formed by decomposition of $MnC_2O_4^+$, on chlorine to form atomic chlorine, and the oxidation of manganous ion to Mn(III) by atomic chlorine.

The catalyst undergoes net reduction by reaction with the reducing intermediate; the re-

ducing intermediate reacts also with ferric ion. The specific rates of reaction of the reducing intermediate with chlorine, Mn_{Cl}^{+++}, $MnC_2O_4^+$, Fe(III) and $Mn(C_2O_4)_2^-$ decrease in that order.

A General Theory of the Mechanism of Emulsion Polymerization[1]

BY WILLIAM D. HARKINS

I. Early Development

The general theory of the mechanism of emulsion polymerization presented here had its origin in ideas developed while the writer was a consultant for the Research Laboratory of the United States Rubber Company at Passaic, New Jersey, and later in work begun on December 15, 1942, for the Rubber Director's Office. In the beginning the consideration of this problem was undertaken at the suggestion of E. Hazell, manager of the Passaic Laboratory, who pointed out that at that time nothing was known as to the loci in which emulsion polymerization occurs. The general features of the theory were presented in a report of the writer (March 20, 1943). In this report data were presented on the increase of polymer particle size with increase in the yield of polymer. It was pointed out that these data were obtained by a soap titration method developed by H. F. Jordan (in 1931) for the determination of the area of carbon blacks.

At the suggestion of Dr. Jordan, this method had been applied by R. H. Ewart and L. M. White[1a] to the determination of particle size in GR-S latex.

The following statements were reported: (1) agreement between soap titration and ultracentrifugal measurements made at the University of Wisconsin; (2) increasing the soap concentration or temperature of polymerization decreases the particle size; (3) increasing the yield increases the particle size; (4) increasing the OEI has very little effect on the size.

By an application of the soap titration method it was found that soap disappears rapidly from the latex as the yield of polymer increases. These facts suggested to the writer that an early locus of polymerization is in the soap micelles and that this is shifted to the polymer particles as the yield increases. One of the reports issued by United States Rubber in March, 1942, showed that styrene vapor, when passed into water which contains potassium persulfate, polymerizes readily.

This shows that soap is not essential if only a very slow polymerization is desired.

Extensive evidence for the theory has been obtained by M. L. Corrin, R. W. Mattoon and R. S. Stearns, who have continued their work since early in 1943, with Stearns and Corrin engaged in the physico-chemical aspects of the problem and Mattoon engaged in the X-ray work. The other co-workers are cited later in connection with their specific researches; Reynolds and his co-workers at the University of Cincinnati were associated with the writer in the early development of the project and did valuable work at that time, especially on solubilization, rate of polymerization, and the effects of salts. Simultaneously and even earlier, work on solubilization was carried out by Professor McBain at Stanford University.

One of the topics investigated in the earliest work at the University of Chicago was the effects of "seeding" or inoculation of a latex with latex formed in another system. It was found that the induction period, often four hours in length, caused by atmospheric oxygen in the polymerization of styrene, could be reduced or removed by the initial addition of latex in which some degree of polymerization had already been attained. This was suggested to McBain as a profitable subject for investigation and he, after the completion of experimental work in this field, considered it to give evidence in favor of the general theory of the writer. Whereas a modification of the "seeding" technique may be made to give powerful evidence for the theory, ordinary seeding itself, as practiced in the early work, seems to speak neither for nor against the theory.

Much encouragement in the researches carried out by the writer and his associates was given by W. A. Gibbons, of the United States Rubber Company, and by the chiefs of the Polymer Research Branch of the Rubber Director's Office and the Rubber Reserve Company: R. R. Williams, Calvin Fuller, R. F. Dunbrook and W. A. Borders.

Although the ideas presented in the paper are believed to be those of the author, he would like to point out that, during the past four years, he has attended numerous research discussion meet-

ings, sponsored by the Office of Rubber Reserve, in which problems related to polymerization locus theory were discussed at great length. Certain ideas expressed by others in those meetings may have been helpful in suggesting means for obtaining evidence for the theory and the author is pleased to acknowledge any such help. Wherever ·possible in the text, he has made specific reference to the pertinent suggestions of others. The present paper gives merely a bare outline of the general theory with a presentation of some of the pertinent evidence for it. The more extensive evidence will be presented later in supplementary papers by the various collaborators and the writer.

II.　Earlier Theories

At the time this theory was developed two earlier theories, neither of which was correct, were favored by different workers in the field of emulsion polymerization. These were:

A.　The older theory which assumed that the monomer emulsion droplet itself polymerizes. This theory disregarded the fact that the emulsion droplet commonly has initially a volume more than a thousand times, often more than a million times, that of the polymer particle.

B.　Theory of Fikentscher[2]: the locus of the reaction is the aqueous phase. Unfortunately Fikentscher did not specify what he considered as the aqueous phase.

In the present paper the aqueous phase is considered to be limited to the aqueous true solution, excluding oil emulsion droplets, polymer latex particles, and soap micelles. If this is what is considered by Fikentscher as the aqueous phase, then his theory is incorrect, while if his "aqueous phase" includes the polymer and soap micelles then the theory does not specify the locus.

III.　Outline of the Theory

The principal function of the monomer emulsion droplets, according to the theory of the writer, is not, as in the older theory, to be a locus of polymerization, but to act as a storehouse of monomer from which its molecules diffuse into the aqueous phase and from this into either soap micelles or polymer–monomer latex particles.

The two principal loci of polymerization are (Fig. 1): (1) Principal locus for the initiation of polymer particle nuclei: the extremely small amount of solubilized oil (monomers) which in a soap micelle is surrounded on all sides by a monolayer of soap molecules with their hydrocarbon groups toward the oil and their ionic-polar groups (as $-COO^-K^+$) toward the water outside. (2) Principal locus for formation of polymer: the polymer particle itself. Nearly all of the polymer particle nuclei are formed by polymerization of the monomer or monomers in the oil cores inside soap micelles (Locus 1). The polymer molecules grow larger than the micellar cores and appear in-
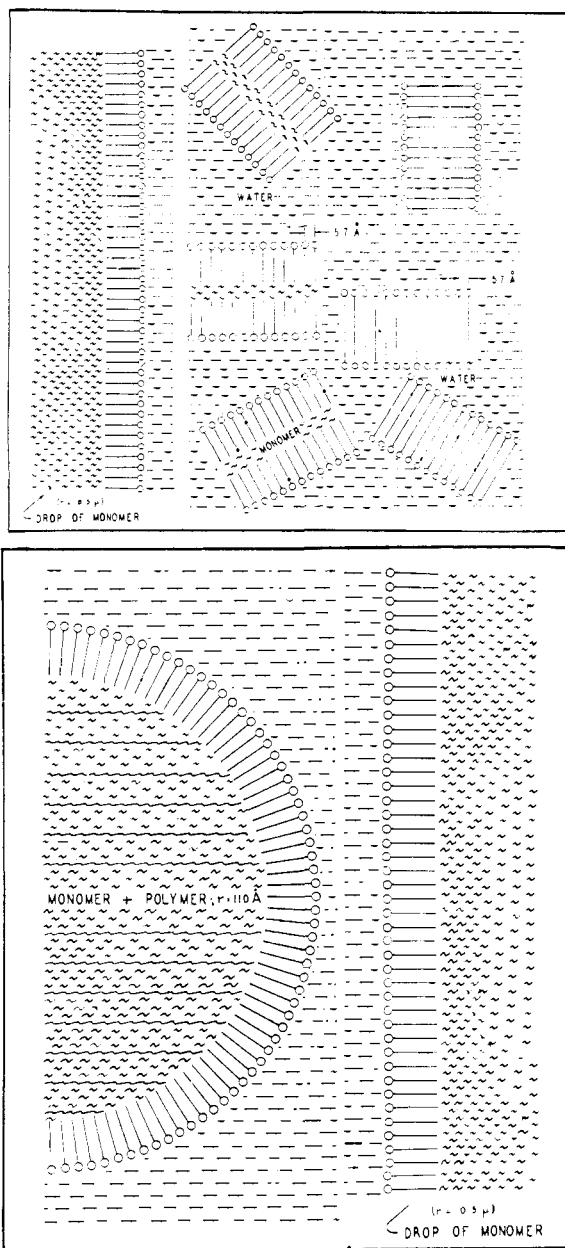
(2) H. Fikentscher. Angew. Chem., 51, 433 (1938).

Fig. 1.—Highly idealized representation of the diffusion from a monomer droplet through a monolayer of soap into (a) micelles, and (b) into a polymer–monomer droplet. All of the monolayers of soap and also the soap in the micelles exhibit the structure of a liquid with its irregularity and "holes," whereas the drawing, for the sake of simplicity shows a regular structure. The micelles which contain monomer should be shown as containing many more soap molecules than the others.

side the aqueous phase as excessively small polymer particle nuclei. These capture monomer molecules from the aqueous phase and 'are thus polymer–monomer particles in which monomer polymerizes while more monomer is being captured. There is also a minor locus in which poly-

mer particle nuclei are initiated. This is: (3) The aqueous phase: *i. e.*, water which usually contains very small amounts of catalyst, dissolved monomer, ionic non-micellar soap, and often mercaptan. This locus is responsible for the formation of practically all of the polymer particle *nuclei* when no soap is present, but becomes much less prominent than (1) when micellar soap is present, losing relative importance as the amount of soap increases. (4) A very minor locus is the emulsion droplet.

IV. The Emulsion

Upon agitation, a two-phase system of aqueous soap solution and an oil usually forms an oil in water emulsion. The droplets exhibit a distribution in size such as that shown in Fig. 2, in which the y-axis gives the percentage of the number of particles within a given range of drop diameters and the x-axis gives the area. The position of the peak of this curve is dependent upon the type of agitation, the concentration and nature of the soap, the temperature and the viscosity of the oil. With 0.1 N soap, about the concentration commonly used in emulsion polymerization, the peak for diameters with benzene and similar oils often lies in the region from 0.5 to 1.0 micron.[2a,3,4]
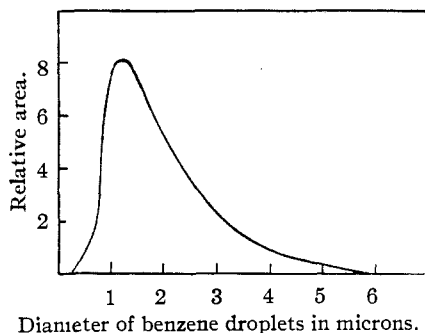

Fig. 2.—Distribution of area with diameters; emulsions of benzene in a 0.1 N solution of sodium oleate.

The distribution curve for butadiene has not been determined, but the viscosity of the liquid is so small that the peak should be found at a relatively small diameter.

In the presence of 0.1 molar soap each emulsion droplet and also each polymer–monomer particle formed is surrounded by a liquid, but moderately tightly packed, monomolecular layer of soap molecules oriented with their hydrocarbon chains toward the oil and their ionic-polar groups toward the water. On account of the slight repulsion between these ionic polar groups the average area occupied per molecule of soap is greater than that for a liquid condensed film of stearic acid, in which

(2a) W. D. Harkins and Norvil Beeman, THIS JOURNAL, **51**, 1674 (1929).

(3) E. K. Fischer and W. D. Harkins, *J. Chem. Phys.*, **36**, 98 (1932).

(4) W. D. Harkins, Colloid Symposium Monograph, Vol. V, 1927, pp. 19–48.

at 20° the area is 24 sq. Å. at low pressure (π) and about 20 sq. Å. at the highest pressure at which this phase of the film exists.[5] This area decreases slightly with increase in the length of the hydrocarbon chain. At the present time the area per soap molecule in the monolayer around an emulsion droplet in 0.1 N soap seems from preliminary evidence obtained in this laboratory by Corrin to be about 24 sq. Å. This problem is at present under further investigation.

It is shown in Section XI that, as the polymerization process proceeds, soap disappears from the aqueous phase so rapidly that, beginning with 0.1 molar soap, practically all micellar soap has usually disappeared by the time the yield of polymer has reached 13 to 20%. As a consequence of this disappearance of soap, the area per soap molecule around each emulsion droplet increases at first very slowly and later more rapidly, as the reaction proceeds. It has been shown in this Laboratory that this results in a reduction in the stability of the emulsion and an increase in particle size, especially if the agitation is not very vigorous.

