus attention upon one particular particle P (see diagram), which is imagined to be stationary in the first instance, and consider the overall rate of passage of particles across a spherical surface of radius r , centre the centre of P. The problem then immediately becomes one of spherical symmetry, and this greatly simplifies the mathematics. Thus the concentration, c , of particles at a distance r from the centre of P is then a function of r only.



The particle P is considered to be a sink for all particles flowing inward towards it which actually reach its surface. This implies the existence of a particle-concentration gradient, dc/dr . Particles tend to flow inward across the spherical surface because of Brownian diffusion. The rate of flow is $4\pi r^2 D dc/dr$, where D is the diffusion coefficient of the particles. Particles tend to flow outward across the spherical surface if there is a repulsive force, $f(r)$, between any two particles, $f(r)$ being in general a function of r . The rate of flow is $4\pi r^2 uc$, where u is the outward velocity of the particles under the influence

of the force $f(r)$; this follows because the number of particles which flow outward across the spherical surface in unit time is equal to the number of particles contained in the concentric shell between radii $r = r$ and $r = r-u$. The net rate of flow of particles across the spherical surface towards P is therefore given by

$$\frac{dN}{dt} = 4\pi r^2 D \frac{dc}{dr} - 4\pi r^2 uc \quad \dots(1)$$

It is now assumed that a steady-state is rapidly established, so that dN/dt has a constant value, say J . This is a reasonable assumption which has been justified by Smoluchowski(2). We also put u equal to $f(r)/g$, where g is the frictional coeff-

icient for the particles in the disperse phase of the lyophobic colloid. With these two substitutions, equation (1) becomes

$$\frac{dc}{dr} - \frac{f(r)}{\xi D} \cdot c = \frac{J}{4\pi D} \cdot \frac{1}{r^2} \quad \dots(2)$$

If J is assumed to be independent of r , equation (2) is a first-order linear differential equation in c and r , in which the coefficient of c is a function of r . It can readily be solved by the standard method of multiplying by the integrating factor

$$e^{-\int f(r) dr / \xi D}$$

and then integrating. The result is

$$c = \frac{J}{4\pi D} \cdot e^{\int f(r) dr / \xi D} \int \frac{1}{r^2} e^{-\int f(r) dr / \xi D} dr + A e^{\int f(r) dr / \xi D} \quad \dots(3)$$

where A is a constant.

The boundary conditions for the problem are

- i) $c = 0$ when $r = 2a$, because the surface of P is a sink for all the other particles
- ii) $c = c_\infty$ when $r = \infty$, where c_∞ is the uniform concentration of particles at a great distance from P.

The second of these boundary conditions gives

$$c = e^{\int f(r) dr / \xi D} \left\{ c_\infty + \frac{J}{4\pi D} \int_{2a}^{\infty} \frac{1}{r^2} e^{-\int f(r) dr / \xi D} dr \right\} \quad \dots(4)$$

This equation can be written in the simplified form

$$c = e^{-V(r)/kT} \left\{ c_\infty + \frac{J}{4\pi D} \int_{2a}^{\infty} \frac{1}{r^2} e^{V(r)/kT} dr \right\} \quad \dots(5)$$

where $V(r)$ is the potential energy of two particles when the distance between their centres is r , relative to $V(\infty) = 0$. This follows because

$$V(r) = -\int_{\infty}^r f(r) dr \quad \dots(6)$$

Also $\xi D = kT$ by the Einstein equation.

The first of the above boundary conditions substituted in equation (5) gives

$$0 = e^{-V(2a)/kT} \left\{ c_\infty + \frac{J}{4\pi D} \int_{2a}^{\infty} \frac{1}{r^2} e^{V(r)/kT} dr \right\} \quad \dots(7)$$

$$\text{i.e.,} \quad c_\infty + \frac{J}{4\pi D} \int_{2a}^{\infty} \frac{1}{r^2} e^{V(r)/kT} dr = 0 \quad \dots(8)$$

$$\text{i.e.,} \quad J = \frac{4\pi D c_\infty}{\int_{2a}^{\infty} \frac{1}{r^2} e^{V(r)/kT} dr} \quad \dots(9)$$

For an unstabilised lyophobic colloid, $V(r)$ is everywhere zero, and the value of J is

$$J_0 = 4\pi D c_\infty \int_{2a}^{\infty} \frac{dr}{r^2} = 8\pi D a c_\infty \quad \dots(10)$$

as given by the Smoluchowski theory for rapid flocculation. The stability factor, W , for a stabilised lyophobic colloid is defined as the ratio J/J_0 . Combining equations (9) and (10) immediately gives the Fuchs result, namely

$$W = 2a \int_{2a}^{\infty} \frac{1}{r^2} e^{V(r)/kT} dr \quad \dots(11)$$

An interesting observation, which may or may not be significant, is that the exponential factor in the integrand of the Fuchs expression for W enters as the integrating factor for a first-order linear differential equation with variable coefficients.

References

1. N. Fuchs, Z. Physik, 1934, 99, 736
2. M. von Smoluchowski, Physik. Z., 1916, 17, 557, 585

Lyon, France 6-9 March 1981

The final programme consisted of 15 invited lectures, 15 Short Communications, 2 General Discussions, 9 Posters and an apparatus and book exhibition, not to mention social events and the activities of an intrepid photographer so that it is only possible to mention a few of the highlights in a brief report. There will be many other points of interest in the printed texts when they appear.

In other hands, difficulty has been experienced in getting Ugelstad's technique for selling latex particles to work although it seems to be O.K. in Australia. However the relevant patents have now been issued (Norwegian 142032 (1978), U.S. 4 336 173) and John was able to disclose that acetone is NOT used in his two stage swelling process; the secret is in getting very small emulsion droplets which have a higher swelling rate and a higher equilibrium swelling; 100 μm monodisperse particle can be made and the use of these enables the time required for H.P.L.C. to be reduced from 9 h to 2 min with improved separation! (cf. 'Nature' 303 (1983) 95). Magnetic particles have been very successful in treating cancer of the bone marrow (cf. 'Lancet' January 1984) and this is in a large part a result of Alan Rembaum's work (cf. J. Immunol. Methods 52 (1982) 341).

Dave Bassett has been drafted from latex preparation to water-soluble polymers; he gave a very effective 10 min. presentation on Union Carbide's associative thickener 'Ucar' SCT-200 in the course of the final Panel Discussion chaired by John Vanderhoff. Associative thickeners can prevent emulsion paints spattering during application because of the way the viscosity of their solutions varies with rate of shear. They are generally polyurethane polyethers which associate; their apparent molecular weight depends on rate of shear unlike hydroxyethyl cellulose which has been commonly used till now. They also confer sag resistance whilst retaining good flow and levelling but there are severe problems in devising formulations using them because of interactions; the viscosity of resins at the same solids concentration with the same concentration of thickener could vary by a factor of 5!

Abstracts of the papers presented by D. Aasser, Ottewill, and Vanderhoff are included as their contributions to this Newsletter.

Jaromir Snparek (Czechoslovakia) was the only participant from Eastern Europe. He discussed some features of semi-continuous emulsion polymerisation in monomer-starved conditions in which, by contrast with batch copolymerisation in which copolymers with a wide distribution of composition may be obtained, the composition of the product is the same as the composition of the monomer feed. He emphasised the importance of coalescence in determining particle numbers. The fact that ethyl acrylate produces smaller particles than butyl acrylate in semi-continuous emulsion polymerisation (cf. Preprints by Snparek and by Sütterlin for the IUPAC Macromolecular Symposium at Strasbourg, 1981, Vol 1 pp 341, 45) seems to be a result of the more facile acid hydrolysis of ethyl acetate which produces a greater number of surface carboxyls which decrease the rate of particle coalescence.

Battelle (École Polytechnique de Montreal) described a continuous tubular reactor using a 0.63 cm or 2.54 cm diameter teflon tube 155 m in length formed into 4 coils used for the copolymerisation of styrene and α -methyl styrene; the best flow rate was in the region of the transition from laminar to turbulent flow. Although the Continuous Loop Reactor invented in Canada by Raymond Anthier (U.S. 3 551 396 (1970)) he regarded this process as impracticable and did not seem to be aware of its subsequent successful commercialisation by the Crown Polymer Group (cf. K. Geddes, Chem. & Ind. (1983) 223)

B. Emelie (CNRS Vernaison) mentioned an interesting application of the recently developed FAB (Fast Atom Bombardment) technique in Mass Spectrometry to the determination of chain length distribution in a commercial C20 polyoxyethylene nonylpheno ether non-ionic surfactant; polyoxyethylene chain lengths were between 9 and 28. According to Medvedev et al. (J. Macromol. Sci. Chem. 7 (1973) 715) polymerisation occurs in monomer droplets when the polyoxyethylene chain length of this emulsifier is less than 20 but Smith-Ewart kinetics apply when it is greater than 20. More than half the commercial emulsifier was found to be dissolved in the monomer in the methyl methacrylate-butyl acrylate copolymerisation.

J. Claude Daniel (Rhône Poulenc, Aubervilliers) gave a very thorough review of the structure of latex particles including core/shell structure, framboidal particles, and anomalous particles containing voids. He concluded that in emulsion homopolymerisation the outer layer of the latex particles is the locus of polymerisation but the particles which are formed are homogeneous. In copolymerisation, different structures can be promoted by appropriate processing but the structure of the final particles is critically dependent on the relative hydrophilicity of the monomers and cannot be predicted with much confidence.

Sütterlin (Röhm, Darmstadt) explained that a core/shell structure of copolymer particles could improve the impact resistance of materials formed from them; the differences which could be achieved were impressively demonstrated with two samples of plastic sheet of similar appearance. He was incredulous that some people still doubted the existence of core/shell structures; convincing evidence had been available for years in the paper of Keppler, Wesslau & Stabenow (Angew. Makromol. Chem. 2 (1963) 1) although this was in German which nowadays seemed to mean that it would not be read outside Central Europe. (However an English translation is available from R.A.P.R.A., Shaubury, nr. Shrewsbury, Shropshire, SY4 4NR - Translation 1623; this was issued to participants in the 1969 Manchester 'Emulsion Polymers' Symposium and I still have a few surplus copies which Group members could have on request).

The problem of obtaining reliable values for reactivity ratios came in for some discussion. Apart from the necessity of bringing in the partition coefficient in emulsion polymerisation when the monomers differ in water solubility (Ham et al. J. Polym. Sci. 3 (1949) 991) it now appeared that values differed depending on the polarity of any solvent used (Saini et al. Makromol. Chem. 344 (1971) 235, Minak et al. J. Polym. Sci. Polym. Chem. Ed. 11 (1973) 35, Otsuka et al. J. Appl. Polym. Sci. 26 (1981) 1637). In discussion, Ritchie Wessling reported that O'Driscoll had shown that the linear least squares analysis of the Finemann-Ross plot, widely used in the literature, was invalid and that a non-linear least squares regression using the integrated SKEI equation was required (cf. O'Driscoll in the Alfrey Symposium - in the press). Analyses of polymer composition were often unreliable and it was better to analyse the monomer remaining at high conversion by gas chromatography.

One theme reiterated by several speakers (Ottewill, Vanderhoff, Guyot) was the difficulty in relating results obtained under conditions chosen primarily for experimental convenience to the behaviour of practically useful concentrated latices. Thus ζ -potentials have usually to be determined by microelectrophoresis under conditions of extreme dilution and it is doubtful whether these values are still applicable at 50% solids. There is a need to find scientific approaches which can be applied under conditions of practical interest; neutron scattering (cf. Ottewill) provides one such method.

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AMPHOTERIC POLYSTYRENE LATICES

by I. H. Harding and T. W. Healy

Pursuant to the work of Homola and James [1], the preparation and characterization of amphoteric polystyrene latices have been studied in some detail. The following forms the basis of a Ph.D. thesis submitted by Mr. Harding in this University.

