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The Kinetics of Styrene Emulsion Polymerization[1a]

BY WENDELL V. SMITH

Introduction

Recent papers[1,2,3] in discussing the kinetics of styrene polymerization in emulsion have emphasized the similarity between emulsion and bulk polymerization. While there is a similarity in the chain propagation reaction,[4] this discussion will emphasize the very important and interesting differences.

The excellent work which Professor Harkins[5] has done in elucidating the locus of the emulsion reaction and in describing the general nature of the processes involved serves as the logical basis for working out the kinetics. Smith and Ewart,[6] adopting Harkins' picture, have discussed in a rather general manner the kinetics of reaction of free radicals in isolated loci when the radicals are generated in a medium outside of the loci. This discussion is used in interpreting the experimental data reported herein.

In order to present a clear and coherent picture of the essential results obtained from this investigation a brief discussion of a typical emulsion polymerization follows.

Just before polymerization starts, an emulsion system used for polymerization consists of a water solution of persulfate and styrene containing emulsified styrene droplets and small, numerous soap micelles which have dissolved styrene in them. Free radicals are generated at the rate of about 10^{13} per second per cc. of water solution by a reaction which presumably involves persulfate and styrene dissolved in the water. Practically all of these radicals enter soap micelles or polymer particles.

Having entered a soap micelle, a free radical starts the styrene contained therein to polymerize at the rate of about 10^3 molecules per second. The surrounding water solution saturated with styrene is capable of supplying styrene to the polymerizing free radical at a rate very much greater than this. Consequently, the growing free radical behaves as a polymer particle swollen with styrene, the styrene in the particle being substantially in equilibrium with the styrene in the surrounding water solution. This polymer free radical continues to polymerize until another free radical (probably a small one) happens to enter the swollen polymer free radical which may now be called a polymer particle.

As more and more particles are formed and continue to grow, their interfacial area will adsorb more and more of the available soap until finally all of the soap is adsorbed on polymer particles, leaving none as micelles. The total number of particles formed up to this time under typical conditions is 10^{14} to 10^{15} per cc. of water solution. Since free radicals are formed at the rate of 10^{13} per sec., the period in which the particles are being formed will not be very long. Thus, if all the free radicals entered soap micelles, this period would require only 10 to 100 seconds. Actually, it is longer, since after some particles are formed, there is competition between the polymer particles and the soap micelles for the free radicals being produced.

After the micelles have disappeared, practically all the free radicals formed enter polymer particles and substantially no new particles are formed. Now, since the 10^{13} free radicals produced per sec. have a choice of entering any of the 10^{14} to 10^{15} polymer particles present, on the average a free radical enters a particular particle once every 10 to 100 seconds. So after entering a particle, a free radical causes polymerization for 10 to 100 seconds until another radical enters. After the second enters, the two react to terminate mutually in a very small fraction of a second ($<10^{-3}$ sec.). Then after a period of 10 to 100 seconds of inactivity, another free radical enters and starts polymerization again. Thus to a good approximation, a particle contains a free radical one-half of the time. Since the intervals of growth are 10 to 100 seconds and the rate of growth per free radical is about 10^3 molecules per sec., one interval of growth results in the polymerization of 10^4 to 10^5 molecules corresponding to molecular weights of 10^6 to 10^7.

After the initial period in which new particles are being formed, the rate of polymerization is substantially constant for a time and is given by one-half the number of particles present (10^{14} to 10^{15} per cc.) times the rate per free radical (10^3 molecules per sec.), which gives an over-all rate of 10^{17} to 10^{18} molecules or 10^{-5} to 10^{-4} g. of styrene per second per cc. of water solution. This rate continues until the separate styrene phase disappears, after which the rate falls off due to a decrease in activity of the styrene.

Effect of Polymerization on Number of Polymer Particles

In order to determine if the number of polymer particles remains constant after their principal generators (soap micelles) have disappeared, a study was made of the number of particles present after polymerizing varying amounts of styrene in a

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[1a] Presented at the High Polymer Forum of the Chicago meeting of the American Chemical Society, April, 1948.

[1] I. M. Kolthoff and W. J. Dale, THIS JOURNAL, **67**, 1672 (1945).

[2] C. C. Price and C. E. Adams, *ibid.*, **67**, 1674 (1945).

[3] M. L. Corrin, *J. Polymer Sci.*, **2**, 257 (1947).