An increase in particle size gives a reduction of the total area of the surface of the monomer droplets through which monomer molecules diffuse into the aqueous phase.

V. Diffusion of Monomer Molecules into the Aqueous Phase and their Capture by Soap Molecules and by Polymer–Monomer Particles

An important step in the polymerization process is the transfer of monomer molecules from emulsion droplets in which little polymerization takes place into the aqueous phase in which some polymer particle nuclei are initiated, and from this into soap micelles in which most of the nuclei are initiated, and to a much greater extent into polymer particles.

Of great importance to the polymerization process is the thickness of the diffusion layer around each monomer droplet. If extremely thin (ca. 50 Å.), as one investigation indicated, the layer would not extend over the diameter of a single polymer particle or a single soap micelle. The method used is very simple, as outlined by Vinograd, Fong and Sawyer.[6] They obtained a linear relation between time and the diameter of an oil droplet suspended in a soap solution.

In this Laboratory Stearns found the very different relation (Fig. 3) that the rate of decrease in the diameter of a drop of ethylbenzene in 12.2% potassium laurate solution at 40° was changed from −0.0026 to −0.0043 mm. per minute by a decrease in diameter from 1.4 to 0.25 mm. with a rate twice as high at 40° as at 25°.

In a private communication to the writer,

(5) G. C. Nutting and W. D. Harkins, THIS JOURNAL, **61**, 1183 (1939).

(6) Meeting of the American Chemical Society, September 11–15, 1944.

Professor P. Debye has developed a theory for the diffusion from the surface of an oil drop into a soap solution. From one of our curves, similar to that of Fig. 3, but for a 10.6% solution of potassium laurate, Debye calculated the thickness of the diffusion layer to be of the general order of 0.06 mm. or 6×10^5 Å. While manifestly this cannot be at all exact, due to the fact that a small change of curvature gives a relatively large change in the thickness, the result is very important in connection with the polymerization in indicating a thick layer in which many micelles and also many polymer particles can capture monomer molecules.

Experiments on the diffusion of an oil into polymer and into polymer–monomer suspensions (latex) are much more difficult but indicate diffusion rates of the same general order of magnitude, but slower than with soap. Since very many times more monomer is, in the whole process, captured by polymer–monomer particles than by soap micelles, this process is of great importance. A problem closely related to this is the change in value of the monomer–polymer ratio as a function of the yield of polymer. If the rate of polymerization in the particle exceeds the rate at which monomer enters it, then the monomer-polymer ratio (M/P) must decrease, as it is found to do in the case of styrene–polystyrene.

In this connection it is of interest to note that the rate of diffusion was found to be twice as high $(2 \times 10^{-3}$ mm. decrease per minute) into a latex which already contained 33% of monomer (67% yield) as that (1×10^{-3}) into a latex which contained only 2% of monomer (98% yield). Presumably, the polymer network is less stiff at the lower yield.

VI. The Monomer–Polymer Ratio

The fact that, in general, more than 99% of all of the polymer produced in emulsion polymerization is formed by the reaction of monomer while inclosed in a network of polymer gives a considerable importance to the ratio of monomer to polymer (M/P). When the initial solution is about 0.1 molar with respect to soap and 100 g. of monomers is used per 180 g. of water, it is found that when the yield of polymer has reached a value of 60% (sometimes less than this) diffusion has carried all of the monomer into the polymer. As a result, the monomer–polymer ratio in the particle at a 60% yield is 40/60 or 2/3. At any higher yield (y) the ratio has the value, $(100 - y)/y$, so at a yield of 80% it has fallen to 0.25.

It is important to know the value of this ratio in the particles while some free monomer remains in the aqueous phase.

It seems obvious, since M/P is determined by the rate of diffusion of monomer into and through the water and from this into the monomer-polymer particle and by the rate of polymerization inside this particle, that M/P should vary
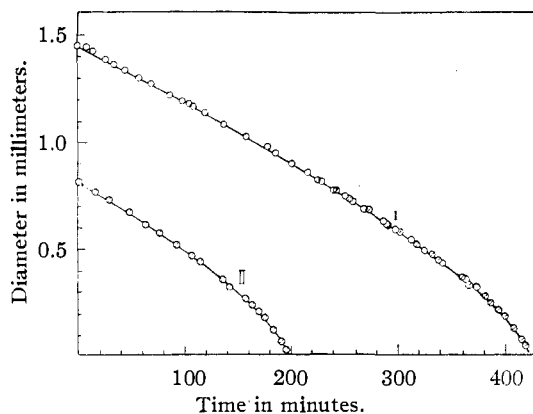

Fig. 3.—Diffusion from droplets (I) of ethylbenzene of diameters 1.45 mm. and 0.81 mm. into a 12.2% solution of potassium laurate at 40°; (II), imposed on Curve I by adding 226 mm. to the time axis in order to exhibit the agreement between the two experiments (Stearns).

greatly as various factors are changed. For example, abnormally low values of M/P were obtained in cases in which the polymerization was abnormally slow. A single curve can be obtained only when the conditions are not varied. Important factors are both the size and the shape of the molecules and their solubility in the polymer. The concentration and nature of the soap play a role, especially since the micelles compete with the polymer in trapping the monomer. Butadiene has a much smaller molecule than styrene, so its diffusion is much more rapid.

Figures 4a and b represent values of the M/P ratio obtained by Stearns, and by Corrin and Miss Roginsky for styrene as the yield of polymer increases. The ratio is highest at low yields and falls as the yield increases. The ratio at any yield, y, is given by

$$M/P = [100 - (y + d + m)]/y \qquad (1)$$

in which d is the percentage of the initial monomer present in emulsion droplets and m that in micelles. Above about a 13 to 17% yield the value of m is zero. The yield of polymer at which all free monomer disappears was determined by experiment in which the latex was centrifuged to throw out the emulsion droplets. In each case there is a yield of polymer above which no monomer can be centrifuged out, even at 25,000 g. If the mutual formula is used, this yield usually lies between 50 and 60%, so d becomes zero. Above this, no monomer droplets remain in the latex. It seems evident that below this the rate of diffusion into the particle is somewhat less than the rate of polymerization inside it.

VII. Structure of the Soap Micelle

The soap micelle plays a most important role in emulsion polymerization, since it dissolves monomers, which polymerize while inside it, and because the quantity of micellar soap determines
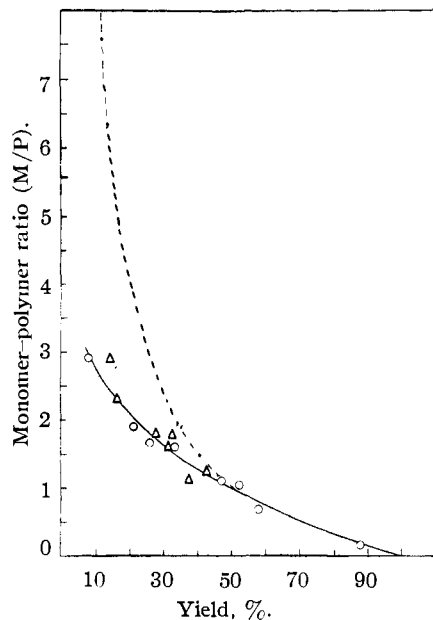
Fig. 4a.—Monomer-polymer ratio with styrene by a spectrophotometric method (Stearns). The dotted line gives the ratio if all the monomer were in the polymer.
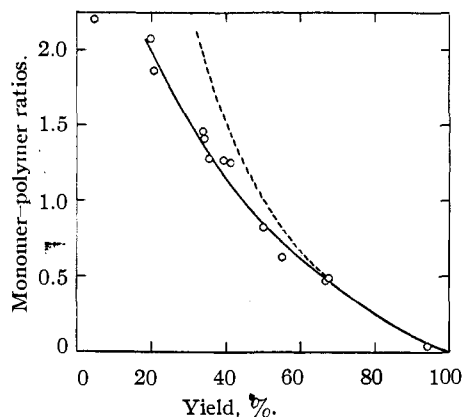

Fig. 4b.—Monomer–polymer ratio for styrene by a gravimetric method (Corrin and Roginsky).

the number of polymer particles formed and, thereby, the rate of the polymerization reaction and the size of the polymer particles, even long after all of the micelles have disappeared.

Reychler,[7] McBain,[8] and Hartley[9] have all assumed that not too dilute soap solutions contain spherical micelles, but McBain,[10] in addition, advanced the idea that large lamellar micelles also exist. The first evidence which seemed to support the idea of the existence of these lamellar

(7) A. Reychler, Kolloid.-Z., 12, 277 (1913); Bull. soc. chim. Belg., 27, 213, 300 (1913).

(8) J. W. McBain and T. R. Bolam, J. Chem. Soc., 113, 825 (1918); J. W. McBain, Trans. Faraday Soc., 9, 99 (1913).

(9) G. S. Hartley, "Aqueous Solution of Long Chain Salts," Hermann et Cie, Paris, 1936, p. 🔳.

(10) See review by McBain in "Advances in Colloid Science," Interscience Publishers, Inc., New York, N. Y., 1942, p. 124.
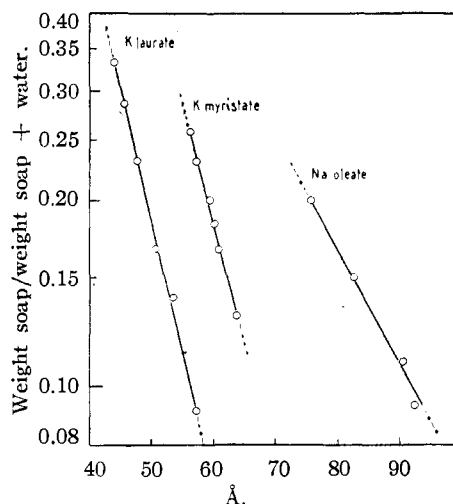
Fig. 5.—Logarithmic plot for the distance between micelles in aqueous solutions of potassium laurate, potassium myristate, and sodium oleate (Mattoon).

"Grossmizellen" was that obtained by X-ray measurements.[11]

In the second[12b] of two papers, Harkins, Mattoon and Corrin[12] depart from this point of view. Plate I represents photographs by Mattoon which show broad lines which represent the d_1 band, which gives the distance (d_1) between the double layers of soap micelles in the micellar solution. The value of d_1 (Fig. 5) is given by the relation·

$$d_1 = 2l + k \log (1/c)$$

which for this photographic film is 58.5 Å. In this equation, l is not very different from the length of the soap molecule, and c is the concentration of soap. When the soap solution $(c = 25\%)$ was saturated with styrene, d_1 increased to 74.4 Å., which gives an increase of spacing Δd_1 of 15.9 Å. This had been considered by the German investigators and McBain as the thickness of the layer of oil. However, in this paper,[12b] Harkins, Mattoon and Corrin introduced a new thickness, τ, as the mean thickness of the oil layer. This was obtained by dividing V, the total volume of the oil dissolved in the double layers, by Σ, the total area of the layer. Σ was taken as half the number of molecules of soap $(N/2)$ multiplied by the area (σ) occupied per double molecule, which from X-ray evidence may be taken as 28 sq. Å. Thus

$$\Sigma = 28 \times 10^{-16} N/2 \text{ sq. cm.}$$

(11) (a) K. Hess and J. Gunderman, Ber., 70, 1800 (1937); (b) W. Philippoff and K. Hess, ibid., 70, 1808 (1937); K. Hess, H. Kiessig and W. Philippoff, Naturwissenschaften, 26, 184 (1938); K. Hess, W. Philippoff and H. Kiessig, Kolloid.-Z., 88, 40 (1939); (c) J. Stauff, ibid., 89, 224 (1939); (d) J. Stauff, Naturwissenschaften, 27, 213 (1939); (e) H. Kiessig and W. Philippoff, ibid., 27, 593 (1939); (f) H. Kiessig, Kolloid-Z., 96, 252 (1941); W. Philippoff, ibid., 96, 255 (1941); H. Kiessig, ibid., 98, 213 (1942); K. Hess, Fette u. Seifen, 49, 81 (1942).