1. Preparation

Amphoteric polystyrene latices probably form via an "oligomer - micelle" mechanism. A typical recipe for such latices is:

Styrene	10.00 cm ³
Methacrylic Acid (M.A.).	0.500 g
Dimethyl Aminoethyl Methacrylate (D.M.A.M.)	0.500 g
Potassium Persulphate (K.P.S.).	0.200 g
Water to Give Total Volume of	100 cm ³
pH	1.15
Temperature	70°C

Highly monodisperse, spherical particles were manufactured in sizes ranging from 100 nm to 600 nm diameter. The average particle size was shown to increase with increased initiator concentration, increased temperature, increased pH, addition of surfactant and in the presence of radioactive monomer. The exact relationship between the final particle size and the initiator concentration (given, otherwise, the conditions

above) was:

$$\log[d_w] = - 0.67 \log[I] + 0.316$$

where d_w is the weight average diameter and I is the (K.P.S.) initiator concentration (mol dm⁻³).

2. Purification

Dialysis, ion exchange and activated charcoal cloth cleaning were shown to be unsatisfactory for use with amphoteric polystyrene latices. Centrifugation/decantation and ultrafiltration were, however, found suitable. Details of this section have been published elsewhere [2].

3. Characterization

The latices formed by the above recipe are distinguished from more traditional polymer latices in that they yield an isoelectric point (pH_{i.e.p.}). The charge and potential of amphoteric polystyrene latices were adequately described by the simple Gouy-Chapman model of the electrical double layer but not by the more sophisticated models of Stern and Grahame. The i.e.p. of a given preparation depended mostly on the ratio of amine (D.M.A.M.) to acid (M.A.) used. Increasing the M.A. content decreased the measured pH_{i.e.p.}. The pH_{i.e.p.} was also decreased when the initiator concentration was decreased.

It was shown that traditional electrical double layer models predict a shift in the pH_{i.e.p.} of a latex in which counter-ion binding is significant, and in which the surface acid/base ratio is not unity. Such a shift was not observed for latices having different acid/base ratios in the presence of KNO₃ as background electrolyte. Thus counter-ion binding of simple 1:1 electrolytes, such as KNO₃, onto amphoteric polystyrene latices is not significant. This is in contrast to the majority of studies of counter-ion binding onto other polymer colloids and onto mineral oxides.

4. Adsorption of Cadmium (II) from Solution

Some debate exists amongst adsorption chemists as to the relative importance of electrostatics to the adsorption, from solutions, of transition, or heavy, metal cations. Associated with this is confusion as to which is the dominant adsorbing species - the free metal ion or its hydrolysis species (that is, for carbon dioxide - free systems). Amphoteric polystyrene latices were shown to be an ideal substrate for studying the relative importance of electrostatics to a given property since samples could be synthesized differing in their $pH_{i.e.p.}$, but similar with respect to most other chemical and physical properties.

The adsorption of a given metal ion, cadmium (II), from solution, and as a function of pH, onto a series of amphoteric polystyrene latices was shown to result in a series of curves which were, to a first approximation, identical to each other but displaced along the pH axis in apparent response to the isoelectric point. When normalized with respect to the isoelectric point, the curves were identical. This evidence was used to show that the dominant adsorbing species was Cd^{2+} , and not its hydrolysis species. Electrostatics were shown to play a vital role in determining the extent of adsorption but were also shown to be insufficient to describe the full extent of adsorption and a specific, or chemical, free energy term was required.

- [1] Homola, A. and James, R.O., *J. Colloid Interface Sci.*, 59, 123-133 (1977).
- [2] Harding, I.H. and Healy, T.W., *J. Colloid Interface Sci.*, 89, 185-201 (1982).

23 MAR Recd

Internal Structure of Latex Particles Formed by Two-Stage Feed Polymerization of Ethyl Acrylate-Methacrylic Acid Mixture

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Our previous paper¹⁾ reported on the internal structure of latex particles formed by two-stage feed polymerization of an ethyl acrylate (EA)-methacrylic acid (MAA) mixture and a methyl acrylate (MA)-MAA mixture. The latex particles thus formed were dissolved progressively from the surface by raising the pH of the latex gradually. The dissolved polymer was separated cumulatively from the undissolved particles and subjected to compositional analysis. In all cases the results showed the particle shells to be comprised of poly(MA-MAA) and the cores of both poly(MA-MAA) and poly(EA-MAA), in agreement with the results of a study by Lee²⁾. They also showed the ratio of EA/MA to be nearly constant from the surface to the center of latex particles formed by two-stage polymerization of MA-EA-MAA mixture, and showed MAA units to be present at the particle surface in high concentration and decrease rapidly with proximity to the center, as is the case with carboxylated latex particles formed by one-stage feed polymerization^{3, 4)}.

The present paper describes the internal structure of latex particles formed by two-stage polymerization of two types of monomers or monomer mixtures with the same or closely similar hydrophilicity, as indicated by investigation of latex particles formed by two-stage polymerization of a monomer mixture of EA-MAA (90:10 in weight ratio) and another of EA*-MAA containing EA labelled with ¹⁴C. The sample latexes were prepared by polymerizing the EA-MAA mixture in the presence of poly(EA*-MAA) seeds in a 50:50 ratio (EA*-MAA/EA-MAA latex), and by the reverse procedure (EA-MAA/EA*-MAA latex). The resulting latex particles were dissolved progressively from the surface. The dissolved polymer was separated cumulatively in the manner described in the previous paper¹⁾ and then submitted to analysis by liquid scintillation counter and acid titration.

Table 1 shows the degree of dissolution of the latex particle as related to the pH and the specific radioactivity (RAp) of the cumulated fractions expressed as the integral weight fraction (Fw). For reference, the fraction separated at the pH of polymerization is entered in the table as Fraction No. 0. For both types of sample latexes, the RAp tended to increase initially and then level off as the succeeding fractions of the dissolved polymer cumulated. The MAA concentration had been shown in our previous paper¹⁾ to be high in the initial fractions and decrease in succeeding fractions, and the specific radioactivity RA_{EA} was calculated for the EA units on this basis. Fig. 1 shows the product of this RA_{EA} and Fw as a function of Fw, and thus indicates the integral distribution of EA* within the latex particle. The straight line through the origin in Fig. 1 indicates a homogeneous distribution of EA* from surface to center of the two-stage feed polymerized latex particle regardless of the order of the feed stages.

Table I Integral weight fraction of progressively dissolved polymer (Fw) and its specific radioactivity (RAP)

Fraction No.	EA* - MAA / EA - MAA			EA - MAA / EA* - MAA		
	pH	Fw	RAP (μC/g)	pH	Fw	RAP (μC/g)
0	-	0.0026	6.2	-	0.0027	12.3
1	8.17	0.010	23.5	7.72	0.010	30.7
2	8.43	0.023	31.7	8.03	0.018	28.4
3	8.50	0.046	34.5	8.14	0.043	29.2
4	8.60	0.077	36.2	8.30	0.096	30.1
5	8.67	0.107	37.8	8.40	0.149	29.6
6	8.73	0.159	39.3	8.52	0.209	31.9
7	8.80	0.207	39.5	8.62	0.268	33.4
8	8.83	0.232	39.8	8.72	0.361	32.6
9	8.84	0.286	34.5	8.83	0.639	33.1
10	8.91	0.407	39.6	8.97	0.848	34.7
11	8.96	0.462	38.6	9.65	0.969	36.4
12	9.00	0.611	31.9	10.70	0.985	35.3
13	9.45	0.886	35.7	-	1.000	36.4
14	10.50	0.990	32.8	-	-	-
15	-	1.000	36.7	-	-	-

This indication that post-feed monomer is diffused even into the seed centers and then polymerized is supported by the results of an independent study on the formation of inversed core-shell morphology²⁾. On the other hand, it is in disagreement with the results of other studies which indicate the occurrence of shell layer formation by the post-feed monomer in the polymerization of monomers with same or similar hydrophilicity^{5, 6)}. It appears that this disagreement can be resolved only by assuming the glassy state of polymer seeds such as those utilized in those studies prevents the diffusion of the post-feed monomer inside the seeds.

References

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- 4) *Ibid.* 26, 424 (1969)
- 5) L. J. Hughes, G. Brown, *J. Appl. Polymer Sci.*, 5, 580 (1961)
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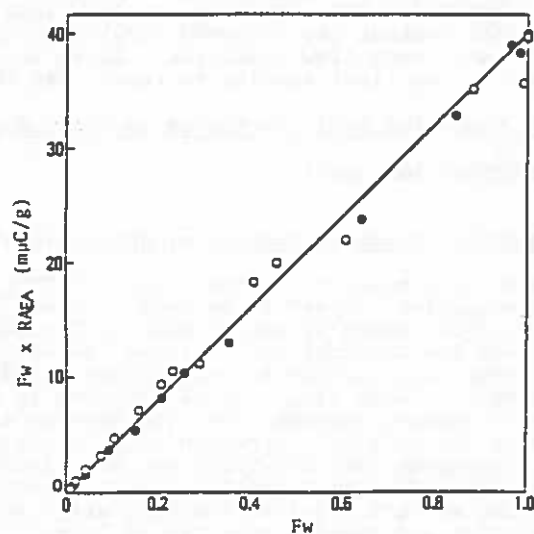


Fig. 1 Product of specific radioactivity on EA unit (RAEA) and Fw, as a function of Fw (O : EA*-MAA/EA-MAA, ● : EA-MAA/EA*-MAA)

Compiled by Bob Gilbert

Styrene emulsion polymerization: particle size distributions

G. Lichti, B.S.Hawkett, R.G.Gilbert, D.H.Napper, & D.F.Sangster
J. Polym. Sci. Polym. Chem. Edn. 19 (1981) 925-938.

Emulsion copolymerization theory: kinetics and sequence distributions

M.J. Ballard, R.G.Gilbert, & D.H.Napper

J. Polym. Sci. Polym. Chem. Edn. 19 (1981) 939-954

Analysis of Interval III data for emulsion polymerizations

B.S.Hawkett, D.H.Napper, & R.G.Gilbert

J. Chem. Soc. Faraday Trans. 1, 77 (1981) 2395-2404

Theoretical prediction of particle size distributions and molecular weight distributions in emulsion polymerizations

G. Lichti, R.G.Gilbert, & D.H.Napper

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Emulsion copolymerization theory: kinetics and sequence distributions

R.G.Gilbert, M.J. Ballard, & D.H.Napper

J. Dispersion Sci. and Tech. 2 (1981) 163-173

Improved methods of solving the Smith-Ewart equations in the steady state

M.J. Ballard, R.G.Gilbert, & D.H.Napper

J. Polym. Sci. Polym. Phys. Edn. 19 (1981) 533-537

The molecular weight of emulsion polymers

D.H.Napper, G. Lichti, & R.G.Gilbert

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A.C.S. Symposium Series 165 (1981) 105-120

Radical capture efficiencies in emulsion polymerization

B.S.Hawkett, D.H.Napper, & R.G.Gilbert

J. Polym. Sci. Polym. Chem. Edn. 19 (1981) 3173-9

Polymerization in emulsion droplets

B.J. Chamberlain, D.H.Napper, & R.G.Gilbert

J. Chem. Soc. Faraday Trans. 1, 78 (1982) 591-606

Seeded emulsion polymerizations of styrene: the fate of exited free radicals

B.C.Y. Whang, D.H.Napper, G. Lichti, M.J. Ballard, & R.G.Gilbert

J. Chem. Soc. Faraday Trans. 1, 78 (1982) 1117-1126

Effects of chain transfer agents on the kinetics of seeded emulsion polymerization of styrene

G. Lichti, D.F.Sangster, B.C.Y. Whang, D.H.Napper, & R.G.Gilbert

J. Chem. Soc. Faraday Trans. 1, 78 (1982) 2129-2145

Mechanisms of latex particle formation and growth in the emulsion polymerization of styrene using the surfactant sodium dodecyl sulfate