[4] W. V. Smith, THIS JOURNAL, **68**, 2059 (1946); R. G. Fordyce and E. C. Chapin, *ibid.*, **69**, 581 (1947).

[5] W. D. Harkins, *ibid.*, **69**, 1428 (1947).

[6] W. V. Smith and R. H. Ewart, *J. Chem. Phys.*, **16**, 592 (1948).

persulfate solution containing a known number of polystyrene particles but no soap micelles. The experiment was made by first preparing a seed using the usual ingredients for emulsion polymerization (water, soap, potassium persulfate and styrene). This was polymerized to about 95% conversion of the styrene to polystyrene under which conditions practically all the original soap was adsorbed on the polystyrene particles and none remained in the form of micelles. A sample of the latex was used to obtain electron microscope pictures of the particles present. Using these pictures the diameters of 100 particles were measured, from which the average volume of a particle was calculated. The particular latex used had particles with an average volume of 0.618 × 10^{-16} cc. This latex was then diluted with water containing 0.175% potassium persulfate, and varying amounts of styrene were added; the charges were kept at 50° until substantially all the added styrene had polymerized. These resulting latices were then examined with the electron microscope and again the average volume of the particles were determined from measurements of the diameters of 100 particles. The results are given in Table I.

TABLE I

INCREASE IN SIZE OF POLYSTYRENE SEED PARTICLES DUE TO ADDITIONAL POLYMERIZATION

Average initial volume of seed particles = 0.618 × 10^{-16} cc.

Final pol./ initial pol.	2.09	2.2	3.57	4.86	9.6	17.3	17.9	32.7	70.5
Final $\bar{v}$, cc. × 10^{16}	2.11	1.77	3.72	3.23	5.98	8.27	17.1	14.9	32.8
n_f/n_f[a]	0.62	0.77	0.60	0.94	0.99	1.29	0.65	1.35	1.33

[a] n_f/n_i = ratio of number of particles in the polymerized latex to the initial number present.

The first row gives the ratio of polymer present after the additional polymerization to that initially present due to the seed; while the second row gives the average volume of the particles after the additional polymerization.

From the ratio of the final number of particles present after additional polymerization to the number of particles originally added, third row, it is seen that, even when polymerization is carried out to increase the amount of polymer by as much as seventy-fold, the number of particles does not change by more than about 30%. The relatively small number of particles found in the first three charges probably results from unsatisfactory control in taking the electron microscope pictures. It has been found that very small particles of polystyrene sometimes become flattened due probably to heating in the gold shadowing process; when this happens, it can be detected by the appearance of the shadows.

Rate of Polymerization per Particle

Having established that it is possible to carry out polymerization of styrene in persulfate solutions seeded with polystyrene particles without substantially altering the number of particles, the next step is to determine the effects of the number and size of seed particles (polystyrene) on the rate of polymerization. For this investigation, four different polystyrene latices were prepared and the particle sizes of each determined from electron microscope pictures.

Typical data used in calculating the average particle volumes are given in Table II for the largest and smallest particle size latices.

TABLE II

POLYMER PARTICLE SIZES IN TWO POLYSTYRENE LATICES

Small		Large			
d × 48,000. cm.	No.	d × 48,000. cm.	No.	d × 48,000. cm.	No.
<0.10	2	0.35	1	0.59	5
.11	7	.38	0	.62	2
.14	7	.41	3	.65	7
.17	5	.44	0	.68	21
.20	19	.47	0	.71	31
.23	15	.50	1	.74	16
.26	36	.53	2	.77	7
.29	9	.56	1	.80	3
	100				100

v = 0.595 × 10^{-16} cc. v = 15.9 × 10^{-16} cc.

From these data the average values of the cube of the diameters were calculated and these in turn were used in calculating the average volumes. The standard deviation for the distribution of volumes indicated by the data for the small particle latex is 5.6%, so the probable error for the average volume obtained by measuring 100 particles is 3.8%. In like manner for the large particle latex the probable error for the average volume is 1.9%. Thus the errors introduced from lack of infinite sampling are small compared with other errors such as errors in measurement of the diameters of the individual particles.