(12) (a) W. D. Harkins, R. W. Mattoon and M. L. Corrin, THIS JOURNAL, 68, 220 (1946); (b) J. Colloid Sci., 1, 105 (1946).

and

$$\tau = V/\Sigma$$

Now, both τ and Δd_1 are very nearly proportional to the amount of oil dissolved (solubilized) by the micelles.

The very interesting fact which emerged from this work is that $\tau/\Delta d$ exhibited values which in 25% potassium laurate solutions at 25° increased only from 0.42 to 0.43 for n-heptane and from 0.39 to 0.41 for triptane, in both cases over a very large increase of the amount of oil solubilized. Also, in a 15% solution of ethylbenzene the value of the ratio was found to be 0.43. Thus, the ratio is essentially constant for these three oils, even when the soap concentration is varied over a wide range. This seemed to indicate either

1 Δd_1 is not, as had been commonly assumed, a measure of the thickness of the oil layer; or

2 the structure of the micelle is very different from that commonly assumed.

A consideration of these possibilities led the writer to ask Professor Debye to consider if the X-ray evidence is compatible with the idea that the double layer of soap molecules is itself the micelle. He developed equations for the attraction and repulsion between the double layers and found them to be equal, as represented below. Let p_0 be the hydrostatic pressure midway between the layers, then Debye finds that there is for 1 sq. cm. an excess pressure

$$+ \frac{D}{8\pi} \left(\frac{d\Phi}{dx} \right)^2$$

and an electric force

$$- \frac{D}{8\pi} \left(\frac{d\Phi}{dx} \right)^2$$

which exactly compensate each other. Here, the coördinate perpendicular to the layers is x, and $x = 0$, midway between them. D is the dielectric constant, and Φ the potential.

If each double layer is a micelle, the relations in emulsion polymerization become much more simple, as indicated below.

A new X-ray diffraction band has been discovered by R. W. Mattoon, R. S. Stearns, and W. D. Harkins,[12c] which gives the thickness, d_2, of a double layer of soap. This is found to be essentially equal to double length of the molecule of the particular soap involved, $i. e.$, 36.6 Å. for the eight carbon atom soap and 49.6 for the 14 carbon atom soap. On solubilization of an oil, this thickness is increased by from 7 to 12 Å. being dependent upon the solubility of the oil, as, for example, 10 Å. for heptane and 12 to 13 Å. for benzene.

The picture now becomes that of a small micelle ($ca.$ 20 to 300 soap molecules) which consists of a double layer of soap whose thickness can be measured by X-rays even at soap concentrations as low as 2.5%. However, the distance between the micelles which is determined by the distance d_1

(12c) R. W. Mattoon, R. S. Stearns, and W. D. Harkins, $J.$ $Chem.$ $Physics$, **15**, 209 (1947).

cannot, in general, be found below 9% of potassium laurate (7% with myristate), since the corresponding band does not appear until the concentration reaches this value. However, if an oil is dissolved, this band may become visible down to 7.5% of laurate, since the number of soap molecules in a micelle is increased by solubilized oil (doubled in some instances). Presumably, below concentrations of this order the micelles, each of which consists of a single double layer of soap, are subject to a violent Brownian vibration and rotation so that X-rays do not exhibit any d_1 band below this concentration.

These and other interesting features of the theory and observations will be presented in a later paper by Stearns, Mattoon and the writer, so they are not considered further here, except to point out that the d_1 band does not appear until the soap solution has attained a concentration of 7 to 10% of soap, even though the previously unobserved d_2 band appears at a concentration of 2%, or possibly less.

Several conferences with Debye have been held, and the point of view has developed that there is little restriction of motion of the micelles until the soap attains a concentration of about 7 to 10%. The new point of view is of importance, since in solutions 0.1 N (3%) with respect to soap, even if saturated with monomers, the micelles occupy only about 0.04 of the volume, with 0.96 of the solution free for diffusion of monomer molecules from the emulsion droplets. The Brownian motion keeps the micelles in rotation as well as oscillation and at this concentration prevents them from lining up. Not until the soap concentration becomes several times larger (about 8% soap) do the micelles have their rotation restricted sufficiently to cause them to give a sufficiently localized intensity in the d_1 band to give the distance between the micelles (double layers of soap). Since 3% is the usual initial concentration commonly used in emulsion polymerization, diffusion is much more free than if the lamellar model were valid.

VIII. Critical Concentration for Micelle Formation

Since nearly all of the polymer particle nuclei are formed in soap micelles, it is of fundamental importance to understand the relations involved in their formation. Even though both of the following phenomena are dependent upon the decrease of free energy involved in removing the interface between hydrocarbon chains and water: the adsorption of a monolayer of polar–non-polar molecules at the surface of water, or the interface between oil and water, is gradual, the onset of micelles is sudden. When the hydrocarbon chains come into contact, this free energy mostly disappears. There is a smaller increase of free energy involved in bringing together the polar groups and especially the ions of like sign.

TABLE I

CRITICAL CONCENTRATION FOR MICELLE FORMATION IN SOLUTIONS OF PURE DETERGENTS (EQUIVALENTS PER LITER)

	No. of C atoms (n)	Detergent	Critical concn. $t = 25.8°$	Factor R_m for $\Delta n = 2$
		Anionic detergents		
Corrin	14	K myristate	0.006	4.0
	12	K laurate	.024	4.0
	10	K caprate	.095	3.7
	8	K caprylate	.035[a]	
	16	Na cetyl sulfate (35.8°)	.0004	4.0
	12	Na dodecyl sulfate	.0065	

Na alkyl sulfonates

	(n)	Detergent	Critical concn. 40°		R_m	60°	R_m	80°	R_m
Wright, Abbott, Sivertz and Tartar[b]	10	Decyl	22.6° = 0.040	0.0400	3.6	0.0430	3.58	0.0580	4.14
	12	Dodecyl	31.5° = .0098	.0110	4.4	.0120	3.64	.0140	3.04
	14	Tetradecyl	39.5° = .0027	.0025	4.0	.0033	3.61	.0046	3.59
			Average						
	16	Hexadecyl	47.5° = .00105						
	18	Octadecyl	57° = .00075						

	(n)	Detergent	Critical concn. $t = 25°$	R_m
		Unsaturated soaps		
Corrin	18	K oleate	7–12 × 10⁻⁴	
	18 + 18	K dilinoleate	2.5 × 10⁻⁴	
		Cationic detergents		
Corrin	12	Dodecylammonium chloride	0.013	
	13	Dodecyltrimethylammonium chloride	.062	
	13	Decyltrimethylammonium bromide	.064	
Scott and Tartar[c]	16	Hexadecyltrimethylammonium bromide	.0010	3.96
	12	Dodecyltrimethylammonium bromide	.0016	4.0
	10	Decyltrimethylammonium bromide	.065	2.1
	8	Octyltrimethylammonium bromide	.137	

[a] Not specially purified. [b] K. A. Wright, A. D. Abbott, V. Sivertz, H. V. Tartar, THIS JOURNAL, 61, 549 (1939). [c] A. B. Scott and H. V. Tartar, ibid., 65, 692 (1943).

After the adsorbed monolayer has attained nearly its full population of molecules, the following relation is found to hold for any special series of normal primary alcohols, acids, amines and esters whose molecules contain 10 carbon atoms or less: for the definite decrease in free energy involved the concentration of the solution increases by a factor (R_f) of 3.7 for each increase by one in the number (n) of carbon atoms in the molecule. The factor increases somewhat when n becomes close to unity.

The question which arises is this: does a similar relation hold for the concentrations at which soap ions segregate from the aqueous phase in groups designated as micelles? If so, the value of R, the constant for micelles, should be smaller than R_f, since R is not associated with a constant decrease in free energy but with a decrease which decreases as the hydrocarbon chain becomes shorter. Values of R are given in Table I.

It should be noted that at room temperature the critical concentration for ordinary soaps and for the alkyl sulfates exhibits a fourfold increase for each decrease by two in the number of carbon atoms. The only exception ($R = 3.7$) occurs in the case of a soap which was not specially purified. The value 4 corresponds to a doubling for each carbon atom added. The data of Tartar show that there is only a slight increase in the critical concentration with temperature.

At 40° the average value of R for the sulfonates is 4.0, or the same as for the ordinary soaps and sulfates at room temperature, but at 60 and 80° the mean value given by the data is slightly lower (3.6). This appears to agree with the fact that the free energy change per carbon atom decreases with temperature.

Since the usual initial molar concentration of soap used in emulsion polymerization is 0.1, it is apparent that no micelles would be obtained from potassium caprate, and none from potassium caprylate at a concentration three times higher. Thus, the values of the critical concentrations of these 8 and 10 carbon atom soaps indicate that they are unsuitable for emulsion polymerization unless additives are used.

Now, Fig. 6 shows that the critical concentration of a soap is greatly reduced by the addition of inorganic salts. Thus, it should be possible to decrease the critical concentration of the 8 carbon
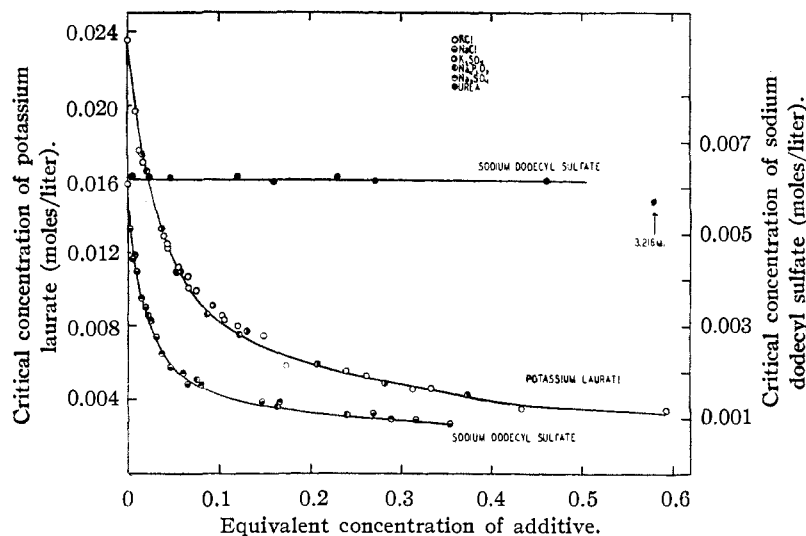
Fig. 6.—Effect of potassium chloride, sodium chloride, potassium sulfate, sodium pyrophosphate and sodium sulfate on the critical concentrations of potassium laurate and sodium dodecyl sulfate. The figure also exhibits the fact that the addition of a non-electrolyte has almost no effect (Corrin).
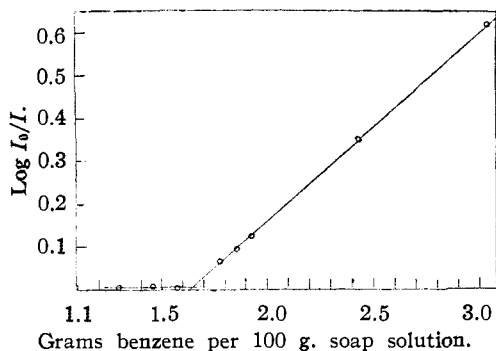
atom soap to that of the 12 carbon atom soap

Fig. 7.—Effect of benzene on the turbidity of solutions in 6.89% potassium laurate. The turbidity remains extremely small until the critical concentration is reached, after which it increases rapidly due to light scattering by droplets of benzene at 25° (Stearns).
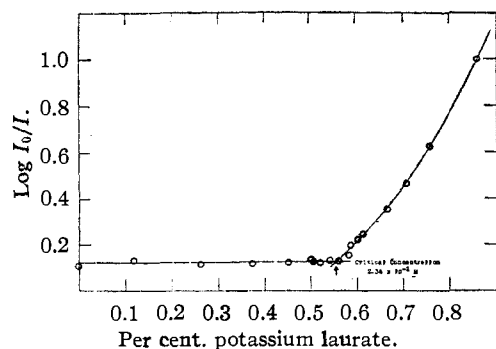

Fig. 8.—Solubilization of 2-nitrodiphenylamine in dilute potassium laurate solutions [0.005 N potassium hydroxide at 25° (Stearns)].

(laurate) and easy to do this with the 10 carbon atom soap.