J. Polym. Sci. Polym. Chem. Edn. 21 (1983) 269-291

Styrene emulsion polymerization: kinetics and particle size distributions in highly swollen latex systems

D.F. Wood, B.C.Y. Whang, D.H.Napper, R.G.Gilbert, & G. Lichti

J. Polym. Sci. Polym. Chem. Edn. 21 (1983) 935-997

Styrene emulsion polymerization: the effect of initiator charge

I.A. Penboss, D.H.Napper, & R.G.Gilbert

J. Chem. Soc. Faraday Trans. 1, 79 (1983) 1257-1271 12 (1986) 2247

The direct determination of kinetic parameters in emulsion polymerization systems

R.G.Gilbert & D.H.Napper

J. Macromol. Sci. - Rev. Macromol. Chem. Phys. C 21 (1983) 127-186

Coagulative nucleation and particle size distributions in emulsion polymerization

P.J. Feeney, D.H.Napper, & R.G.Gilbert

Macromolecules, in press 17 (1984) 2520, 20 (1987) 2922

The application of electron spin resonance spectroscopy to emulsion polymerization

M.J. Ballard, R.G.Gilbert, D.H.Napper, P.J. Pomery, & J.H.O'Donnell

Macromolecules, in press

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Contribution to the Polymer Colloid Group Newsletter

by

Mamoru Nomura, Department of Industrial Chemistry,
Fukui University, Fukui, Japan1. Kinetics of Batch Emulsion Copolymerization

The batch emulsion copolymerization of vinyl acetate and methyl methacrylate is now carrying out to demonstrate the validity and utility of the simulation model proposed by us (J. Appl. Polym. Sci., 27, 2483 (1982), *ibid*, 28, 2767 (1983)). It was found that in this system, desorption of both oligomeric radicals from the polymer particles was also very important factor in determining the rate of emulsion copolymerization of each monomer. It was also found that our reaction model could explain the kinetic behavior of this emulsion copolymerization system although reactivity ratio for each monomer is very different with each other ($r_{MMA}=20$, $r_{VAC}=0.015$).

2. Kinetics of the Continuous Emulsion Copolymerization

The continuous emulsion copolymerization of MMA and ST is now carrying out in CSTR's. The purpose of this work is to clarify the kinetic behavior of this emulsion copolymerization system, and to make clear whether the proposed simulation model can be applicable to continuous flow operation. Since the experiments are now going on, no final results to report are obtained.

3. Simulation Model for Semi-Continuous Emulsion Copolymerization

No further progress to report.

The 3rd Polymer Microspheres Symposium, Japan (biennial)

We (Nomura, Muroi and Matsuo) are now organizing "The 3rd Polymer Microspheres Symposium, Japan" to be held in Fukui University in November 8-10, 1984, which is cosponsored by The Society of Polymer Science, The Chemical Society, -the Division of Colloid and Surface Chemistry, and The Adhesive Society and other two academic societies. This time, we are planning to invite Dr. Vanderhoff as a plenary lecturer from the members of Polymer Colloids Group, and he kindly accepted our invitation. The members of our Polymer Colloids Group who are planning to visit Japan around the time of this meeting are welcome to present an invited lecture, and are provided transportation expenses between Fukui and Tokyo(?) and staying expenses in Fukui.

Fundamental Studies of the Behaviour of Concentrated Latices

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An important factor in determining the colloid stability of a latex is the existence of repulsive forces between the particles. In the case of aqueous based systems this frequently arises from the presence of ionized groups on the surface which lead to an electrostatic field around the particle and long range interactions. In the case of non-aqueous latices where the dispersion medium has a low relative permittivity then stability can frequently be conferred on the particles by the adsorption or grafting of surface active or polymeric molecules to the surface. These provide what is now usually called steric stabilization.

The nature of colloid stability in both aqueous and non-aqueous systems is frequently investigated in dilute dispersions. In general, however, dispersions of industrial interest usually contain a high volume fraction of latex particles. It is only in recent years that some progress has been made in studying the structure of concentrated latex dispersions. The various techniques utilised include, optical diffraction (1,2,3,4); light scattering (5,6), photon correlation spectroscopy (5), osmotic compressibility (7) and in the last few years small angle neutron scattering (8). In the latter case using cold neutrons the wavelength range (3 - 16 Å) is much shorter than that available using visible light (4000 - 6500 Å) and in addition the weak nature of the interaction of neutrons with matter (i.e. scattering by nuclei rather than electrons) allows deep penetration with little attenuation of the radiation. Consequently it is a very suitable technique for use with concentrated latices and avoids many of the problems of multiple scattering which are encountered using light.

Basically the small angle neutron scattering technique measures the intensity of neutrons $I(Q)$ falling on a detector at an angle θ to the direction of the incident beam. The scattering vector, Q , which has dimensions of reciprocal length is defined by the scattering angle and the wavelength of the incident beam, λ , as,

$$Q = \frac{4\pi}{\lambda} \sin(\theta/2) \quad \dots (1)$$

An example of an experimental curve for a dilute latex is given in Figure 1a. The change in intensity with Q is, for a spherical particle, directly related to the radius of the particle by the form factor $P(Q)$ as

$$P(Q) = \left[3(\sin QR - QR \cos QR)/(QR)^3 \right]^2 \quad \dots (2)$$

so that the intensity is given by

$$I(Q)_{\text{dilute}} = \text{Const. } \phi_{\text{dilute}} V_p P(Q) \quad \dots (3)$$

where ϕ = the volume fraction of the latex and V_p = the particle volume. Equation (3) provides a direct means of sizing latex particles (9) in the radius range up to ca .25 μm .

Once a concentrated latex is examined the form of the experimental curve changes and an example for a polystyrene latex with $R = 160 \text{ \AA}$, $\phi = 0.14$ in $10^{-4} \text{ mol dm}^{-3}$ sodium chloride solution is given in Figure 1b. The different form of the curve is due to the strongly interacting particles forming a structure in the system so that the scattering from the particles is correlated. This can be represented by a factor $S(Q)$, which is equal to

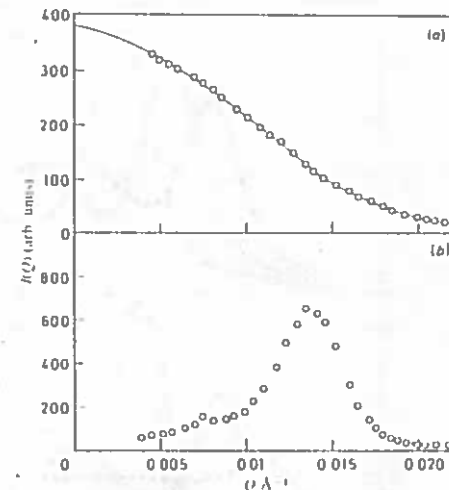


Fig. 1. (a) Plot of $I(Q)$ against Q for latex at $\phi = 0.011$ in $1.3 \times 10^{-4} \text{ mol dm}^{-3}$ sodium chloride solution. (b) Plot of $I(Q)$ against Q for latex at $\phi = 0.14$ in $10^{-4} \text{ mol dm}^{-3}$ sodium chloride solution.

unity for dilute dispersions and becomes a function of Q for concentrated systems (8). For the latter we must rewrite equation (3) as

$$I(Q)_{\text{conc}} = \text{Const. } \phi_{\text{conc}} V_p P(Q) S(Q) \quad \dots (4)$$

so that $S(Q)$ becomes

$$S(Q) = \frac{I(Q)_{\text{conc}} \phi_{\text{dilute}}}{I(Q)_{\text{dilute}} \phi_{\text{conc}}}$$

Examples of the form of $S(Q)$ against Q are shown in Figure 2 for different electrolyte concentrations and volume fractions. As can be seen as the volume fraction increases, so the primary peak becomes more pronounced indicating a substantial increase in order in the system as a consequence of the stronger repulsive forces acting between the particles.

The nature of the results is more easily visualised if the data is transformed into real space as represented by the distance of separation, r , between the particle centres. This can be done in terms of the distribution function $g(r)$ which is related to the number concentration of the system, N_p , by

$$g(r) = N(r)/N_p$$

where $N(r)$ is the number concentration of the particles at a distance r from a reference particle. $g(r)$ is obtained directly from $S(Q)$ by Fourier transformation using,

$$g(r) = 1 + \frac{1}{2\pi r^2 N_p} \int_0^{\infty} [S(Q) - 1] Q \sin(Qr) \cdot dQ$$

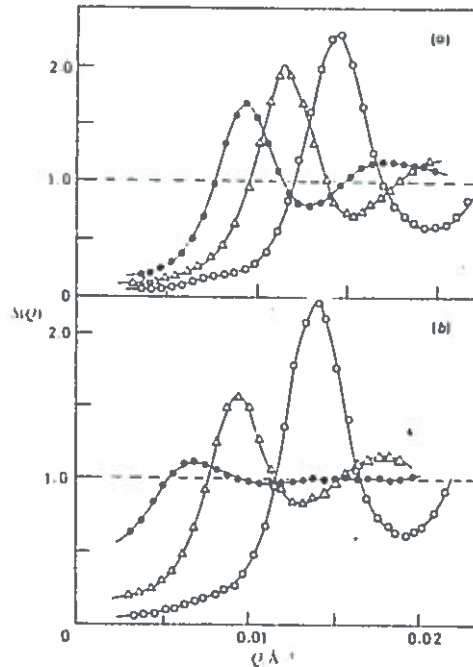


Fig. 2. (a) Plot of $S(Q)$ against Q for a non-exchanged latex: \bullet , $\phi = 0.04$; Δ , $\phi = 0.08$; \circ , $\phi = 0.13$. (b) Plot of $S(Q)$ against Q for latex in 10^{-4} mol dm^{-3} sodium chloride: \bullet , $\phi = 0.01$; Δ , $\phi = 0.04$; \circ , $\phi = 0.13$.

Some examples showing $g(r)$ as a function of r are shown in Figure 3 for a polystyrene latex ($R = 160 \text{ \AA}$) in 10^{-4} mol dm^{-3} sodium chloride solutions at various volume fractions.

In Fig. 3a, the curve closely resembles that expected for a vapour-like system; the exclusion region is clearly visible and the first peak is rather small. At $\phi = 0.04$ (Fig. 3b) the initial slope has increased and the exclusion region has decreased; a clear shell of particles now surrounds the central particle as evidenced by the strong first peak and a second shell is beginning to form. At $\phi = 0.13$ (Fig. 3c) the exclusion region has decreased still further and the initial gradient is even steeper indicating a much stronger interaction. The form of the curve indicates very clearly that there is considerable short-range order but little long-range order, i.e. the overall behaviour is "liquid-like". The excluded volume region in the curves and the low volume fraction at which peaks are observed clearly indicates the long-range nature of electrostatic interactions in aqueous-based lattices.

The same technique has been applied to examine the behaviour in hydrocarbon media of poly-methylmethacrylate lattices stabilised by covalently linking poly-12-hydroxy stearic acid molecules to the surface (10). The results shown in Figure 4 illustrate the form of the $S(Q)$ against Q curves at volume fractions of 0.18 and 0.35. These particles had a core radius ($R = 180 \text{ \AA}$) very similar to that of the polystyrene lattices discussed above. However, in order to induce

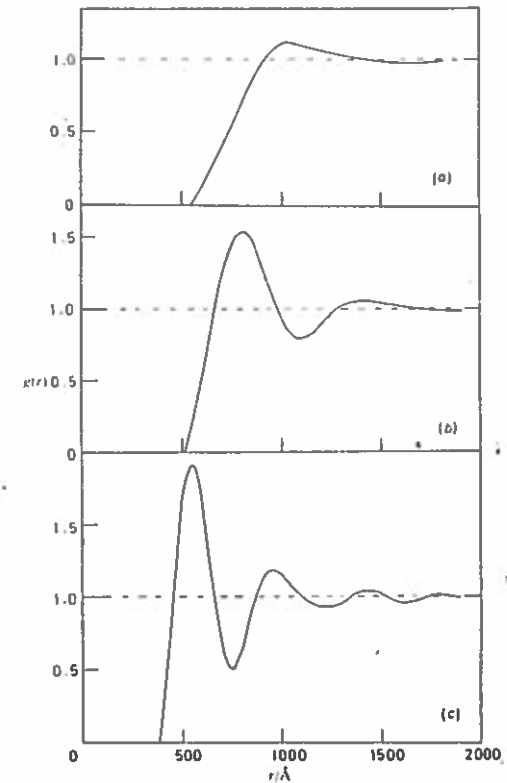


Fig. 3. Plot of $g(r)$ against r for latex in 10^{-4} mol dm^{-3} sodium chloride: (a) $\phi = 0.01$, (b) $\phi = 0.04$, (c) $\phi = 0.13$.

similar structures to those obtained with the aqueous based lattices much larger volume fractions had to be utilized. It can therefore be deduced immediately that the repulsive forces in these nonaqueous dispersions are of much shorter range than those in the aqueous based systems. In fact it was possible to fit the nonaqueous data using a hard sphere model with a hard sphere radius close to that of the radius of the core particle plus its stabilizing layer (10).