In determining the rates of polymerization of styrene in the seed particles, the latices were diluted to varying extents with 0.175% potassium persulfate solution, additional styrene put in, and the rate of polymerization of the styrene determined. In a typical run 5 cc. of the diluted latex and 2 cc. of styrene were added to test-tubes which had been swept out with nitrogen (it was also usual practice to bubble nitrogen through the diluted latex and the styrene prior to using them for charging). After charging, the vapor space above the charge was swept out with nitrogen and the test tubes sealed off. They were placed on a rotating carriage in a water bath thermostated at 50°. Charged test-tubes were withdrawn at convenient intervals and the entire charge transferred to 100 cc. of methanol containing 2 cc. of a 5% aqueous solution of hydroquinone. The precipitated polymer was filtered, dissolved in benzene, reprecipitated with methanol, redissolved in benzene, frozen, dried on a vacuum line and the polymer weighed.

In a run to determine the rate of polymerization five or six charges were removed at convenient in-

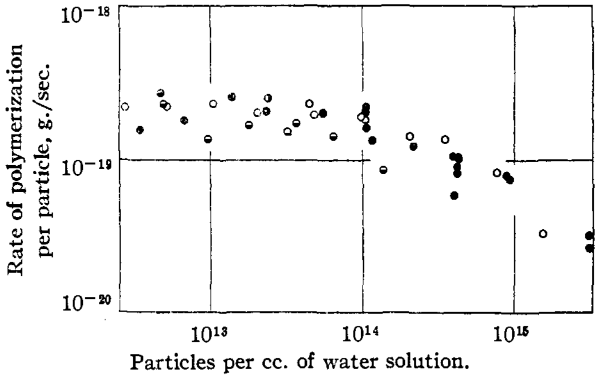

Fig. 1.—Rate of polymerization of styrene in a swollen polystyrene particle suspended in aqueous persulfate solution. Average vol. of particles: O, 0.595×10^{-16} cc.; ●, 0.618×10^{-16} cc.; ◑, 4.89×10^{-16} cc.; and ⊖, 15.9×10^{-16} cc.

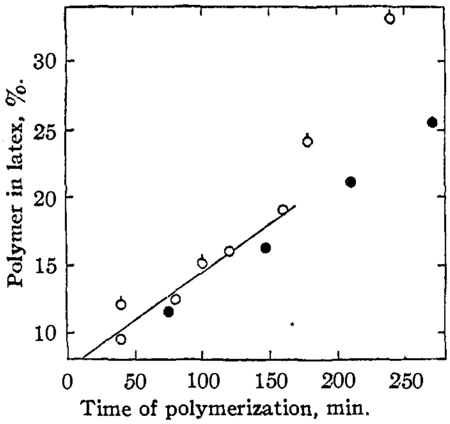

Fig. 2.—Effect of persulfate concentration on polymerization rate of styrene in seeded latex: O and ó, 4 times normal persulfate concn.; —, normal persulfate concn.; ●, $^1/_4$ times normal concn. (normal persulfate concn., 0.175%).

tervals. The polymer yields obtained were usually linear functions of the polymerization time, so the rate of polymerization was determined from the slope of the least squares straight line established by the data. From these rates, the size of the original seed particles, and the known original polymer content of the latex, the rate of polymerization of the styrene per seed particle was calculated. This rate is plotted against the number of seed particles per cc. of water solution (excluding the seed particles) in Fig. 1. The number of seed particles per cc. was varied over a thousand-fold range. For the lower concentrations of seed particles (below about 10^{14} per cc.), the rate of polymerization per particle is substantially constant but this rate decreases with increasing concentration of seed particles for the higher concentration region. This decrease is probably due to the inability of the styrene layer to supply monomer to the system rapidly enough to keep it in equilibrium. It is also seen from Fig. 1 that in the lower concentration range (below 10^{14} particles per cc.) not only is the rate of polymerization per particle independent of the concentration but it is independent of the size of the seed particles too.

To determine the effect of persulfate concentration on the rate of polymerization in a constant number of particles, a particular polystyrene latex was diluted with water solutions of potassium persulfate of three different concentrations, styrene was added and the rate of polymerization of the added styrene determined. The average volume of the particles in the seed latex was 9.02×10^{-16} cc. and dilution was such as to give a particle concentration of 1.35×10^{14} particles per cc. of water solution. Neglecting decomposition of the persulfate in the seed latex the three different dilutions gave persulfate concentrations of $^1/_4$, 1 and 4 times the normal (0.175%).