IX. Solubilization

It was discovered in 1892 by Engler and Dieckhoff[13] that organic substances have a much higher solubility in soap solutions than can be accounted for by the water present. This, designated as solubilization, has been made the subject of a short review by McBain.[14]

W. B. Reynolds of the University of Cincinnati was associated with the writer in the early work on the loci of reaction in emulsion polymerization, and it was arranged that he should make the preliminary investigations on solubilization, particularly in the presence of inorganic salts. His work gave valuable information[15] which will be published by Reynolds and his collaborators. Simultaneously, investigations on solubilization were carried on in this laboratory.
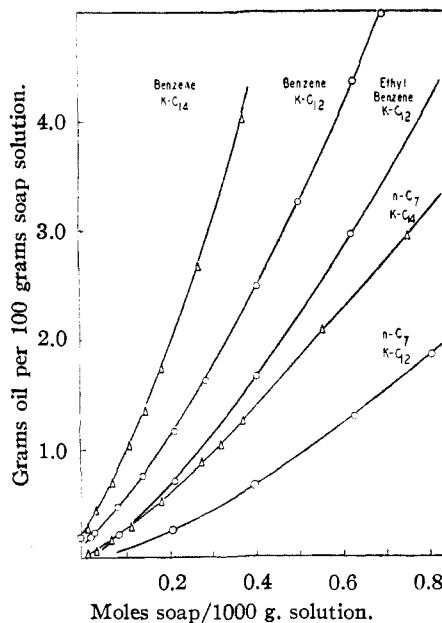

Fig. 9.—Effect of soap concentration upon the solubility of benzene, ethylbenzene, and n-heptane in potassium laurate and potassium myristate at 25° (Stearns, Oppenheimer and Simon).

(13) C. Engler and E. Dieckhoff, *Arch. Pharm.*, **230**, 561 (1892).

(14) J. W. McBain, "Advances in Colloid Science," Interscience Publishers, Inc., New York, N. Y., p. 116.

(15) W. B. Reynolds, E. W. Cotten, P. J. Canterino and J. E. Wicklatz, private communication, August 6, 1943; W. B. Reynolds and P. J. Canterino, private communication, August 17, 1944; R. B. Holland and P. J. Canterino, private communication, March 13–14, 1944; W. B. Reynolds, private communication, April 20, 1945.

However, what is considered below is only a few of the relations obtained by a more accurate turbidimetric method. A paper giving the complete data and the more general aspects of the problem is to be published by R. S. Stearns, H. Oppenheimer, E. Simon and W. D. Harkins, *J. Chem. Phys.*, **15** (1947).

(1) The solubility of an oil, in general, remains constant as soap is added to the water, until the critical concentration is reached. The addition of more soap causes the solubility to increase rapidly (Fig. 7).

(2) The rate at which the solubility increases also increases as the soap concentration increases (Figs. 8 and 9). This appears to be a formerly unknown type of behavior.

Now, (2) seems to indicate either that the size of the micelles increases with soap concentration, or if not, the structure of the micelle changes.

(3) Although the lowering of the critical concentration of a colloidal electrolyte by a salt is independent of the valence of the ion of the same charge as that on the ion aggregate, this is not true of solubilization, for which the increase of solubility is greatest for the univalent ion. For example, the extent of solubilization of ethylbenzene in 0.1 molal potassium myristate was found by Oppenheimer to increase in the order of potassium ferrocyanide, potassium sulfate, with the greatest increase when potassium chloride was added.

X. Polymerization of Monomers while in the Micelle and Growth of the Polymer Molecule from the Micelle into the Aqueous Phase (Plate I, Upper Part)

In the introduction it was mentioned that when the only monomer present is that in the micelles of soap, polymerization occurs. The part of the theory developed earliest was that which considered the growth of the polymer to be started in the monomer solubilized inside the soap micelles. In support of this idea much evidence was obtained. For example, nearly all of the polymer particles were found to be formed before the soap disappears. In early work with X-rays Mattoon

found the increase (Δd_1) in the long spacing to be relatively large for short exposures, whereas with long exposures polystyrene appeared as evidenced by an increase in the turbidity of the solution, and the value of Δd_1 was found to decrease with the time of exposure to X-rays. This indicated that the styrene was polymerized in the micelles by the action of the X-rays and that the polymer disappears from the micelles and appears in the water. In one experiment in which Δd, produced by the styrene layer, was 7.2 Å. after centrifuging to remove all excess of styrene, all of the styrene was dissolved in the micelles. The styrene was polymerized, the polystyrene formed adsorbed soap, and when a correction is made for the amount of soap adsorbed it is found that most of this thickness has disappeared. This shows that the polystyrene produced grows out of the micelle. On shaking with ethylbenzene or styrene it was found that the micelles which did not disappear and had been utilized for polymerization were able again to take up these oils, since the total long spacing (Δd_1) was increased in two experiments by 14 and 16 Å., respectively, above the initial long spacing of the soap.

In the discussion of this section the values of Δd_1 are used. However, if Δd_1 becomes zero, Δd_2 also becomes zero, and either indicates the disappearance of the oil from the micelles. This shows that the micelles left in the solution may be used over and over again, as the reaction proceeds. Thus, the soap micelles would continue as a locus through the entire course of the polymerization reaction if it were not for a factor introduced by the polymer particles formed. These absorb monomer, and the polymer–monomer particles, which have a greater area per unit mass, adsorb a monolayer of soap. By this process some of the soap present in the micelles changes into adsorbed soap. This causes the disappearance of the micelles at some yield of polymer, which with the standard formula appear to occur at about 13 to 20% yield of polymer, but with double the amount of soap (6%) the micelles persist up to the highest yields. The sum of the molecular weights of the monomer in the micelle is of the order of 10^4,

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PLATE I (Top): A. Exhibits two lines, one on each side of the center, which give the distance ($d_1 = 58.5$ Å.) between the centers of micelles in a 0.784 molar solution of potassium laurate and myristate (0.392 molar in each soap). The background contains a band which gives the thickness of the micelle ($d_2 = 35.3$ Å.) B. On saturation with styrene, d_1 increases by 15.9 to 74.4 Å. and d_2 by 11.5 to 46.8 Å. C. On polymerization, with no free monomers present, the increase in thickness disappears, and the spacings become practically those found in the micelle without styrene.

When the polymerization is produced by X-rays, the thickness of the monomer layer decreases with the time of exposure to the X-rays, the d_1 band remains as sharp as before, but merely shifts in position. The soap in the micelle in which a free radical starts to grow becomes adsorbed soap associated with the new molecule, and monomer is taken from other micelles until equilibrium with respect to monomer is established between the remaining micelles. D On solubilizing styrene again, the value of d_1 rose to 76.8 Å., or essentially that found for micelles whose styrene had not b-en polymerized.

PLATE I (Bottom): Electron microscope photograph (Eckart) at a magnification of 55,000 of polystyrene polymerized to a 0.75% yield in a potassium laurate solution in the absence of soap micelles, since the soap concentration was only one-fourth of the critical concentration for the formation of micelles. The peak in the distribution curve is at 1850 Å (Fig. 14). See Plate II for results obtained in a 0.1 molar soap solution.

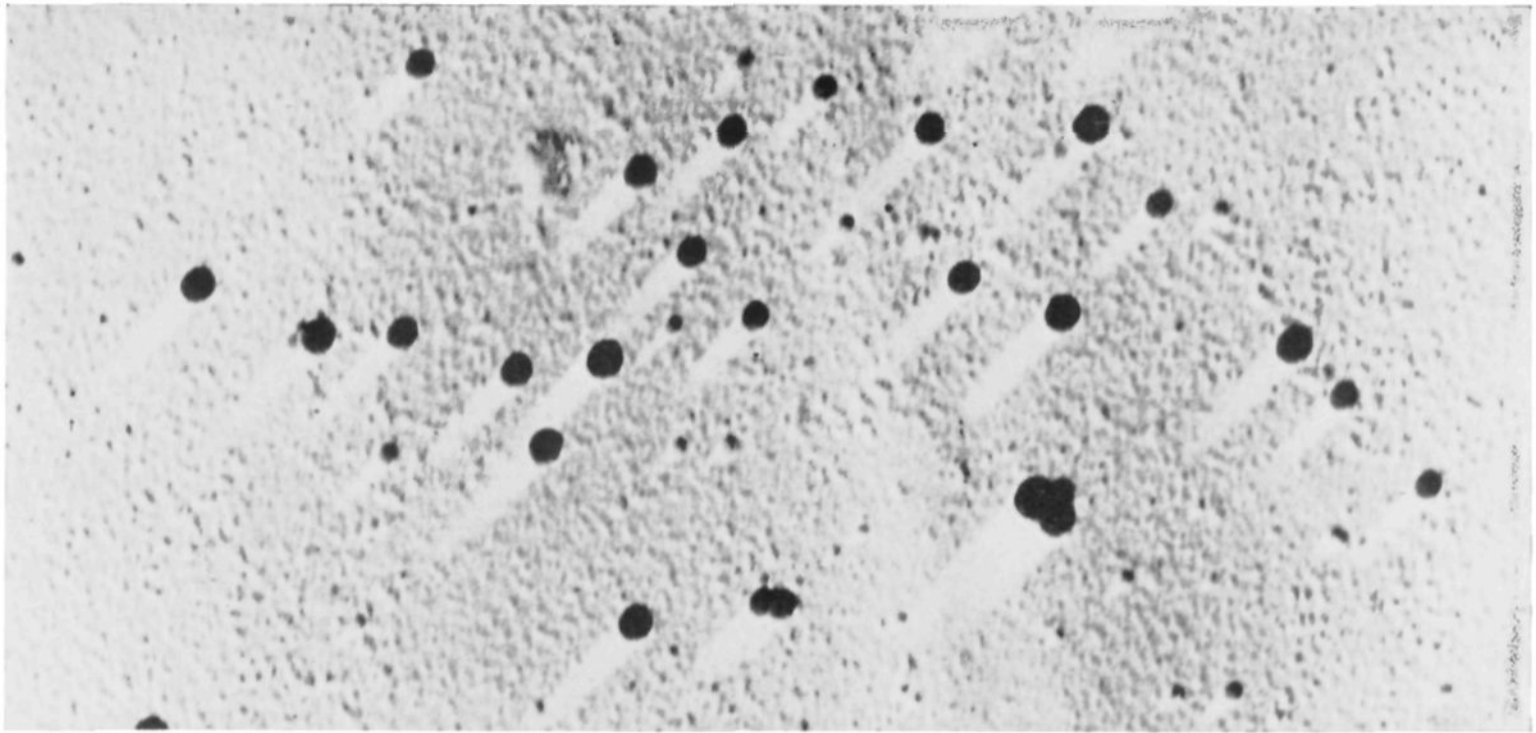Polymerization reduces the styrene layer in the micelle.

		d_1 A.	Δd_2	Δdn
A	soap soln. 0.784 m.	58.5	t_0	0
B	+ styrene	74.4	15.9	11.5
C	polystyrene	60.7	2.2	1.9
D	+ more styrene	76.8	18.3	—