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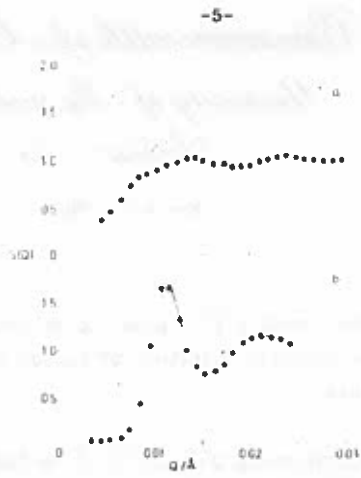


Fig.4. S(Q) against Q curves for poly methyl methacrylate particles stabilised by poly-hydroxy stearic acid. a) $\phi = 0.18$; b) $\phi = 0.35$. —, hard sphere calculations.

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In order to further establish that phase inversion during polymerization is the cause of the observed two constant rate regions in the conversion vs. time plots and is also the reason for the corresponding bimodality in the particle size distribution found in these latexes, two sets of experiments were carried out with results discussed below.

The polymerizations were done at 26°C with two commercial available nonionic surfactants Emulphogene BC-840 (HLB = 15.3) and Igepal CO-710 (HLB = 13.6). These surfactants are chemical

Emulphogene BC-840:
 a polyoxyethylated tridecyl alcohol ($C_{13}H_{27}O(CH_2CH_2O)_{15}H$)
 Igepal CO-710:

a polyoxyethylated nonyl phenol ($C_9H_{19}-\text{C}_6\text{H}_4-\text{O}-(CH_2CH_2O)_nH$,
 $(n = 10-11)$).

At 26°C the first surfactant gives an oil-in-water emulsion (Fig. 1) with a wide range of monomer-to-water ratios $\phi = 0.15$ to 0.48^* . Igepal CO-710, however, produces a water-in-oil, (at first a water-in-oil-in-water) type emulsion (Fig. 2) in the range of ϕ values of 0.27 to 0.48. The emulsion polymerizations conversion vs. time plots (Fig. 3) for the Emulphogene BC-840 shows rate curves, normally observed in emulsion polymerizations. Rates of polymerization are faster with higher monomer concentrations. The particle size distributions are all unimodal (Fig. 4). With the Igepal CO-710 as the surfactant where the starting emulsion is not of the oil-in-water type, the conversion vs. rate curves show two constant rate regions (Fig. 3) and the corresponding HDC curves indicate bimodality in particle size distributions up to ϕ value of 0.48. Only the $\phi = 0.15$ is the exception, here the monomer concentration is too low to support a water-in-oil type emulsion too long and inversion occurs very close to the start of polymerization

* $\phi = \frac{\text{wt. of monomer}}{\text{wt. of monomer} + \text{wt. of water}}$

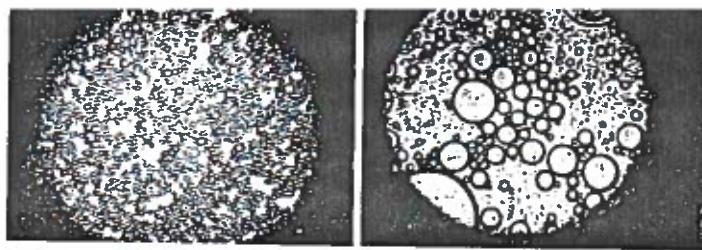


Figure 1. Optical microscope picture of emulsion of $\phi = 0.45$ with Emulphogene BC-840 at 23°C.

Figure 2. Optical microscope picture of emulsion of $\phi = 0.45$ with Igepal CO-710 at 23°C.



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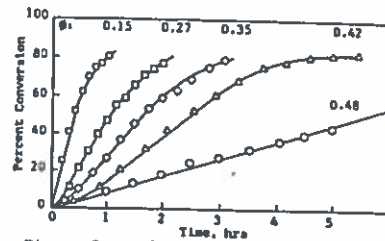


Figure 3. Polymerization of styrene at 26°C. Recipe (mol/liter water): Emulphogene BC-840, 0.063; potassium persulfate, 0.0126; and sodium bisulfite, 0.0126.

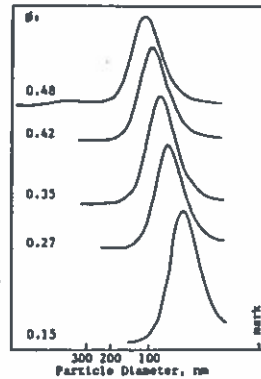


Figure 4. HDC analyses of final latices from polymerization of styrene at 26°C. Recipe: See Figure 3.

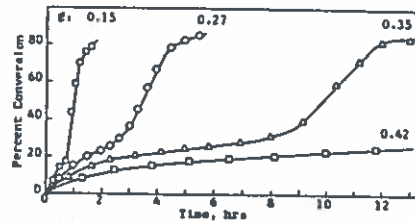


Figure 5. Polymerization of styrene at 26°C. Recipe (mol/liter water): Igepal CO-710, 0.063; potassium persulfate, 0.0126; and sodium bisulfite, 0.0126.

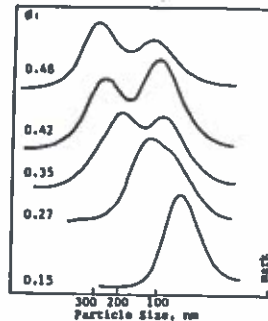


Figure 6. HDC analyses of final latices from polymerization of styrene at 26°C. Recipe: See Figure 5.

We report the following summary of a paper to be presented at the 67th Annual Meeting of the Canadian Institute of Canada International Symposium on Polymer Colloids:

"Dependence of the Hydrodynamic Diameter of Expandable Layer Polymer Latexes on pH" by A.A. Morfesis and R.L. Rowell

Low acid copolymer acrylic acid latexes have been studied as a function of pH by photon correlation spectroscopy, wide angle light scattering and electrophoretic mobility distribution. Expansion curves have been found as in earlier work but the expandable layer has been shown to be of low polymer chain density. The general explanation describes chain expansion due to electrostatic repulsion between ionized carboxyl groups followed at higher pH by a partial contraction arising from a chain relaxation caused by the shielding at higher electrolyte concentration. Electrophoretic mobility measurements were negative in the pH range examined showing the presence of carboxylate anions in the plane of shear at all pH. Inflection points in the mobility-pH curve correlated well with inflection points in the hydrodynamic diameter-pH curve. Since the particles were monodisperse the charge distribution in the diffuse layer must have been uniform and symmetric at the inflection points.

SWELLING OF LATEX PARTICLES WITH SOLVENT EMULSIONS

by

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Polymer-solvent systems which are miscible in all proportions in macroscopic domains behave quite different than polymer-solvent systems in which the polymer is subdivided into colloidal particles; i.e., a latex. When a solvent for the polymer is added to a latex, the solvent molecules diffuse through the continuous phase and swell the latex particles. If the solvent and continuous phase are immiscible and if the solvent is present in large droplets, this swelling is limited because of the free energy required to expand the surface of the polymer-solvent particles. This problem was first treated in a quantitative manner by Morton, Kaizerman and Altier (1). They derived a relationship similar to Eq. 1 by using the Flory-Huggins equation for the free energy of mixing and the Gibbs-Thomas equation for the interfacial free energy.

$$\frac{\Delta G_s}{RT} = \ln \phi_{s,1} + \left(1 - \frac{J_s}{J_p}\right) \phi_{p,1} + \phi_{p,1}^2 X_{sp} + \frac{4\bar{V}_s\gamma}{RT} \left(\frac{1}{d_1} - \frac{1}{d_2}\right) \quad (1)$$

The subscripts s and p denote solvent and polymer and 1 and 2 the particle and solvent phases, respectively. ΔG_s is the difference

in free energy of the solvent in these two phases, T is absolute temperature, R is the gas constant, the ϕ parameters are volume fractions, \bar{V}_s is the molar volume of the solvent, d_1 and d_2 are the diameters of the two disperse phases, X_{sp} is the Flory-Huggins interaction parameter per mole of solvent, J_s and J_p are the equivalent number of molecular segments in the molecules of solvent and polymer, respectively, and γ is the interfacial tension between the polymer-solvent particles and the continuous phase. Morton et al (1) applied Eq. 1 to emulsion polymerization where monomer is the solvent, $\phi_{s,1} + \phi_{p,1} = 1.0$ and $J_s/J_p \approx 1/\bar{X}_n \approx 0$. If the monomer droplets are large $1/d_2$ can be removed from Eq. 1 since $1/d_2 \ll 1/d_1$. Tseng, El-Aasser and Vanderhoff (2) have expanded the Morton treatment to include the effect of water solubility in the organic phases. This is not a major effect for monomers such as styrene. Tseng et al. reported experimental styrene: polystyrene swelling ratios of 3:1 to 7:1 for particles in the latex size range (0.1 to 10 μ m).

Latex particle swelling has received considerable attention during the past several years; primarily because of the interest in producing large particles with narrow size distributions. Ugelstad and coworkers (3,4) have obtained swelling ratios several orders-of-magnitude greater by incorporating water-insoluble swelling agents into the latex particles. Vanderhoff et al. (5) have conducted experiments in space with larger latex seeds.

Jansson, Wellons and Poehlein (6) have recently shown that higher degrees of monomer swelling can be achieved when monomer

emulsions with small droplet size are used. Eq. 1 reduces to the following relationship for this situation.

$$\frac{\Delta G_m}{RT} = \ln \phi_{m,1} + \phi_{p,1} + \phi_{p,1}^2 X_{mp} + \frac{4\bar{V}_m \gamma}{RT} \left(\frac{1}{\bar{d}_1} - \frac{1}{\bar{d}_2} \right) \quad (2)$$

where the subscript m denotes monomer

The specific question to be addressed in this brief paper

is:

Given: An initial latex containing N_1 polymer particles of size $d_{1,0}$ and a target monomer:polymer swelling ratio of R_s in the absence of swelling agents.

Determine: The emulsion droplet size $d_{2,0}$ and number N_2 that will completely diffuse into the particles to achieve the target monomer:polymer swelling ratio.

In the normal swelling situation an excess of monomer in the form of large droplets is used. As the swelling process takes place, the free energy of the monomer in particles increases with monomer concentration while the free energy of the dispersed monomer remains nearly constant. When $\Delta G_m = 0$ the swelling stops. However, if the monomer is dispersed in very small droplets, the surface free energy contribution can cause the monomer activity in these droplets to increase dramatically as they shrink due to diffusion losses. In such cases, the droplets will disappear completely and large swelling ratios can be achieved without the use of a swelling agent.

In order to examine the question concerning emulsion droplet size limitations, one must utilize the following volume conservation relationships.

$$V_p = (\pi N_1 d_{1,0}^3 / 6) \quad (3)$$

$$V_m = V_{m,1} + V_{m,2} = (\pi N_2 d_{2,0}^3 / 6) \quad (4)$$

$$V_{m,1} = (\pi N_1 / 6) (d_{1,t}^3 - d_{1,0}^3) \quad (5)$$

$$V_{m,2} = (\pi N_2 d_{2,t}^3 / 6) \quad (6)$$

where V_p and V_m are total volumes of monomer and polymer respectively, $V_{m,1}$ and $V_{m,2}$ are the volumes of monomer in the polymer particles and emulsion droplets respectively, and $d_{1,t}$ and $d_{2,t}$ are the time-dependent diameters of the two phases.

When these volume-balance relationships are combined with Eq. 2 the free energy difference can be written as a function of a single variable; specifically the size of the swelling latex particles.

$$\frac{\Delta G_m}{RT} = \ln \left(1 - \frac{1}{d^3} \right) + \frac{1}{d^3} = \frac{X_{mp}}{d^3} + \frac{4\bar{V}_m \gamma}{RT d_{1,0}} \left\{ \frac{1}{d} - \frac{1}{(d_0^3 - N^* (1-d^3))^{1/3}} \right\} \quad (7)$$

where $d = (d_{1,t} / d_{1,0})$ is a dimensionless latex particle diameter which is a function of swelling time, $d_0 = (d_{2,0} / d_{1,0})$ is the ratio of initial emulsion droplet size to initial polymer particle size and N^* is the dimensionless ratio N_1 / N_2 .

Figure 1 contains three plots of $(\Delta G_m / RT)$ vs d for different

values of N^* . The following parameters were used for the calculations.

$$\bar{V}_m = 1.0 \times 10^{-4} \text{ m}^3/\text{gmol}$$

$$\gamma = 5.0 \times 10^{-3} \text{ N/m}$$

$$X_{mp} = 0.35$$

$$R = 8.315 \text{ N}\cdot\text{m}/\text{gmol}\cdot\text{K}$$

$$T = 323 \text{ K}$$

$$d_{1,0} = 1.0 \text{ }\mu\text{m}$$

$$d_0 = 6.0$$

The end positions on each of the curves represent the points where the monomer droplets have completely disappeared. The bottom curve ($N^* = 5.0$) contains a relative maximum well below the position of equilibrium, $\Delta G_m = 0$. In this case the emulsion droplets were small enough to completely disappear well before equilibrium was approached.

The top curve ($N^* = 0.146$) passes through the equilibrium line. This would not be observed experimentally since the swelling would stop at $\Delta G_m = 0$. Hence, in this case, the initial monomer droplets were too large to completely disappear and limited swelling would occur.

The middle curve ($N^* = 1.464$) satisfies all of the following relations at one point on the plot.

$$\left(\frac{\Delta G_m}{RT}\right) = 0; \quad \frac{d}{dd} \left(\frac{\Delta G_m}{RT}\right) = 0; \quad \frac{d^2}{dd^2} \left(\frac{\Delta G_m}{RT}\right) < 0 \quad (8)$$

This curve, therefore, represents the largest emulsion droplet size that will completely disappear during swelling.

In this case that droplet size and the resulting swelling ratio (R_s) are:

$$d_{1,2} = d_{p,0} \cdot d_0 = (1.0)(6.0) = 6.0 \text{ }\mu\text{m} \quad (9)$$

$$R_s = d_0^3/N^* = (6.0)^3/1.464 = 147.5 \quad (10)$$

The relationship between the swelling ratio R_s , the initial droplet:particle size ratio d_0 , and the seed latex particle size $d_{1,0}$ can be obtained from a series of plots such as Figure 1 or by numerical methods which utilize the relationships given in Eq. 8. Modified Newton-Rapson procedures have been used with Eq. 8 to determine the relationship between R_s , d_0 , $d_{1,0}$ and X_{mp} . Figure 2 contains calculated curves for four different values of $d_{1,0}$.

The following example illustrates how such curves can be used to answer the initial question raised in this paper.

Given: $N_1 = 10^{10}$ latex particles

$$d_{1,0} = 0.5 \text{ }\mu\text{m}$$

$$R_s = 800 \text{ (desired swelling ratio)}$$

Determine: N_2 and $d_{2,0}$

Step 1: Use the ($d_{1,0} = 0.5 \text{ }\mu\text{m}$) curve and the $R_s = 800$ scale value to determine d_0 . In this case $d_0 = 6.0$ (See Fig. 2).

Step 2: Compute $d_{2,0} = d_{1,0}d_0 = (0.5)(6) = 3.0 \text{ }\mu\text{m}$

Step 3: Compute $N_2 = N_1/N^* = 10^{10}/1.464 = 0.683 \times 10^{10}$

Figure 3 is an expanded-scale plot of the curvature area from Figure 2. It would be more precise for some computations.

In summary, the application of the techniques outlined in this paper will permit one to compute the approximate maximum emulsion droplet size that will be necessary to generate a desired swelling ratio for specific seed latex when swelling agents are not present.

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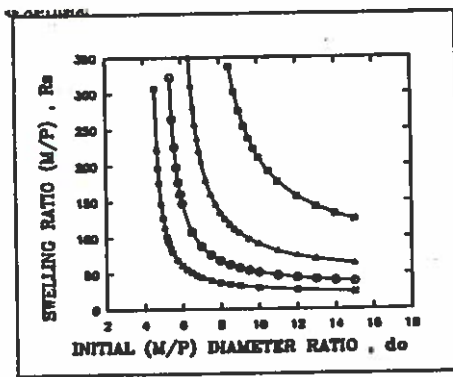


Figure 3. Swelling Ratio Correlation for $X_{mp} = 0.35$

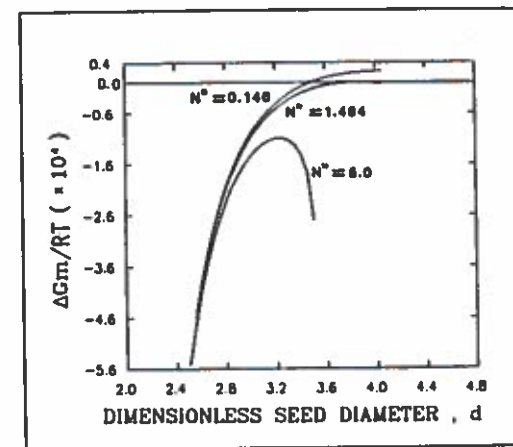


Figure 1. Profiles of Monomer Free Energy Difference as a Function of Polymer Particle Swelling.

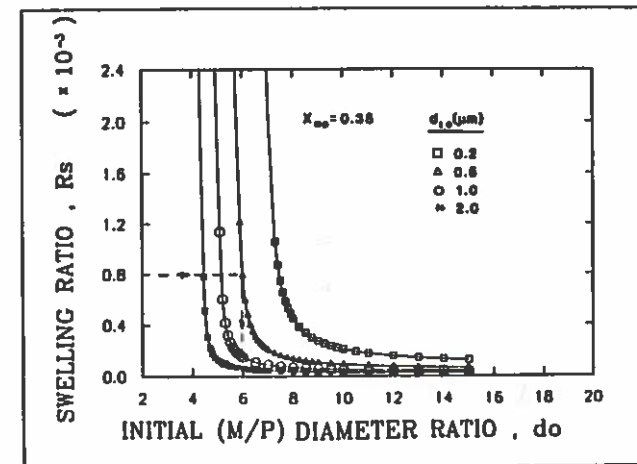


Figure 2. Swelling Ratio Correlation for $X_{mp} = 0.35$

Effect of Chain Transfer Agents on Seeded
Continuous Emulsion Polymerization

20 MAR 7 1968

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The effect of chain transfer agents (CTA) on styrene emulsion polymerization in a seed-fed continuous stirred-tank reactor (CSTR) has been investigated in this laboratory. In the present work, carbon tetrachloride (CCl_4) is used as a chain transfer agent. The reactor system is composed of a tubular prereactor and a CSTR. The tubular prereactor is operated in a plug-flow mode to generate seed particles with narrow size distribution for the CSTR at downstream. CCl_4 is directly added to the CSTR by a syringe pump.

Figure 1 shows the effect of addition of CCl_4 with different amounts on the course of polymerization. In Figure 1, T denotes CCl_4 and M styrene; X_1 stands for the conversion of the seed latex from the tubular prereactor and has an averaged value about 9.6%; dimensionless time is defined as reaction age divided by the mean residence time of the CSTR which is about 37 minutes. Figure 2 illustrates the influence of CCl_4 concentration on the particle size distribution (PSD) of the latex product particles in the effluent stream from the CSTR. The smoothed PSD's are based on the measured particle size histograms. Typical particle size histograms of the seed particles and the product particles are presented in Figure 3. Note the PSD data are expressed in terms of the dimensionless diameter which is defined as particle diameter divided by the mean diameter of the seed particles (about 390 Å). Particle sizes are determined by a transmission electron microscope. About 3200 particles are counted to construct the PSD for product particles, and about 600 for seed particles.

The experimental results shown in Figures 1 and 2 clearly indicate that addition of chain transfer agents to continuous emulsion polymerization not only decreases the rate of polymerization but also changes the PSD of product particles significantly. This reduction effect is mainly due to the loss of free radicals from the monomer-swollen polymer particles. When CTA is added to emulsion polymerization, the free radical at the end of a propagating polymeric chain may be transferred to a neighboring CTA molecule and generate a CTA radical. Because of the high mobility of a CTA radical and the small size of a polymer particle, the CTA radical may diffuse out of reaction site into the continuous phase. This radical "exit" effect would cause a decrease in the free radical concentration in the particles and leads to a decreased rate of polymerization.

The PSD data obtained in this work can be used to quantify the radical transport mechanism. This has been achieved by fitting the computer-simulated PSD to the experimental PSD. Computer simulations are carried out based on the mathematical model developed earlier [Brit. Polym. J., 14, 143(1982)]. According to our model, the PSD of the product particles from a steady-state seeded CSTR depends upon four dimensionless groups: Q_c , β , γ , and Y_c . The definitions of these dimensionless groups were given in the paper. Typical example of the fitting procedure is shown in Figure 4 in which γ (which accounts for transport of radicals out of particles) is used as a curve fitting parameter. Preliminary results obtained so far indicate that the method introduced here can be an useful diagnostic tool in the study of radical transport phenomena in emulsion polymerization.

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Fig. 1. Effect of addition of CCl_4 at different concentration levels on the conversion histories.

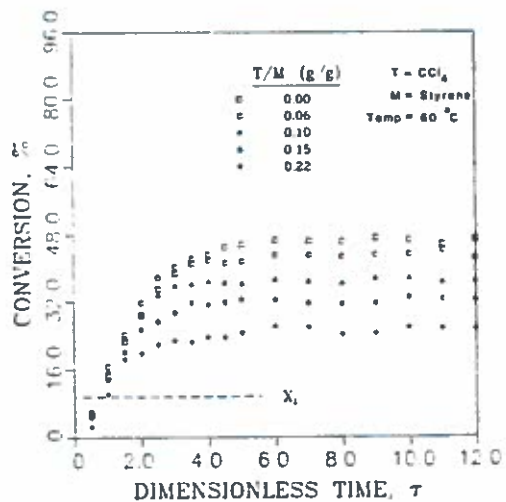


Fig. 3. Particle size histograms of seed particles and product particles at steady state.

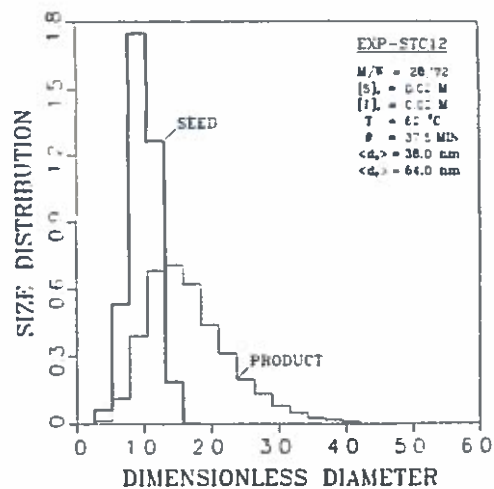


Fig. 2. Effect of addition of CCl_4 at different concentration levels on the product PSD.