Identical exposures throughout by R. W. Mattoon.
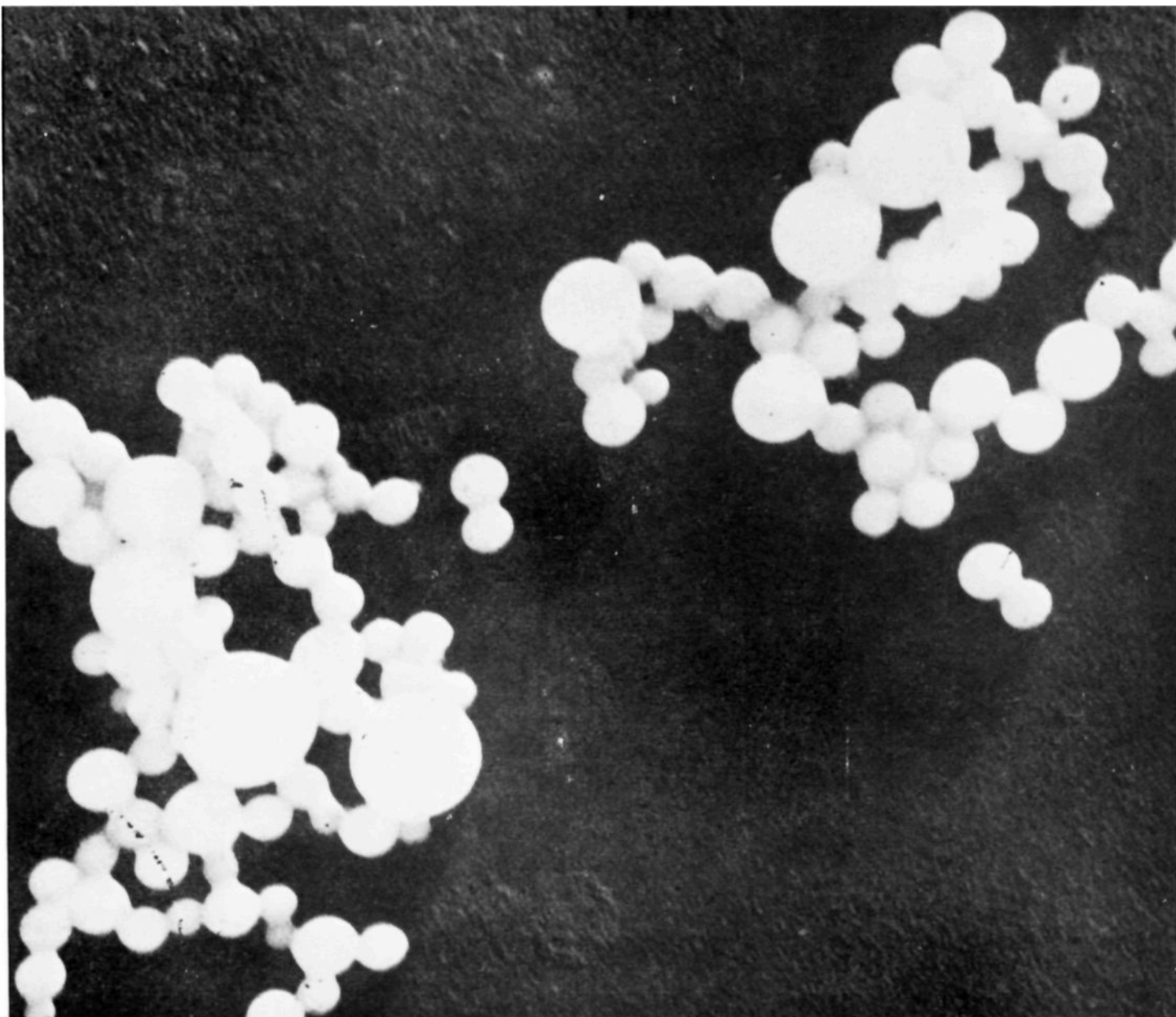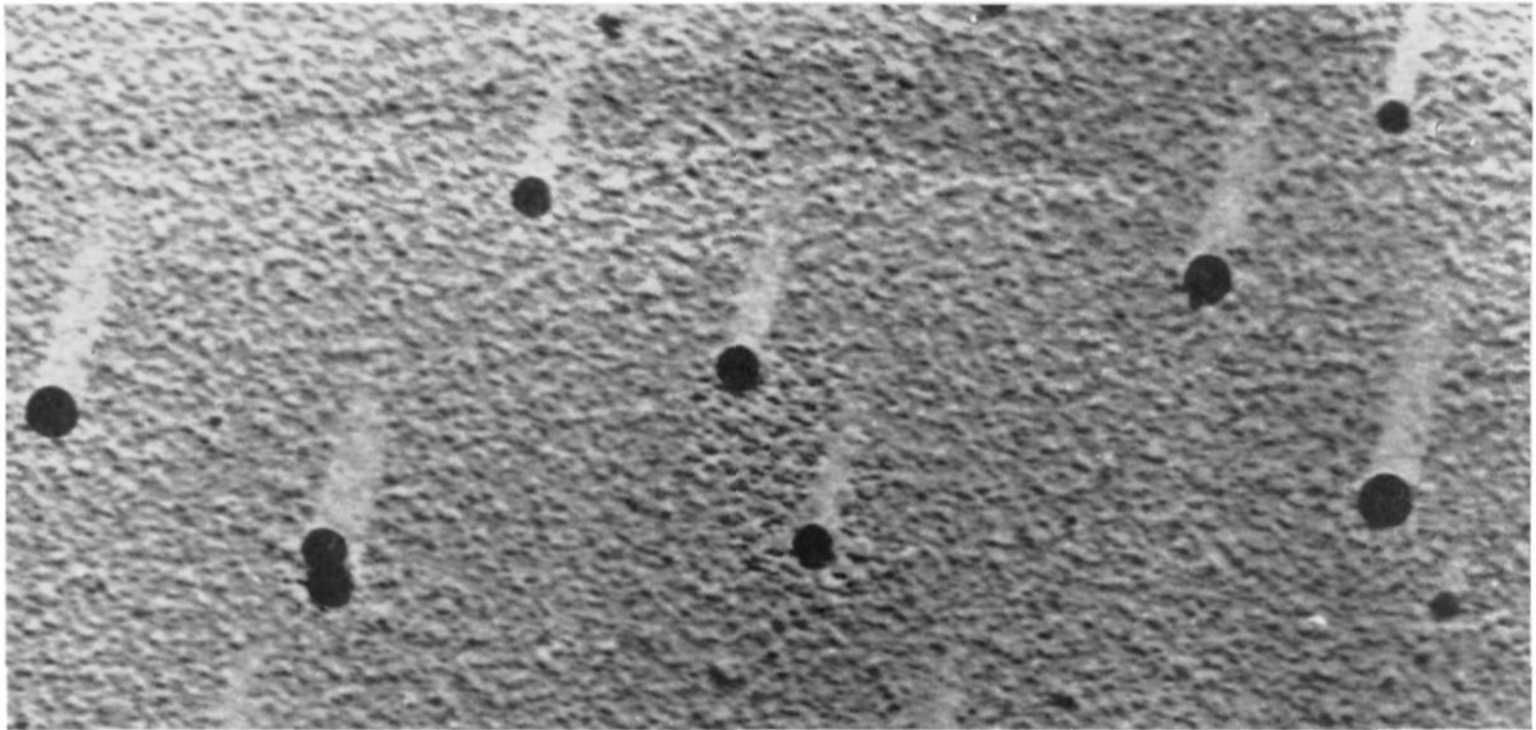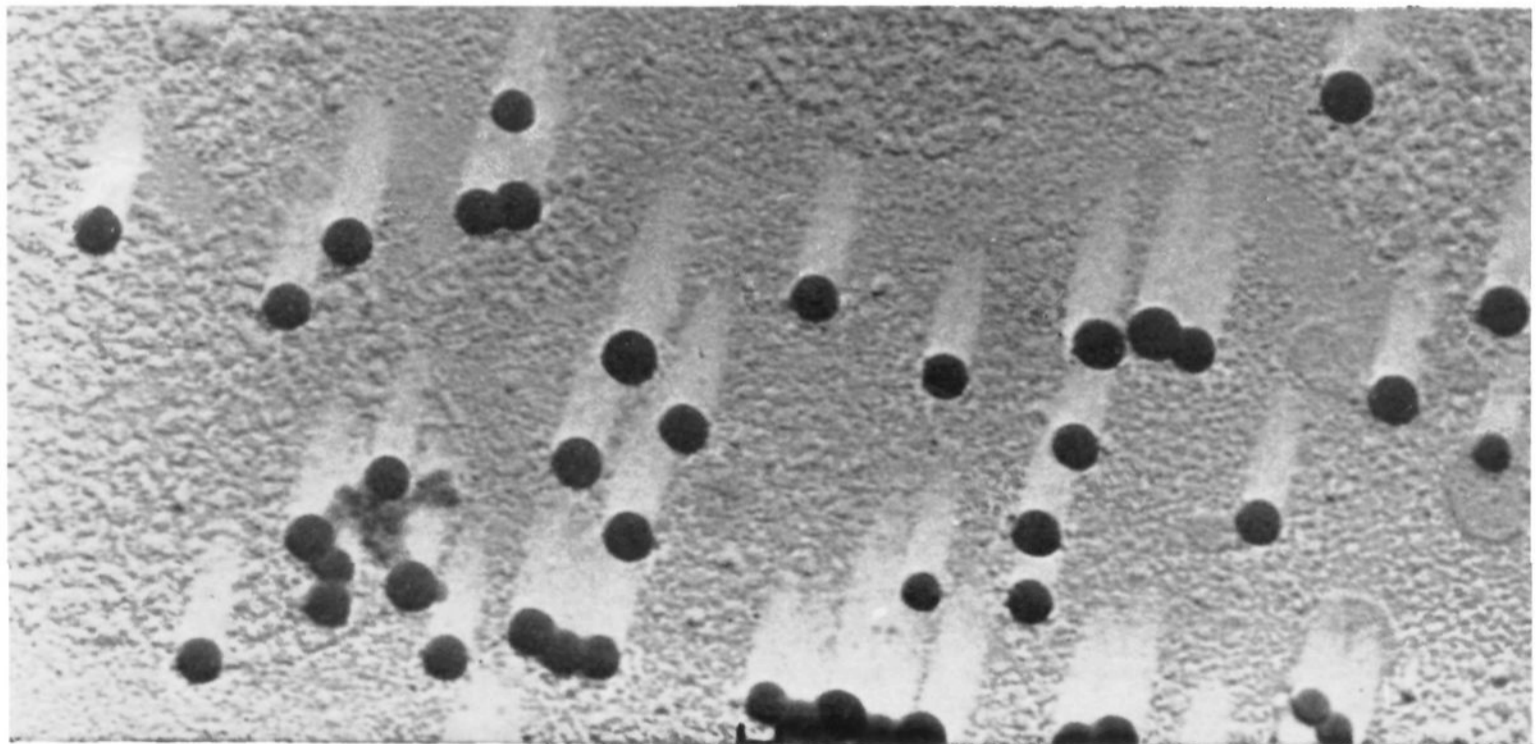

1000 Å.

Plate I.

A

B

C

1000 Å.

Plate II.

whereas the molecular weight of the polymer is of the order of 10^5. Thus, when the monomers are "insoluble" in water and emulsion droplets are absent, a polymer chain initiated in one micelle must continue to grow from monomer diffusing out of other micelles.

Much more striking results are obtained with higher concentrations of soap, for example, with 0.784 mole of soap, equimolar in potassium laurate and potassium myristate, per 1000 g. of soap solutions the initial long spacing with the soap alone was 58.5 Å. On shaking this with styrene at 25° the spacing increased to 74.4 Å. This indicates a Δd_1 of 15.9 Å., which is relatively large. On polymerization the long spacing was reduced to 60.7 Å. Thus, from this measurement alone Δd_1 decreases from 15.9 to 2.2 Å. The changes in the spacing of the X-ray diffraction lines in such a set of experiments is shown in Plate I. In the interpretation of this photograph it should be kept in mind that a decrease in distance of a diffraction line from the middle line indicates an increase in the actual spacing.

However, when a calculation is made for the decrease in concentration of the soap solution by adsorption on the latex particles which are formed, it is found that, within the limits of error of experimental work, Δd_1, due to the monomer, *has disappeared completely*. Experiments of this type demonstrate conclusively that the oil dissolved in micelles constitutes one locus of the polymerization reaction.

Hughes, Sawyer and Vinograd[16] also report a decrease in the long spacing due to polymerization of dissolved styrene. They state, "These micelles are then capable of solubilizing more styrene and continuing their role in emulsion polymerization." However, they do not point out that the micelles lose this role by disappearing rapidly as the yield increases. Also, Vinograd[17] considered that the further course of the reaction is in the aqueous phase, whereas the writer considered it to be in the polymer phase.

XI. Disappearance of Soap and Its Micelles from the Aqueous Phase: Change to Adsorbed Soap

In earlier sections of this paper it has been assumed that soap present in the aqueous phase largely in the form of micelles is rapidly transformed into a monolayer of soap which surrounds every one of the minute polymer–monomer latex

(16) E. W. Hughes, W. M. Sawyer and J. R. Vinograd, *J. Chem. Phys.*, **13**, 131 (1945).

(17) Meeting of the American Chemical Society, New York, September 13, 1944.

particles formed by the polymerization reaction. There are now two experimental methods known for the determination of the disappearance of the soap from the aqueous phase. One of these, the first to be developed, is dependent upon the change of surface tension of the aqueous phase with soap concentration.