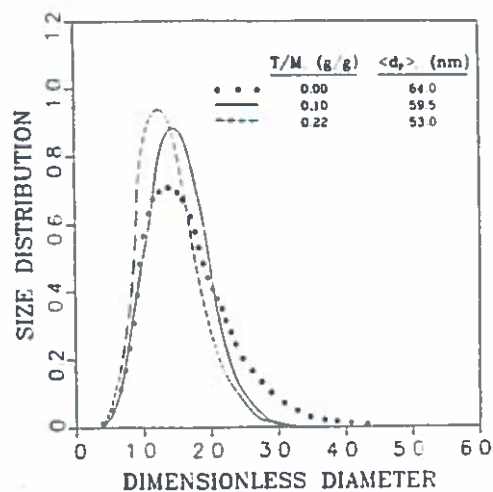
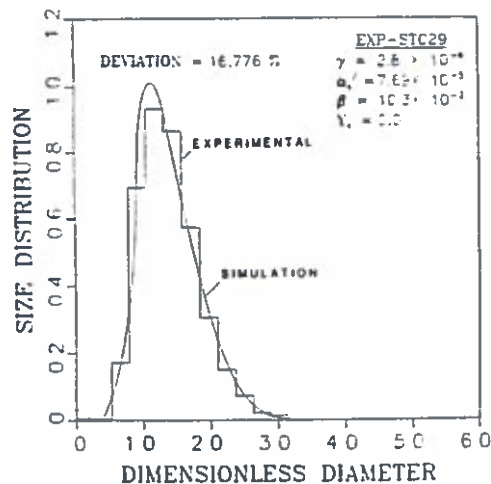


Fig. 4. Comparison between model-predicted PSD and experimental PSD for a selected τ value.



(Accepted for publication in TAPPI Journal)

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COMPETITIVE ADSORPTION PHENOMENA IN PAPER COATINGS

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ABSTRACT

The adsorption of anionic surfactant (sodium dodecyl sulphate SDS), nonionic surfactants (polyethyleneoxide nonylphenol ethers NPEO_n), sodium hexametaphosphate (SHMP) and polyethylene oxide (EO_n) in a model coating color system (kaolin + polystyrene latex (PSL)) has been investigated. The adsorption strengths of NPEO_n on kaolin and PSL are of the same order of magnitude. SHMP adsorbs on kaolin, but is strongly desorbed when NPEO_n is added. SDS adsorbs much more weakly than NPEO_n on PSL and hence may be desorbed and cause foaming problems if NPEO_n is added. The desorption effect can be predicted from the critical micelle concentrations of SDS and NPEO_n . When a latex (containing NPEO_n) and a clay dispersion (stabilized with SHMP) are mixed (as is frequently the case in the preparation of coating colors) redistribution of the NPEO_n and strong desorption of SHMP will take place. This may flocculate the dispersion. This effect has been confirmed by measurements of the flow properties.

(Submitted to J. Colloid Interface Sci.)

THE EFFECT OF SURFACE POLARITY ON THE ADSORPTION OF
NONIONIC SURFACTANTS

I. THERMODYNAMIC CONSIDERATIONS

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ABSTRACT

A thermodynamic model is used to predict the adsorption of nonionic surfactants on latexes with different polarity. The model, which is based upon the Flory-Huggins theory of polymer mixing, predicts that the adsorption decreases as the polarity of the latex increases. It is predicted that adsorption should occur even when it is unfavorable to replace a surface-water contact with a surfactant-water contact. This is due to a lower number of unfavorable hydrocarbon-water contacts when the surfactant is adsorbed, compared to when it is free in solution.

It is also predicted that it is in principle possible to determine the latex polarity or solubility parameter, from adsorption measurements, provided that a similar experiment is carried out on a latex with known polarity, or solubility parameter.

(Submitted to J. Colloid Interface Sci.)

THE EFFECT OF SURFACE POLARITY ON THE ADSORPTION OF
NONIONIC SURFACTANTS

II. ADSORPTION ON POLY(METHYL METHACRYLATE) LATEX

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ABSTRACT

Adsorption isotherms of three nonionic surfactants on PMMA latex has been obtained. The surfactants are nonylphenolpolyethylene oxides with 10, 20, and 50 ethylene oxide units in the chain.

The adsorption isotherms are compared with the adsorption of the same surfactants on polystyrene latex. The adsorbed amount on PMMA is consistently slightly lower than on PS latex for the three surfactants.

The results are discussed first in terms of a Langmuir type equation and second in terms of a new thermodynamic model for the adsorption on nonionic surfactants. Using this model a solubility parameter of 22 MPa^{1/2} is obtained for PMMA from the adsorption results.

The model reveals that the principal driving force of adsorption is not the interaction of the surfactant with the surface but is caused by the orientation of the surfactant molecules at the surface. This orientation, with the surfactant hydrocarbon directed towards the surface and the hydrophilic moiety directed towards the aqueous solution, causes fewer unfavorable hydrocarbon-water contacts compared to a surfactant molecule free in solution.

(Submitted to J. Colloid Interface Sci.)

CHARACTERIZATION OF $\text{KMnO}_4/\text{H}_2\text{SO}_4$ -OXIDIZED POLYETHYLENE SURFACES BY MEANS OF ESCA AND $^{45}\text{Ca}^{2+}$ ADSORPTION

J.C. Eriksson, C.-G. Gölander, A. Baszkin and
L. Ter-Minassian-Saraga

ABSTRACT

The chemical constitution of $\text{KMnO}_4/\text{H}_2\text{SO}_4$ oxidized (sulphated) polyethylene (PE) surfaces has been explored by means of ESCA utilizing chemical shifts, peak intensity data and chemical tagging reactions. In addition, the adsorption of Ca^{2+} ions on sulphated PE was quantified by radiotracer measurements. Comparisons have been made with $\text{KClO}_3/\text{H}_2\text{SO}_4$ and $\text{K}_2\text{Cr}_2\text{O}_7/\text{H}_2\text{SO}_4$ as oxidizing agents and through replacing polyethylene by polystyrene. According to the present study the main chemical groups on a $\text{KMnO}_4/\text{H}_2\text{SO}_4$ -treated PE surface are: $-\text{OSO}_3\text{H}$, OH , $-\text{O}-\text{OH}$, $-\text{C}=\text{O}$, $-\text{C}-\text{O}-\text{C}-$ and $-\overset{\text{C}}{\parallel}-\text{O}-\text{R}$ (ester). In the oxidation grooves, dissociable $-\text{COOH}$ groups are also present in appreciable amounts. By annealing, a smoother and more homogeneous sulphated surface is produced, the composition of which strongly depends upon the state of the ionic groups at the heat treatment.



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4 APR 1984

CONTRIBUTION TO THE POLYMER COLLOID GROUP NEWSLETTER

Submitted by Donald C. Sundberg
Spring 1984

INFLUENCE OF LATEX PARTICLE MORPHOLOGY UPON EMULSION POLYMERIZATION KINETICS

Two stage polymerization of immiscible polymers within the same latex particle is known to produce a variety of possible particle morphologies. These include core-shell structure, hemispheric structure, etc. We have been studying the reactor kinetics of two phase latex particles by swelling a seed latex of polymer A with monomer B and monitoring the resultant batch reaction. This technique avoids new particle formation and allows one to concentrate upon the influence of developing particle structure on the speed of the reaction. Here it is necessary to be concerned with the transport of free radicals across the interface between the two phases and with the individual reaction rates within each phase. We have determined that the polymer phase which is at the outside surface of the particle (i.e. the shell in the core-shell morphology) is the phase which primarily controls the reaction kinetics, although there may be significant polymerization occurring within the other phase. It is expected that the more hydrophilic of the two polymers will become the outside phase even if it was the seed polymer.

THE EFFECT OF CHAIN TRANSFER AGENTS UPON REACTION RATES IN EMULSION POLYMERIZATION

Experiments show that the addition of chain transfer agents to an emulsion polymerization recipe causes noticeable to significant reductions in reaction rates. Using the seed latex technique in which a seed polymer particle is swollen with its own monomer, our experiments show that rates decrease with increasing levels of chain transfer agents. Our experiments have been in the particle size range of 1200-2000Å for which radical desorption from the particle to the water phase is insignificant due to the low particle surface to volume ratio. We believe that the rate reduction is due to the production of a greater number of short chain length free radicals (via the transfer reaction) and that these radicals diffuse much easier than long chain length radicals thereby leading to increased termination rates and lower numbers of free radicals per particle. This postulates that the termination rate constant is chain length dependent--a concept which has been shown to be useful in analyzing the gel effect in bulk polymerization of vinyl polymers. We are now working to quantify this effect in our kinetic models.

In our previous efforts to study the gel effect in emulsion polymerization we have always used the steady-state radical population balance proposed by Smith and Ewart. This has been accepted by nearly all of those working in the area and most of us use one of the general descriptions offered by Stockmayer, O'Toole, and Ugelstad. In working with systems which display strong gel effects (e.g. MMA) we note such a rapid buildup in free radicals within the particles that the pseudo steady-state analysis would appear to be violated. With the interaction of Dr. S.K. Soh at the University of Detroit, we are working on a transient analysis for the radical population balance and hope to be able to identify the general sets of conditions for which the pseudo steady-state approach is inappropriate.

OTHER POLYMER WORK AT UNH

Two projects are being carried out in the area of fast polymerization reactions with application to the reactive processing of polymers. The first is a detailed study of the styrene crosslinked polyester system. It is an example of a rapid copolymer reaction in which extensive crosslinking takes place. Our objective is to provide a mechanistically based kinetic model which can be used to gauge curing times in industrial molding operations. We will report on this work at the Atlanta AIChE meeting in March of this year.

The second project in this area is concerned with the anionic polymerization of ϵ -caprolactam to form Nylon - 6. This system is becoming important in the reaction injection molding business and its kinetics are not well understood at all. It is of interest to note here that a polymer chain degradation reaction appears to be responsible for causing a marked increase in the number of reactive chain ends. This reaction becomes more probable with increasing conversion and results in a dramatic auto-acceleration in the reaction rate. This is analogous to the gel effect in free radical polymerization but occurs for a completely different reason.

CONTRIBUTION TO THE POLYMER COLLOID GROUP NEWSLETTER

Mohamed S. El-Aasser, Andrew Klein, F. J. Micale, Cesar Silebi,
and J. W. Vanderhoff
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We have currently thirty-four active projects, the titles of which are included in the enclosed Index of our Graduate Research Progress Reports, issue No. 21, January 1984. We do not have enough copies for distribution to all members; however, any member interested in a particular project will be provided with a copy of that progress report. Requests should be addressed to Ms. Karen Hicks at the above address (a long-awaited, welcome addition to our staff, in charge of the administrative affairs of the Institute).

Also enclosed are extended abstracts of two papers presented at the Colloque International Sur Les Copolymerisations et Copolymeres en Emulsion, CNRS, Lyon, March 6-9, 1984:

"Swelling of Carboxyl Containing Copolymers";
"Emulsion Copolymerization of Azeotropic Styrene-Acrylonitrile Monomer Mixture in Polystyrene Seed Latexes".

Five of our graduate students have finished their Ph.D. Dissertations:

K.J. Chiang, "Electrokinetics, Particle Diffusion and Particle-Bubble Interaction in the Flotation Process";
S. Kiatkamjornwong, "Ink Transfer in the IBM 3800 Printer";
A.I. Ranka, "Fundamental Studies of the Effect of Particle Size and Particle Stability on Critical Pigment Volume Concentration in a Model Latex Coating";
E.D. Sudol, "Toward the Production of Large-Particle-Size Monodisperse Latexes"; and
C.M. Tseng, "Toward the Production of Large-Particle-Size-Monodisperse Latexes - Studies of Swelling and Polymerization Parameters".