The determination of the surface tension of a solution of soap in pure water may be made with considerable accuracy, but is affected by several variables: (1) the presence of acid produced by the hydrolysis of the soap lowers the surface tension, so it is considerably higher if hydrolysis is absent than if it were present[18]; (2) in very dilute solutions a long time is needed for the attainment of equilibrium, the surface tension decreasing with time for a considerable period.[19]

The determination is made more uncertain if oils are present, and this is especially true in the additional presence of latex. The method is dependent upon the fact that, as the concentration of the soap is increased above zero, the surface tension decreases with extreme rapidity but that, at a concentration which is low for the soaps usually used, the surface tension becomes constant, as shown in Fig. 10.
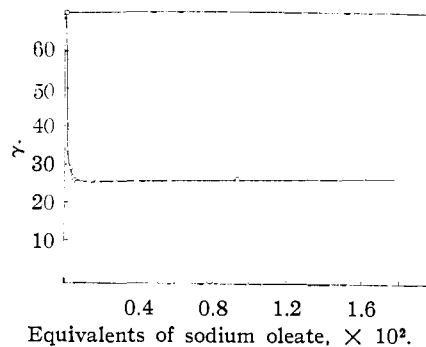

Fig. 10.—Surface tension of solutions of sodium oleate at 20°.

If pure solid sodium oleate is dissolved in water, the surface tension of the soap solution at 20° decreases very rapidly from 72.75 dynes cm.$^{-1}$ at zero concentration to 24.0 dynes cm.$^{-1}$ at about 0.002 molal (or not far from the critical concentration). This surface tension may be a

(18) W. D. Harkins, E. C. H. Davies and G. L. Clark, THIS JOURNAL, **39**, 541 (1917).

(19) N. K. Adam and H. L. Shute, *Trans. Faraday Soc.*, **34**, 758 (1938); K. S. G. Doss, *Kolloid-Z.*, **86**, 205 (1939); J. W. McBain and L. A. Wood, *Proc. Roy. Soc. (London)*, **A174**, 295 (1940); G. C. Nutting, F. A. Long and W. D. Harkins, THIS JOURNAL, **62**, 1496 (1940); H. V. Tartar, V. Sivertz and R. E. Reitmeier, *ibid.*, **62**, 2375 (1940).

PLATE II: Electron microscope photographs (Eckart) at a magnification of 55,000 of polystyrene polymerized in a potassium laurate of an initial concentration of 0.1 molar. Micelles persist to a 20% yield of polymer: A, low yield (*ca.* 7%); B, medium yield (*ca.* 30%); C, high yield (*ca.* 60%). The photographs show increase of size with increase of yield; magnification 55,000. The smaller sizes than those shown in Plate I, even though the yields are much higher, are due to the greatly increased number of polymer particle nuclei. These are initiated mostly in the monomer cores of the micelles.

minimum and may rise to about 27.0 dynes cm.$^{-1}$ at 0.1 molar but is essentially constant. In this latter range the surface film of soap is saturated, and the molecular area per molecule of soap is about 26 sq. Å. The film pressure (π) of this film is extremely high and amounts to 49 dynes cm.$^{-1}$ at 0.1 molal. The Gibbs adsorption equation cannot be used to determine the adsorption of soap in this region, since the equation has here become indeterminate.

In the early stages of the polymerization reaction the amount of soap adsorbed upon the polymer–monomer particles is so small as to have no effect upon the surface tension. However, as the yield increases above that value which reduces the soap to the critical concentration, the surface tension begins to increase rapidly. Some knowledge of the concentration at any such point may be obtained from the curve of variation of surface tension with soap concentration. However, the determination may be made more accurate by adding a soap solution of a given concentration until the surface tension first attains its minimum value.
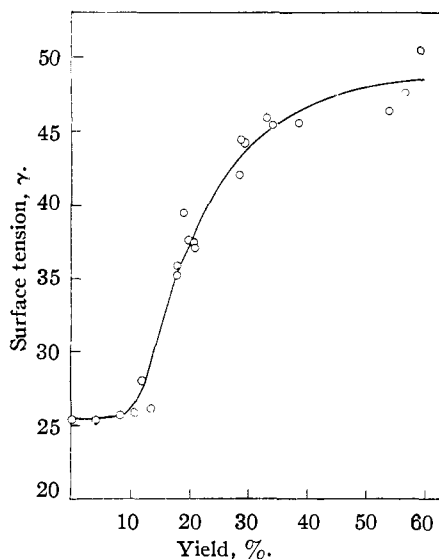

Fig. 11.—Variation of the surface tension with the yield (mutual formula at 50°) of isoprene–styrene copolymer in sodium oleate solutions (Adinoff).

One set of results by Adinoff and the writer is given in Table II. This table gives the diameters of the latex particles as obtained from the data, but the principal object of the work was to obtain the percentages of soap left in the aqueous phase at various yields. The values are given in column 5. Beginning with 2.8% soap at zero yield, the percentage of soap determined had decreased to 0.15% at a yield of 13.5%, 0.05 at a yield of 17.7%, and to other lower percentages as shown in Table III.

The critical concentration of sodium oleate is 7×10^{-4} to 1.2×10^{-3} molar. In Table II at

DISAPPEARANCE OF SOAP (SODIUM OLEATE) FROM THE AQUEOUS PHASE, AND SIZE OF THE POLYMER PARTICLES (50°). (INITIAL CONCENTRATION OF SODIUM OLEATE, 2.8% = 0.091 M)

Time, hr.	Yield, %	Temp., 20°	2% soap, cc. titration	Soap left, %	Molar concn. of soap	Diameter in Å.
0	0			2.8		
3	8.1	24.8		Unknown		
5	13.5	26.1	2.9	0.15	0.0049	310
5.5	17.7	35.2	20.0	.05	.0016	350
6	21.1	36.2	24.4	.04	.0013	400
6.5	20.9	37.4	25.6	.04	.0013	380
8	28.5	42.0	46.8	.025	.0008	430
10	32.8	45.9	57.6	.02	.0007	460
12	37.6	45.8	73.6	.015	.0005	475
14	46.8	50.0	92.1	.015	.0002	550
	95				Calcd. = 700	

13.5% soap, the free soap is already close to the critical concentration.

Adinoff and the writer have determined the surface tension–conversion curve for the copolymerization of isoprene and styrene in the mutual recipe (Fig. 11). The titration curve for a 20.8% latex prepared with sodium oleate and titrated with a 2% solution of sodium oleate is given in Fig. 12. When the constant surface tension value is reached, the surface tension and, hence, the soap concentration corresponds to a point in the conversion–surface tension curve where the surface tension begins to increase at about a 6% yield. When only half this amount of soap is added, the corresponding yield is about 15% and with one-quarter the amount of soap is about 18%.
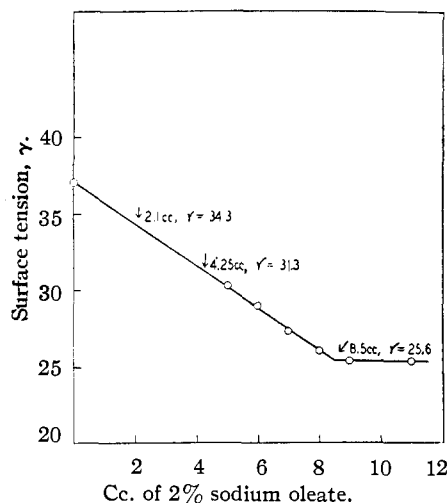

Fig. 12.—Titration of a styrene–isoprene latex at a 21% yield with a 2% solution of sodium oleate (Adinoff).

A determination of the relationship between yield of polymer and concentration of soap by the new dye method developed in this Laboratory is represented in Fig. 13, as obtained by Corrin and

Miss Roginsky. As used in latex this method depends upon the fact that certain dyes exhibit in solution a sharp decrease in fluorescence at the critical concentration when the micelles disappear. Since the rate of disappearance of soap is dependent upon the rate at which the total area of all of the polymer–monomer particles increases, it is evident that the soap disappears more rapidly in polymerizations in which these particles produced are relatively small than when they are relatively large. Obviously, the yield of polymer at which all micellar soap disappears is dependent upon all those conditions in the reaction (e. g., amount of soap, nature of the catalyst, etc.) which control the sizes of the particles. Since the size decreases with the initial amount of micellar soap, the yield at which soap disappears is not so highly dependent upon the initial soap concentration as it would be otherwise.

XII. Initiation of Polymer Particle Nuclei in the Aqueous Phase (i. e., Water plus Catalyst)

Direct evidence that a monomer may polymerize in water alone except for the presence of a trace of catalyst was obtained by the United States Rubber Company in March, 1932, by McBain,[20] and in this Laboratory.[21] The work in this Laboratory by Stearns and Corrin was carried out for the purpose of determining the size of the particles produced in this way. Polymerization occurred either when the two liquids were in contact in a flask, or when the water was in one upright flask and the monomer, in these experiments isoprene or styrene, in another. The two necks of the flasks were connected together by an inverted V tube of glass and the system was evacuated while the liquids were frozen, and the evacuated system was then sealed off. The vapor of the monomer (the liquid monomer kept at a slightly lower temperature than the water) was then allowed to pass over into the water. Under these conditions no monomer droplets formed in the water, so the polymer particles were initiated wholly in the aqueous phase.

In other experiments the monomer was contained in a glass cup sealed at its bottom to the center of the bottom of the flask, which held water around the lower part of the cup. The system was evacuated through the neck of the flask, hich

TABLE III

% K₂S₂O₈	m KCl	$\mu \times 10^2$ (μ = ionic strength)	Conversion, mg./cc.	Mean particle diameter in Å.	Number of particles per cc. $\times 10^{11}$
0.1	0.0	1.11	2.89	1710	1.1
.1	.0025	1.36	2.99	1310	2.5
.1	.005	1.61	3.08	1370	2.3
.1	.01	2.11	2.82	2870	2.3
.1	.05	6.11	2.47		
.1	.10	11.1	1.74		

(20) J. W. McBain, private communication, February 6, 1943.
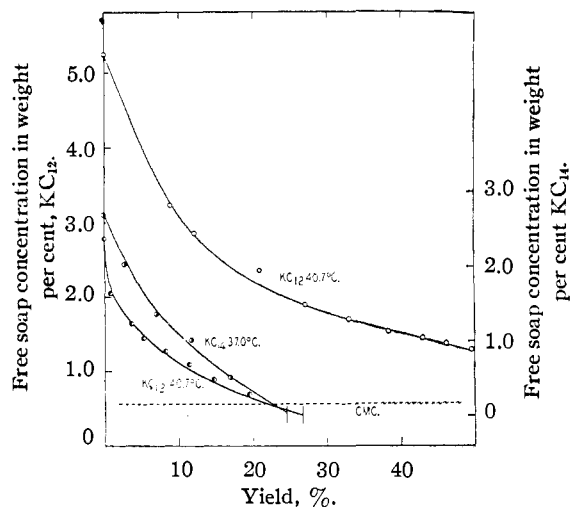(21) W. D. Harkins, private communication, June 17, 1943.

Fig. 13.—Disappearance of soap and monomer during polymerization of styrene: with the normal amount of soap (about 3%), micelles of either potassium laurate or myristate disappeared (curves fall below the CMC—critical micelle concentration) at a yield of polymer of about 23%, while the free monomer disappeared by solution in the polymer particles at a yield of about 50%. With double this amount of potassium laurate at 40.7° the micelles do not disappear at even the highest yields, but the formation of new polymer nuclei was stopped by the disappearance of free monomer at a 30% yield. With any initial soap concentration the soap disappears more rapidly if the polymer–monomer particles produced are smaller. Thus, at a 23% yield of polymer, 2.2% of potassium laurate disappeared when the initial concentration was 2.8%, but much more soap (3.2%) disappeared when the initial concentration was 5.2%, since the particles were finer in the latter and thus gave a larger area.

was then sealed off and held in a thermostat at 50° for eighteen hours. In two experiments of this type by Corrin, the mean diameters of the polymer particles were found to be those listed in Table III, which indicates polymer particle diameters from 1300 to 2900 Å. in the presence of a salt. In the polymerization of styrene at 50° for eighteen hours in the apparatus with several interconnecting tubes, one of which contained lauryl mercaptan, Stearns obtained particles of mean diameters of 1500 and 2000 Å., as measured by Oppenheimer.