Also, three of our graduate students finished their M.S. reports:

M. Agrawal, "Freezing of Coal";
N.J. Earhart, "Freezing of Coal"; and
A. Hadley, "Coating by Electrodeposition".

Copies of these theses abstracts are available upon request.

The most recently submitted and accepted journal articles are:

"Core-Shell Emulsion Copolymerization of Styrene and Acrylonitrile on Polystyrene Seed Particles", J. Polymer Sci. (submitted 1983).
"Mechanical Coagulation in Emulsion Polymerizations", J. Appl. Polymer Sci. (submitted 1983).

"Seeded Semi-Continuous Emulsion Copolymerization of 80:20 Vinyl Acetate-Butyl Acrylate", J. Dispersion Sci. Technol. (submitted 1983).

Manuscript copies are available upon request.

Our 15th Annual Short Course on "Advances in Emulsion Polymerization and Latex Technology" will be held at Lehigh on June 4-8, 1984 and at Davos, Switzerland on August 20-24, 1984.

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EMULSION COPOLYMERIZATION OF AZEOTROPIC STYRENE-ACRYLONITRILE MONOMER MIXTURE IN POLYSTYRENE SEED LATEXES

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ABSTRACT

The emulsion copolymerization of styrene-acrylonitrile mixtures is an important process in the preparation of ABS resins. This copolymerization system is complex: the swelling of the copolymer by the monomer mixture is limited and the acrylonitrile is much more soluble in water than styrene. To investigate this system, the azeotropic styrene-acrylonitrile monomer mixture was polymerized in 190nm- and 300nm-diameter polystyrene seed latexes by batch, batch-with-equilibrium-swelling, and semi-continuous polymerization.

The kinetics of the seeded batch copolymerizations, and the particle growth and morphology, depended upon the polymerization temperature. The final latex comprised two types of particles: the original seed particles grown to a larger size and the new crop of particles formed during the polymerization. The distribution of the second-stage copolymer between the two types of particles, the size and morphology of the particles, and the activation energies of polymerization showed a discontinuity at ca. 65°, indicative of a transition at this temperature. Moreover, the glass transition temperature T_g of the styrene-acrylonitrile copolymer swollen by the azeotropic monomer mixture was found to be 65° (Figure 1), which corresponds to the T_g of the monomer-swollen copolymer latex particles during polymerization. The higher chain mobility above T_g explained the increase in the degree of grafting of the polystyrene seed latex core and the enhanced flocculation of the oligomeric radicals and primary particles in the aqueous phase to give a larger particle size above 65°.

The distribution of the second-stage copolymer between the two types of particles, as well as the number of new particles initiated, depended upon the conversion; with increasing conversion, the total surface area of the particles reached the critical level at which all of the copolymer chains or primary particles formed in the aqueous phase are captured by existing particles and do not nucleate new particles. To confirm this critical surface area concept, a series of seeded copolymerizations was run in which the seed surface area was varied from 113 to 339 m²/dl at constant aqueous sodium dodecyl sulfate concentration, but different monomer-polymer ratios, according to the 190nm or 300nm particle size of the polystyrene seed latex.

The critical total surface area was found to be 260 m²/dl, but even at 226 m²/dl no new particles were formed, and at 170 m²/dl only a few were formed. For a seed surface area greater than the critical value, the number of particles was constant throughout the polymerization and the same as the initial number of seed particles. The initial polymerization rates were directly proportional to the number of seed particles (Figure 2). Thus the particle growth by flocculation can be controlled by adjusting the total initial surface area provided by the polystyrene seed latex particles, to give a homogeneous latex with only one type of particles, the seed particles grown to a larger size.

The particle morphology was characterized by measuring the proportion of the polystyrene seed grafted to the copolymer chains using thin-layer chromatography combined with flame ionization detection. For the same monomer-polymer ratio, the degree of grafting was higher for the smaller seed latex, indicating that it depends on the surface area of the seed particles available to capture the radicals growing in the aqueous phase. The proportion of polystyrene grafted to the copolymer chains increased exponentially with increasing seed surface area (Figure 3), confirming that the grafting reaction is surface-controlled and that the radicals generated in the aqueous phase are captured by the existing monomer-swollen particles. If this hypothesis is correct, the mode of monomer addition should affect the degree of grafting to the polystyrene seed particles. Semi-continuous polymerization should increase the probability of grafting-by-transfer because of the low monomer concentration in the particles; the frequency of capture of radicals from the aqueous phase by the latex particles is lower and so is the termination by combination, which should also increase the probability of grafting. For both the 190nm- and 300nm-diameter seed latexes, the degree of grafting was higher for the semi-continuous polymerizations than when the monomer was allowed to swell the particles for 24 hours before batch polymerization, which in turn was greater than for simple batch polymerization. The degree of grafting increased with decreasing monomer-polymer ratio in the seeded polymerization.

Compression-molded samples of these polymers were characterized by dynamic mechanical spectroscopy; the storage modulus (E'), loss modulus (E''), and the loss tangent (tanδ) were measured, and the T_g's of the samples were determined from the peak of the loss modulus spectrum.

Physical blends of incompatible polystyrene and styrene-acrylonitrile copolymers showed separate T_g's characteristic of the individual polymers (Figure 4), with peaks at 104° (polystyrene) and 120° (styrene-acrylonitrile copolymer), indicating a dual phase continuity. The degree of mixing is improved by increasing the compatibility of the copolymers so that the individual transitions broaden and merge into a single transition. The graft copolymer is a polymeric emulsifier which prevents the two incompatible polymers from separating. Thus 45%-grafted polystyrene (PS-AS-70) showed a single T_g of 112° in comparison with the single T_g of 114°

of the 18% grafted polystyrene (PS-AS-65); the greater the degree of grafting, the closer the single T_g approached that of polystyrene. However, the T_g for the sample with the smaller 190nm seed was 120°, the same as that of the styrene-acrylonitrile copolymer (PS-AS-16). The phase continuity of the individual components of a polymer blend affects its T_g ; the behavior is determined by the more continuous phase. Therefore, these polystyrene particle cores are probably discrete inclusions in a styrene-acrylonitrile copolymer matrix.

Decreasing the monomer-polymer ratio gave more pronounced differences between the smaller and larger seed particles. The 105° T_g of the polymer prepared with the 300nm seed (PS-AS-5) was close to that of polystyrene while the 119° T_g of the polymer prepared with the 190nm seed (PS-AS-19) was close to that of the styrene-acrylonitrile copolymer, indicating that the continuous phase in a polymer blend can be reversed by modifying the seed particle size.

The $\tan \delta$ values (Figure 6) confirmed that the sample prepared with the 190nm seed (PS-AS-5) had a continuous polystyrene phase. Generally, high $\tan \delta$ values over a wide temperature range indicate that the T_g of the inclusions is higher than that of the matrix. The samples with the smaller seed particles gave higher $\tan \delta$ values than those in which the continuous phase was the styrene-acrylonitrile copolymer.

The polystyrene seed preswollen with monomer before batch polymerization to increase the degree of grafting (PS-AS-21) gave a T_g of 112° as well as a small shoulder at 104°, indicating that the sample contained a small amount of ungrafted polystyrene. For the 190nm seed particles, decreasing the monomer-polymer ratio increased the degree of grafting and decreased the T_g to 114° (PS-AS-20). Thus dynamic mechanical spectroscopy characterized the morphology of the core-shell particles and demonstrated that small changes in the reaction parameters can affect the degree of grafting and the emulsification of the two incompatible polymer phases.

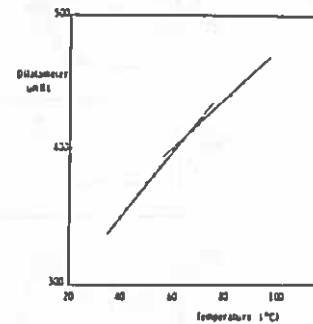


Figure 1. Volume-temperature variation for a styrene-acrylonitrile copolymer swollen by the monomers.

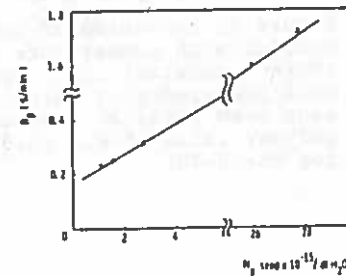


Figure 2. Variation of initial rate of polymerization with number of polystyrene seed latex particles.

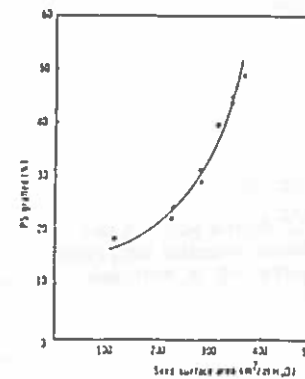


Figure 3. Variation of degree of grafting of the polystyrene seed particles on the total surface area: (x) 190nm; (o) 300nm.

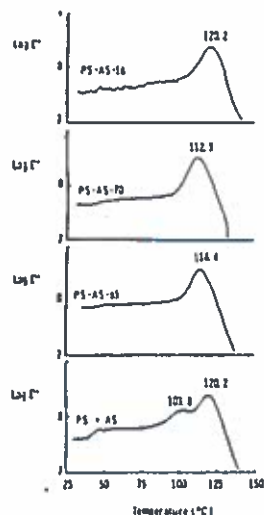


Figure 4. Variation of loss modulus with temperature for styrene-acrylonitrile copolymers prepared with polystyrene seed latex at a monomer-polymer ratio of 4.2.

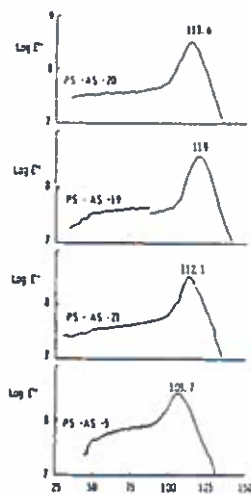


Figure 5. Variation of loss modulus with temperature for styrene-acrylonitrile copolymers prepared with polystyrene seed latex at a monomer-polymer ratio of 6.1 (0.95 for PS-AS-20).

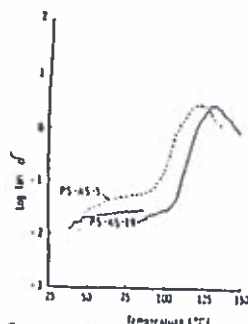


Figure 6. Variation of $\tan \delta$ with temperature for polystyrene-seeded styrene-acrylonitrile copolymers at a monomer-polymer ratio of 6.1.

Swelling of Carboxyl - Containing Copolymers
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In the study of alkali-swella- ble, carboxylated latexes a number of factors concerning the properties of the copolymer must be considered.¹⁻⁸ These factors include molecular weight, the hydrophobicity of the major monomer, the number (or weight fraction) of the carboxyl groups and the T_g of the copolymer. In terms of molecular weight, one must consider the effects of both branching and formation of crosslinked material. This factor in conjunction with the T_g will affect not only the degree of swelling, but also the rate of swelling by limiting the relaxation of the polymer chains. The distribution of the carboxyl groups within the particles will play a role in the swellability of the particles, especially for the case of higher amounts of carboxyls. Early work could only infer this theorem by substituting the more miscible (with the hydrophobic monomer) methacrylic acid (MAA) for acrylic acid (AA). Results by Bassett and coworkers¹⁰⁻¹² indicate that preparing a copolymer latex with a shell rich in carboxyls will give good swelling behavior. One note of caution is that unless care is taken in the preparation, phase separation and/or dissolution of the carboxyl rich layer can occur. In contrast, the work done at Lehigh attempts to prepare a uniform copolymer and subsequently determine the loci of the carboxyl groups in the latex particles.

A variety of experimental techniques are used to determine the degree of swelling of the latex particles. The copolymer latexes are prepared by both a batch and a semicontinuous method where the latter permits monomer(s) to be added into a "starved" system such that the copolymer composition will imitate the comonomer feed ratio. In order to characterize the prepared latex, it must be cleaned of the water-soluble components. The method used is called serum replacement whereby the latex is washed with distilled water in a stirred cell with a submicron membrane filter. This permits construction of a mass balance of the carboxyl groups in the latex system once the serum has been titrated. To determine the loci of the carboxyl groups in the latex particle, a modified conductometric titration is used where an excess of NaOH is added and the conductance vs. time is measured. Back titration and use of the mass balance permits the loci of the carboxyl groups to be assigned to a given region of the latex particle. This method assumes that the time of neutralization of a carboxyl group is a function of the depth because there is a time dependent diffusion rate of the hydroxyl groups into the latex particle.

Once the latex has been cleaned, swelling as a function of pH is determined by different methods. The most obvious method is to measure particle size using the light scattering dissymmetry technique. This experimental method is only useful when the particle size distribution is narrow. For the case of a broad particle size distribution, Transmission Electron Microscopy (TEM) with negative imaging have been of use. However, these particle size measurements must be complemented by a similar series of viscosity measurements in order to determine if the particles are swelling or dissolving. The instrument used for the viscosity experiments is a cone and plate Weissenberg Rheogoniometer, at a constant shear rate. By necessity, the shear rate must be kept low and constant

Contribution to the Polymer Colloid Group

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[19 MAR Recd

The following are abstracts of papers submitted for publication.

Hydrodynamic two-sphere interactions at a wall. (K. Malysa, T. Dabros and T.G.M. van de Ven)

Experimental results are reported on hydrodynamic interactions between a solid plate with a spherical particle attached to it and a rigid sphere moving parallel to the plate. Trajectories and velocities of the moving sphere were determined by taking single frame multiple image photographs using stroboscopic light.

Sphere-sphere hydrodynamic interactions were detectable on the background of plate-sphere interactions for initial dimensionless sphere-wall separations $Z_0 < 4.9$. The sphere trajectories were found to be symmetrical for $Z_0 \geq 2.3$ and asymmetrical otherwise. For asymmetrical trajectories the sphere mobility was larger after the encounter than prior to it. It was concluded that surface roughness of the spheres was responsible for the observed deviations from symmetry.

Theoretical models discussed in the paper were in good agreement with the experimental data for dimensionless distances between sphere centers $r > 2.5$. For $r < 2.5$ results computed by the singularity method were in fair agreement with the data when $Z_0 \geq 2.9$. For smaller Z_0 , theoretical predictions were inaccurate.

Electro-viscoelastic properties of dilute suspensions. (T.G.M. van de Ven)

Suspensions of non-spherical particles can mimic viscoelastic behavior when subjected to an electric field. When a steady shear is superimposed upon an oscillatory shear, different modes of viscoelastic behavior are predicted depending on whether the applied electric field is subcritical or supercritical. For supercritical fields all particles oscillate about a steady state orientation and the system exhibits time independent linear viscoelasticity. For subcritical fields all particles execute complete rotations about their vorticity axis and, except for certain frequencies, the viscoelastic response is in general time dependent. It is predicted that both the intrinsic dynamic viscosity and the dynamic rigidity can attain negative values, depending on particle shape and on the ratio of electric to hydrodynamic torques.

Relaxation phenomena in suspensions of anisometric Brownian particles. (D.S. Jayasuriya and T.G.M. van de Ven)

A general method is presented which in principle can be used to treat theoretically the relaxation of any property of a suspension

that can be expressed in terms of the orientation distribution of the suspended anisometric particles. This method has been applied to various physical properties to obtain expressions relating the relaxation to rotary diffusion coefficients of spheroidal and ellipsoidal particles. Some aspects of the theory are tested by rheo-optical measurements and are found to be in good agreement with the theory.

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in order to prevent deformation of the swelled layer of this non-Newtonian system. The use of these two approaches permits good characterization of the swelling behavior.

Using the above experimental techniques, Nishida⁷ examined methylmethacrylate (MMA) with varying amounts (5 - 25 wt%) of methacrylic acid (MAA). This system is fairly hydrophilic and has a high T_g . At low concentrations (5 & 10 wt%) of MAA, there was little swelling, but a considerable amount of flocculation at higher pH's. Higher concentrations (15 - 25 wt%) of MAA showed very different results between the batch and semicontinuous latexes. For the batch latexes a gradual increase in viscosity and particle size was observed, which indicates the particles are swelling uniformly without dissolution. In contrast, the semicontinuous latexes showed sharp increases in viscosity while the particle size remained constant or even decreased with increasing pH. These results indicate that the particle is dissolving layer by layer instead of swelling. From these results one can infer that batch latexes consist of particles with a core poor in MAA that prevent dissolution while the semicontinuous latexes have an even distribution of MAA which allows the particles to dissolve.

Similar experiments were subsequently carried out replacing MMA with styrene (ST) and varying the MAA content from 5 to 50 wt%. This system increases the hydrophobicity greatly of the base monomer (ST) while keeping the T_g approximately the same. The results show that there is a considerable fraction of the MAA neutralized in the surface region, but very little swelling occurs which results in a large unneutralized core. Only for a few of the high MAA content (40 & 50 wt%) latexes was any viscosity increase seen, but since the samples remained milky, only a small amount of the particles were probably dissolving. Thus, increasing the hydrophobicity for a high T_g copolymer apparently restricts the swelling behavior.

To determine the effect of T_g on the swelling process, 2-ethylhexylacrylate (EHA) replaced styrene.⁸ These two monomers have similar water solubilities, which indicates that both should be similarly hydrophobic. The T_g changes from approximately 100°C for the ST/MAA copolymer system to below 0°C for the EHA/MAA copolymer system. Thus, the copolymer chains should be more flexible which in turn should accommodate diffusing hydroxyl groups for swelling. However, results to date seem to imply that the flexible chains permit a great number of the carboxyl groups to be shifted to the surface region. The results from the conductometric titrations show a similar lack of swelling as the styrene-based systems. Further problems have been encountered in cleaning the soft EHA-based latexes and measuring particle size changes because of the extremely broad particle size distribution. The lack of swelling may also be due in part to the self-crosslinking reaction of the EHA during the polymerization.

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V.I.Eliseeva, S.V.Bogdanova

Aggregatively stable latexes are known to be produced from emulsion polymerization without an emulsifier, if persulfates are used as initiators. The mechanism of particle formation in such polymerization has been investigated elsewhere /1,2/. Ion-radicals $M \cdot M_n SO_4^-$ are supposed to be formed when monomer dissolved in water is initiated by persulfate. These radicals, after the attainment of critical degree of polymerization, precipitate from the solution and form primary particles which flocculate to a charge density needed for stability. This process is known as homogeneous nucleation. While investigating methyl methacrylate (MMA) polymerization in highly diluted solutions /2/, the authors found that the rate of particle formation in such systems (dN/dt) is equal to the initiation rate (R_{in}) minus the radical capture rate (R_c) and the rate of flocculation of primary particles (R_f), $dN/dt = R_{in} - R_c - R_f$.

The radical recombination in water solution yielding oligomer products, like $SO_4^- M_n + m SO_4^- (OH)_1$, with surface-active properties, has not been taken into account in /2/. It has also been neglected in /3/, where the rate of particle formation during water-phase polymerization of a monomer, like styrol, with low solubility in water, was calculated. But when "own" surfactants are formed in a system, one should, obviously, take into account their effect on the rate and mechanism of particle formation.

To ascertain the formation, and to determine the properties of "own" surfactants in emulsion-free MMA polymerization, we made the following experiments. MMA in water phase was polymerized in argon current using the following mixture (part by weight): MMA - 5, ammonium persulfate - 0.05, water - 95, temperature 253°K, and duration 6 hours. The produced latex had the following properties: concentration of dry substances - 4.7%, diameter of particles - 175 nm (light scattering), surface tension - 60.5 mJ/m². Latex was dried at room temperature to constant weight. Using the Allen method, we have determined the sol-fraction in water at room temperature in a dry polymer. The content of sol-fraction was 1.4% of the total polymer weight; surface tension of 1.4% of sol-fraction solution in water was 51.5 mJ/m². Figure shows an isotherm of a sol-fraction surface tension in semilog coordinates. The isotherm shows a similarity between investigated water-soluble oligomers and low-molecular micelle-forming surfactants.

Thus, the performed experiments show that the emulsion-free MMA polymerization with persulfate initiation yields in latex water-soluble polymers with rather high surface activity. These products, being formed as a result of oligomer radical recombination in water phase, can be considered as highly molecular analogs of low-molecular micelle-forming surfactants. Their presence should, apparently, be taken into account in calculating the number of particles and in studying the mechanism of their formation in latex system.

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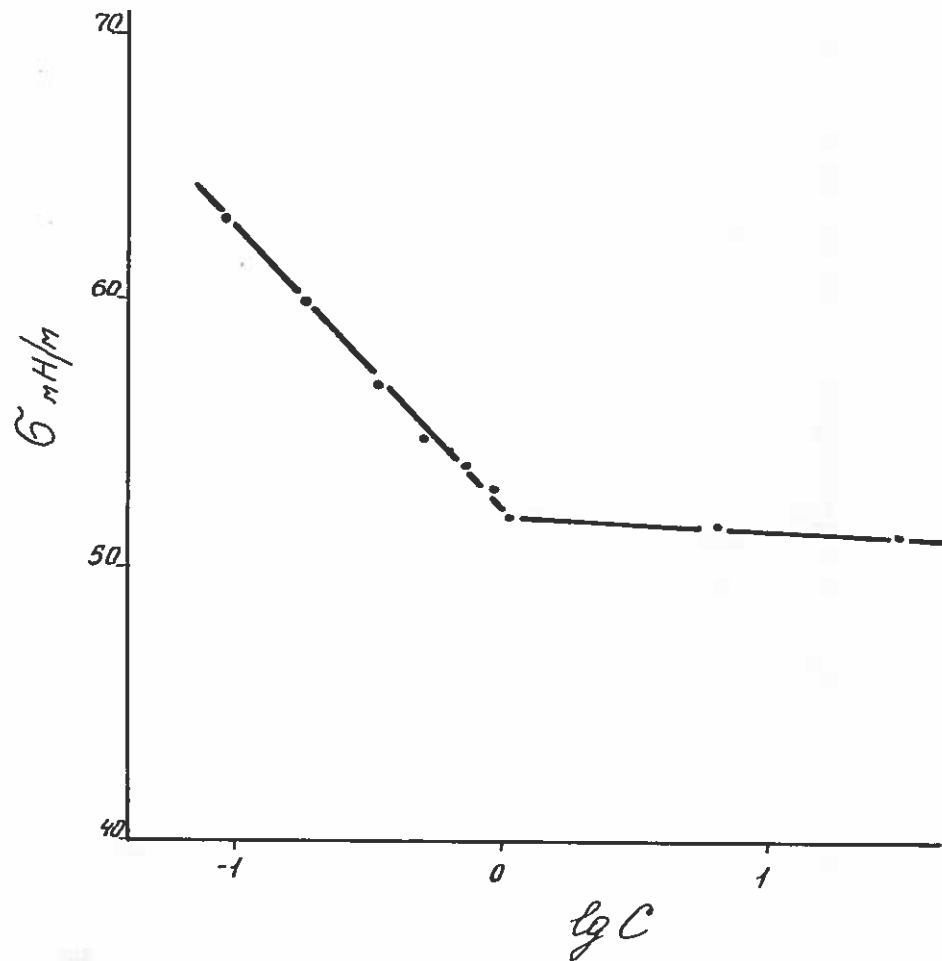


Fig. Isotherm of surface tension of MMA-latex sol-fraction.
C - concentration of sol-fraction in percent.
 $\bar{\sigma}$ - surface tension in mN per meter.