In all of these experiments the latex solution formed was very white and, even though its concentration was very small, opaque, as was found also when soap was present at one-fourth of the critical concentration. In this sample the peak in the distribution curve (Fig. 14) was found to occur at 1850 Å. An electron microscope photograph of this latex, taken by Eckart of the U.S. Rubber Company, is represented in Plate I. In the absence of soap much larger particles are formed, and the latex is much less stable. The distribution above 3000 Å. was not obtained, since all particles above this diameter were removed by
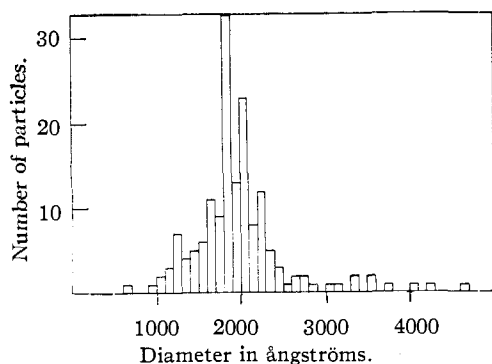
Fig. 14.—Distribution of diameters of polystyrene with a peak at 1850 Å., polymerized to a 0.75% yield in potassium laurate at 0.25 of its critical concentration (from electron microscopic photographs by Eckart, General Laboratories, United States Rubber Company).

a filtration which preceded the preparation of the sample for the electron microscope (Fig. 15). The function of a detergent below its critical concentration and in the absence of monomer droplets is to reduce the extent of aggregation of the polymer particles. Obviously, the large size of the polymer particles produced without soap, or without micellar soap, is due to the relatively small number of polymer particle nuclei formed when the monomer "cores" of the micelles are absent.
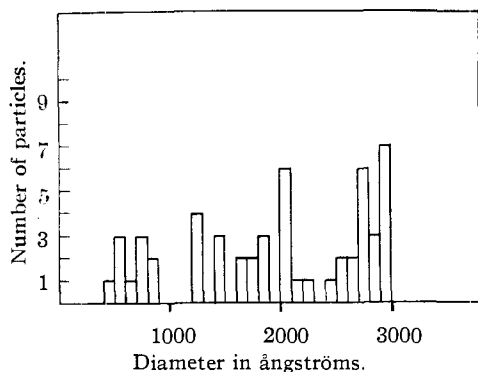

Fig. 15.—Distribution of diameters of polystyrene at 0.75% yield in water without soap. All particles above 3000 Å. in diameter were removed by filtration (Eckart).

XIII. Prediction by the Theory that the Rate of Polymerization Should be Nearly Proportional to the Initial Concentration of Soap

The proportions of the various components commonly used in the synthesis of rubber are given in the "mutual," or standard, formula due to the United States Rubber Company and the Standard Oil Company of New Jersey, as given below

Butadiene	75 g.
Styrene	25 g.
Water	180 g.
Soap	5 g.
Potassium persulfate	0.3 g.
Lauryl mercaptan	0.5 g.

According to the writer's theory, most of the polymer particles are initiated in the soap micelles. Now, if all of them were initiated in the micelles, then doubling the amount of micellar soap should double the number of polymer particles formed per unit time, which should double the rate of reaction at any special yield. Since the critical concentration is low for the soaps used, the rate of reaction should be nearly proportional to the initial amount of soap.

Obviously, since increase in the viscosity lowers the rate of diffusion of monomer into soap micelles and polymer particles, the above relation needs to be modified slightly to account for the viscosity effect. Also, since some polymer particles are initiated in the water, this must be taken into account in the equation for the rate of reaction

$$\frac{dy}{dt} = (k - v - w)s + f(y) \qquad (3)$$

Here s is the amount of soap, k is a constant, v and w are relatively small allowances for the effect of viscosity and of the polymer particles initiated in the water, and $f(y)$ takes account of the variation in the rate of reaction with yield.

With respect to the value of the term $f(y)$ in equation 3, it is of interest that by an extensive series of experiments it was shown that *the rate of the polymerization reaction is determined by the initial amount of micellar soap present, even after the soap has disappeared from the aqueous phase.* With *careful technique*, which necessitated freedom from atmospheric oxygen, the rate between a 5
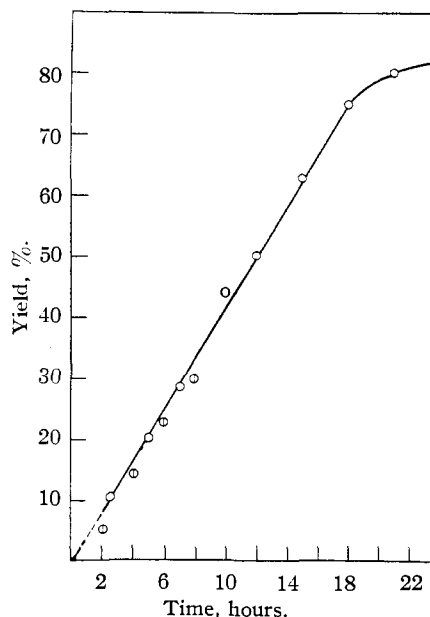

Fig. 16.—Linear increase of yield of polymer with time under extreme vacuum conditions: 75% isoprene, 25% styrene with 3% Procter and Gamble silica-free flakes. Open circles, 0.2%, circles with vertical bar, 0.005% potassium ferricyanide (Corrin).

and 65% yield at certain soap concentrations is found to be *a linear function of the time* (Fig. 16). This is true in the synthesis of GR-S or of isoprene–styrene copolymer at a soap concentration equal essentially to that of the standard formula: 5% by weight as much soap as monomer. This is represented by the equation

$$y = at \qquad (4)$$

in which y is the yield, a is a constant, and t the time.[22] If oxygen is present, this relation changes to

$$y = a(t - b) \qquad (5)$$

in which b is an induction period. The validity of these equations has been confirmed by Dornte, Kharasch and Wall.[23]

The use of more or less than the standard amount of soap and some other factors determine the yield to which the linear relation holds. With standard soap it often remains linear to a yield of 60 to 70%, or slightly more. If much larger quantities of soap are used, the initial rate of polymerization is much higher, but the rate decreases somewhat more quickly with increase of yield. The use of much less soap may throw the curve over into a sigmoid or S-form (Fig. 17).
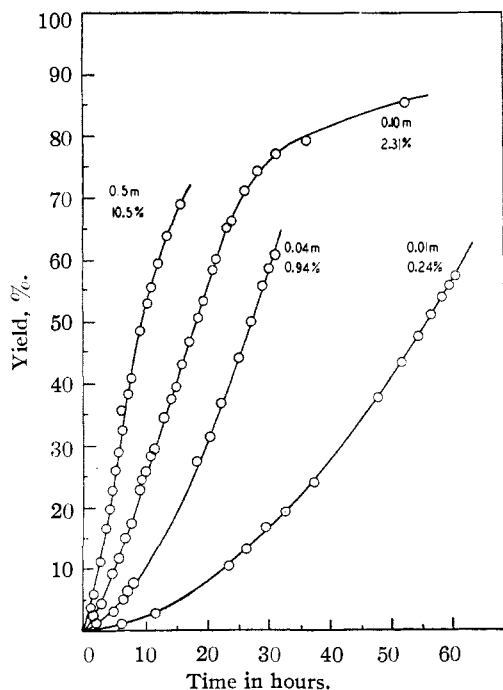

Fig. 17.—Yield of polyisoprene as a function of time and of concentration of potassium laurate: $t = 50°$. The right-hand lower curve with 0.01% soap represents the type obtained below the critical soap concentration. Here, it is approximately 0.5 the critical concentration (Stearns).

(22) W. D. Harkins, R. S. Stearns and M. L. Corrin, private communication, June 17, 1943.

(23) R. W. Dornte, private communication, September 1, 1943; M. S. Kharasch, W. Nudenberg, A. N. Graham, and E. G. Rauh, private communication; F. T. Wall, private communication.

It should be kept in mind that the initial amount of soap in the aqueous phase is less than that which corresponds to the soap employed by the amount adsorbed at the monomer–water interface. This is highly dependent upon the fineness of the emulsion, but with the mutual formula may be of the order of one-seventh of the soap used.

A large number of experiments have been carried out by others on the relationship between yield, soap concentration and time, especially by W. B. Reynolds, private communication, Aug. 6, 1943, etc.; I. M. Kolthoff, private communication, May 25, 1944, etc.

XIV. The Monomer Emulsion Droplet as a Minor Locus of Reaction

Both indirect and direct evidence indicates that the monomer emulsion droplet, contrary to the older theory, is only a minor locus of the polymerization reaction. For example, it was found by Simon that at a yield of 45% of polyisoprene the ratio of polymer to monomer in the styrene was only 0.00940, which represents the production of only 0.23 g. of polymer in 100 g. of initial monomer. In experiments by Stearns, a styrene or isoprene droplet of 1.5 to 0.5 mm. in diameter, suspended in a solution of soap and catalyst, was found to decrease in size by diffusion of monomer molecules into the aqueous phase in which they polymerized, producing a slightly turbid solution. When the diameter of the droplet had decreased to 0.1 mm. or less (Fig. 18), there remained a
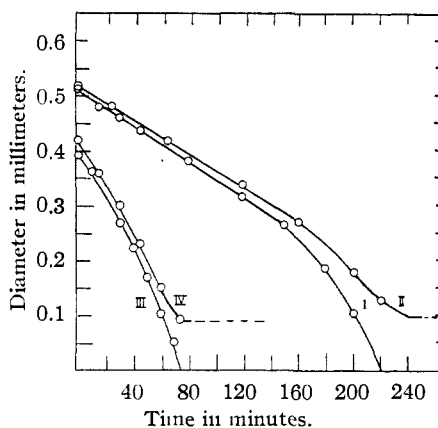

Fig. 18.—Curve I, diffusion of isoprene into water containing 1% sodium carbonate; Curve II, diffusion of isoprene which contains lauryl mercaptan (0.2%) into water with 1% sodium carbonate, 0.3% potassium ferricyanide, and 0.1% potassium persulfate. Curve III, diffusion of isoprene into 3% potassium laurate with 1% sodium carbonate; Curve IV, diffusion of isoprene containing lauryl mercaptan (0.2%) into 3% potassium laurate with 1% sodium bicarbonate, 0.3% potassium ferricyanide, and 0.1% potassium persulfate. The dotted lines show just when distortion of the drop first appears. This indicates that the drop contains a large proportion of polymer.

polymer–monomer particle, now usually non-spherical, which was found to sink finally to the bottom of the soap solution. It is apparent that the amount of polymer thus formed is much less than 1% of the mass of the monomer.

XV. Principal Locus of Polymerization is in the Polymer–Monomer Particle

As indicated in an earlier section, extremely minute polymer particles are initiated in and grow from thin monomer oil layers (order of 10 to 15 Å. thick when saturated). These polymer particles carry soap with them, and, when investigated at very low yields of polymer, may contain as much as six times as much monomer as polymer ($M/P = 6$), a value highly dependent upon conditions. At a low yield as many as 10^{16} such
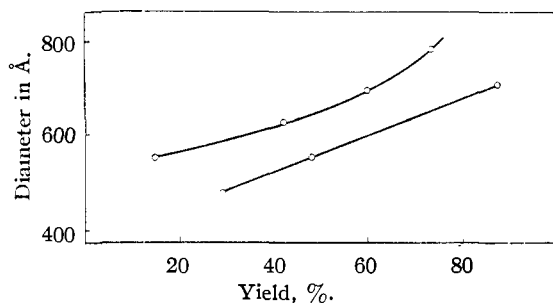

Fig. 19.—Increase in diameter of polystyrene particles with yield. Lower curve with OEI. upper without OEI (= lauryl mercaptan). (Electron microscope photographs, General Laboratories, United States Rubber Company.)
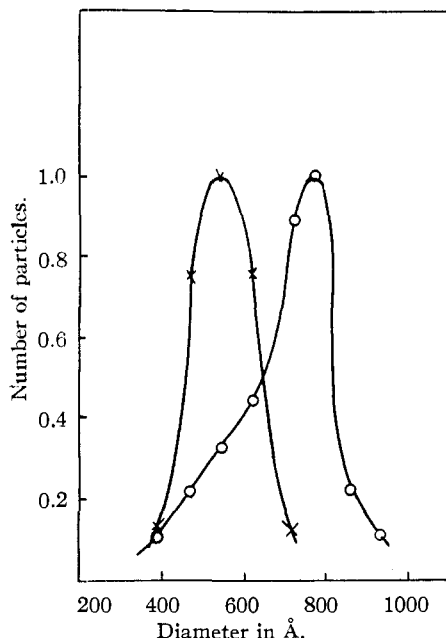

Fig. 20.—Distribution of diameters of polystyrene particles at yields of 15% (left-hand curve) and of 74% (right-hand curve): obtained without OEI (General Laboratories, United States Rubber Company).

particles may be present per initial cu. cm. of monomer. The rate of production of these particles is initially very great, and each of them provides a locus for the monomer present.

As the conversion proceeds, the monomer–polymer particles rapidly become larger. For example, by soap titration by the use of a dye, Corrin found the mean diameter of polystyrene-styrene particles formed at 40.7° with 5% as much initial soap as initial styrene was at a 5.2% yield 850 Å. (590 Å.), while at a 20% yield this had increased to 1340 Å. (960 Å.). The figures in parentheses represent the diameters for the polymer present.

With twice the concentration of soap (10% of the monomer) many more polymer particles are formed, so they are much smaller: i. e., 640 Å. (450) at a 9% yield, whereas with the normal amount of soap the values are 970 Å. (690). In general, the particles are somewhat smaller than with styrene if 75% butadiene and 25% styrene are used and also if isoprene is substituted for butadiene.

The first set of electron micrographs taken to show the increase of size with conversion is represented by Figs. 19 and 20, obtained for the writer by the General Laboratories of the United States Rubber Company. Similar photographs taken later, which exhibit larger sizes, are represented in Plates I and II.

Many experiments on the determination of particle sizes have been carried out in this Laboratory by the following methods: (1) soap titration by the use of (a) dyes or (b) surface tension measurements; (2) light-scattering and use of Debye's theory; and (3) electron microscope (photographs by the United States Rubber Company). All methods, when carried out properly, show that the size of the polymer particles increases rapidly with yield. It is obvious that the size of the polymer–monomer particles cannot be obtained by the electron microscope. In fact,

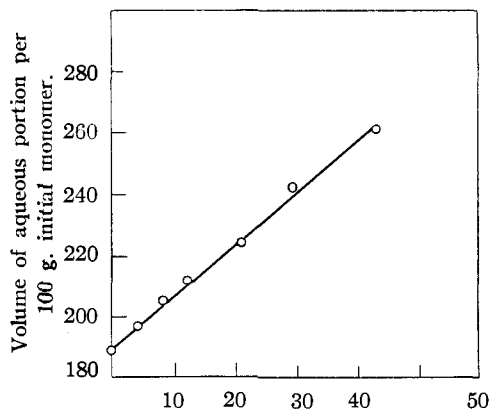Increase in volume of aqueous portion with yield.

Fig. 21.—Increase in the volume of the aqueous phase plus polymer-monomer particles with yield (75% isoprene. 25% styrene, 3% potassium myristate) (Corrin).

no other laboratory than this has paid any attention to the sizes of polymer–monomer particles. Since these particles, in the early stages of the reaction, contain much more monomer than polymer, the probability of coalescence is greater than if they consisted of polymer alone.

It is shown in an earlier section that with the normal amount of soap (3% of the water and 5% of the monomer) the free soap in the water has changed to adsorbed soap sufficiently to cause the disappearance of micelles at a 20% yield. With double this amount of soap the micelles persist to high yields, but the free monomer disappears at 30 to 35%. Either of these types of disappearance reduces the number of new polymer particles initiated to a very low value.

The relations involved are so extensive that they are left to a later paper for a fuller discussion.

Discussion

Since papers on the kinetics of emulsion polymerization have in the past been based on erroneous views of the loci in which the reaction takes place, they cannot be correct. Nearly all of the polymer is formed in the monomer–polymer latex particle in monomer which has been, by the process of diffusion, transferred, first from the emulsion droplet into the water, then from the water into the latex particle. In copolymerization the diffusion rates of the various monomers may be quite different. For example, butadiene diffuses much more rapidly than styrene. In addition, the monomers differ in general in the rate at which they are absorbed in the latex particles. Thus, the value of the ratio R between the amounts of the monomers a and b is in general different in the latex particle from what it is in the emulsion droplet. It is known that the composition of a copolymer formed at a certain time is commonly different from that of the monomer mixture at that time. Commonly, this has been interpreted as due entirely to a difference in the rates at which the different monomers react to give polymer, without any attempt to determine the composition of the monomer mixture in the polymer–monomer particle.

The considerations presented thus far have been given without any reference to the free radical mechanism commonly assumed for polymerization either in an emulsion or in a liquid monomer phase. To extend the theory by the inclusion of the free radical mechanism it would be essential to determine how many free radicals are present at any instant on the average in each polymer–monomer particle, since this is the locus of almost all of the polymerization which occurs.

If the number of free radicals (n_r) in any monomer particle, including the polymer–monomer particle, should prove to be independent (or nearly independent) of the amount of monomer present in it, this would explain the seemingly anomalous slow rate of polymerization (so slow that it may be largely thermal) in the relatively extremely large monomer droplets, as compared with that in the very much smaller polymer–monomer particles. If n_r is constant, it is presumably extremely small, and for polymer–monomer particles often less than unity. For example, a polymer particle of radius 400 Å., of molecular weight 50,000, produced in 1000 minutes contains 3000 molecules or one molecule per 20 seconds, whereas for his polymer Bartlett[23b] found the *life* of a growing chain as 1.3 seconds.

The solubility of styrene or of isoprene in water is very small. Nevertheless, it is shown earlier (Section XII) that in the absence of liquid monomer, but when in contact with its vapor, very large polymer particles are formed. This shows that polymer molecules are formed readily in the solution in water if this contains a small concentration of a catalyst. This occurs in either the presence or absence of a mercaptan or any other promoter and modifier. Thus, a free radical formed from a monomer molecule must often have a sufficiently long life to allow it to collide with another monomer molecule and unite with it to form a larger free radical. Also, the growth of this free radical, even in this extremely dilute solution of the monomer, must continue until a high molecular weight is attained.

When polystyrene is formed in the absence of a mercaptan, its mean molecular weight is often more than three million. Consider that during the growth of the polymer–monomer particle it gains a diameter of 300 Å. at a certain yield. If the molecular weight were this high at this diameter, a straight chain molecule is sufficiently long to stretch across this diameter more than one hundred times, or polybutadiene with a molecular weight as low as 3×10^4, more than eight times. It is, therefore, not pertinent to consider whether the polymerization occurs inside the particle or at its interface with the aqueous phase.

When a droplet of isoprene, for example, from 0.5 to 1.5 mm. in diameter, is suspended in a solution of a composition and at a temperature suitable for polymerization, almost all of the monomer diffuses away and only an extremely small percentage polymerizes in a period of one to six hours. Such a droplet of isoprene has a diameter of the order of 10^4, an area of the order of 10^8, and a volume of the order of 10^{12} times larger than a moderately large polymer–monomer particle. The amount of polymer produced in the monomer droplet does not seem to be greater than that in the polymer–monomer particle by a factor of the same order of magnitude as that indicated by the relative volume or even area. Thus, even with such relatively very large drops the number of free radicals seems not to be very much larger than in very much smaller drops.

At the time the experimental work of this proj-

(23b) P. D. Bartlett and C. G. Swain, THIS JOURNAL, **67**, 2271 (1945).

ect was begun in January, 1943, it was known by the writer from the work of L. E. Copeland of the United States Rubber Company that the onset of polymerization is often delayed by as much as four hours in the presence of air and by a shorter period in nitrogen if dissolved air is present in the water. It was suggested by F. R. Mayo that this effect is due to oxygen. This idea evidently arose in the early fundamental work of M. S. Kharasch[24] on the effect of traces of oxygen on the reactions of organic substances. The influence of oxygen here is to attack the free radicals and thus stop the growth of chains.

In this Laboratory this effect was prevented in the earliest work by: (a) use of a high vacuum system on a vacuum rack. The liquids were frozen in separate bulbs and then distilled into a single bulb. This removed the oxygen. (b) The mixture was *seeded* by adding a small portion of an earlier polymerizing mixture. This may be kept in an ice-box for a long period. Evidently the free radicals thus added remove the oxygen. In industry seeding is now used to change the size of the polymer particles and for other purposes.

The role of free radicals has been discussed by Kharasch,[25] and Reynolds has developed valuable regulators (modifiers).[26] The use of regulators has been investigated extensively.[27]

However, what is of significance for the theory presented by the writer is the work of W. V. Smith,[28] who has discussed the regulator theory in emulsion polymerization and states that "the data can be interpreted satisfactorily, using the picture of emulsion polymerization proposed by Harkins." He finds that the rate of diffusion of the higher molecular weight mercaptans through the aqueous layer plays a predominant role in determining the rate of mercaptan reaction.

Summary

A new general theory of the mechanism of emulsion polymerization is presented. It is shown that there are two types of loci: A, in which minute polymer particles are initiated; and B, locus in which most of the polymer is formed.

A. 1. Early in the reaction nearly all of the polymer particle nuclei are formed in monomers solubilized in the core of oil in the soap micelle. The polymer molecules thus formed grow from the soap micelle into the aqueous phase, the soap of the micelle becoming adsorbed soap. This locus ceases to be active at a yield of about 13 to 20%, when 5% as much soap as monomer is present initially; at lower yields with less soap, and higher yields with more soap.

2. Secondary locus for initiation: the aqueous phase, the relative importance of which rises with decrease in the initial amount of soap. This remains effective to some extent up to a yield which with the mutual or standard formula (5 g. soap to 100 g. monomer) is about 60%, (32% with 10 g. soap) above which all of the monomer is dissolved in the polymer, except a very slight amount of monomer dissolved in the water.

B. Locus in which nearly all of the polymer is formed: the polymer particles themselves. These take up monomer molecules from the aqueous phase and the monomer in the polymer-monomer particles thus formed undergo polymerization, while simultaneously the particles take up more monomer. This is the history of the particle, whether it is initiated in a soap micelle or in the aqueous phase. It is obvious that, when at a yield of about 60% of polymer, all of the monomer has been absorbed by the polymer particles, only that monomer which is dissolved in the polymer is left for polymerization. If this occurs at a 60% yield, the monomer–polymer ratio (M/P) is, obviously, 40/60. Below this yield this ratio cannot be obtained except by experimental determination. Its value increases with decrease of yield. Commonly each polymer–monomer particle contains only one growing chain only a part of the time.

According to the theory, an increase in the ratio of initial soap to monomer (S/M) increases the relative amount of micellar material and should therefore increase the number of polymer particle nuclei formed early in the reaction per unit time. This should increase the number of polymer particles present at any given yield, and thus the rate of the reaction, and should therefore decrease the size of the particles. These predictions are in accord with the experimental results.

Evidence is presented which seems to indicate:

1. Each double layer of soap is an independent micelle, whereas the earlier theory considers the micelle as a pile of double layers.

2. The micelle seems to increase in size with increase of soap concentration.

3. In agreement that the origin of the micelle is the decrease of free energy which accompanies the removal of the hydrocarbon chain from the water, the critical concentration for micelle formation is found to increase by a factor of 2 for each decrease by unity in the number of carbon atoms in the soap molecule.

The principal function of the monomer emulsion droplets is not to serve as a primary locus for the formation of polymer, but as a storehouse from which monomer molecules diffuse into the aqueous phase where they are trapped by soap micelles and polymer particles in both of which they polymerize.

(24) A discussion of the oxygen effect on rate of polymerization is given by M. S. Kharasch and F. H. Westheimer, private communication, December 6, 7 (1943).

(25) M. S. Kharasch, private communication.

(26) W. B. Reynolds, private communication.

(27) W. E. Messer and L. H. Howland, private communication, December 28, 1942; R. H. Ewart, private communication, June 24, 1943; I. M. Kolthoff, private communication, November 12, 1943, etc.

(28) W. V. Smith, THIS JOURNAL, **68**, 2059, 2064, 2069 (1946).