The data on polymerization of the styrene added to these diluted latices are given in Fig. 2. The least squares' straight line established by data on two duplicate runs is given for the normal concentration of persulfate; the slope of this line corresponds to a rate of polymerization of 1.34×10^{-19} g. styrene per sec. per particle, which is consistent with the data in Fig. 1. For the other two persulfate concentrations the individual points are given. It is evident that the persulfate concentration has no measurable effect on the initial rate of polymerization in polystyrene seed particles. The tendency toward increased rate with increased conversion in the case of the high persulfate run may be due to the formation of new particles which cannot be neglected when the persulfate concentration is high enough.

One variable which does affect the rate of polymerization per particle is the temperature, as would be expected. To obtain the temperature coefficient of the rate, a latex having particles with average volume of 0.595×10^{-16} cc. was diluted with persulfate solution (0.175%), so that the concentration of particles was about 5×10^{13} per cc. of water solution. To this diluted latex, styrene was added and its rate of polymerization measured at four temperatures. The rate of polymerization per particle was calculated, using the slope of the least squares straight lines established by the data. The results are given in Table III.

TABLE III

EFFECT OF TEMPERATURE ON RATE OF POLYMERIZATION OF STYRENE IN A SWOLLEN POLYMER PARTICLE

Temp., °C.	Rate of pol. per particle, g./sec.
30	0.593×10^{-19}
40	1.18×10^{-19}
50	2.00×10^{-19}
60	3.06×10^{-19}

These data give an activation energy of 11.7 kcal./mole.

Solubility of Styrene in Polymer Particles

It has been found experimentally that there is a certain finite solubility of styrene in polystyrene latex particles. Apparently this results from a balance between the effect on the styrene activity of the dissolved polymer and the effect of the interfacial tension of the very small particles.

To measure the equilibrium solubility a polystyrene latex was diluted with water containing 3% hydroquinone (to prevent polymerization) and an excess of styrene was added. The initial thickness of the styrene layer was measured; then the test-tube containing the charge was rotated end-over-end on a carriage in a water-bath thermostated at 50°. From time to time the test-tube was withdrawn and allowed to stand for a few minutes to permit separation of the excess styrene layer; then the thickness of the styrene layer was measured. Data on a typical experiment are given in Table IV.

TABLE IV

DETERMINATION OF SOLUBILITY OF STYRENE IN POLYSTYRENE LATEX

Charge: 10 cc. of diluted latex containing 1 g. of polystyrene, 2.5 cc. of styrene.

Time, hr.	0	0.75	1.75	3.75	5.75	22.25
Styrene layer thickness, mm.	16.0	12.5	9.6	6.5	5.0	5.0

The styrene layer decreased to a constant thickness. Interpreting the decrease as being due to solubility of the styrene in the polymer latex particles, the above data give, for the equilibrium solubility, 1.55 g. of styrene per gram of polystyrene.

In addition to this determination, similar experiments were made using two other dilutions of this latex and three dilutions of another latex having a slightly larger particle size. The results are summarized in Table V.

TABLE V

SOLUBILITIES OF STYRENE IN POLYSTYRENE LATEX (50°)

Size of latex particle	3×10^{-16} cc.			4.6×10^{-16} cc.		
Polymer in diluted latex, %	5	10	20	5	10	20
G. styrene/g. polymer	1.62	1.55	1.56	1.57	1.57	1.33

The same type of experiment was made on two other latices of considerably different particle sizes; the results on the four different latices studied are given in Table VI.

TABLE VI

EFFECT OF SIZE OF POLYSTYRENE PARTICLE ON SOLUBILITY OF STYRENE IN THE PARTICLE (50°)

Average volume of particle, cc. × 10^{16}	0.6	3	4.6	14
Solubility, g. styrene/g. polymer	1.2	1.6	1.5	1.9

This indicates a possible trend toward increasing solubility of styrene with increasing size of the polystyrene particle. Some similar experiments were carried out using excess soap which indicated a higher solubility (possibly about 2.5 g. of styrene per g. of monomer).

Formation of Free Radicals

The primary initiation step is still being studied so a more complete discussion will be given in a subsequent paper. At present, it appears that it must involve reaction of the persulfate since sulfur-bearing fragments of the persulfate have been shown to be attached to the polystyrene.[7] More recent quantitative data have shown that the number of sulfur atoms per polystyrene molecule is about two (providing no transfer agent is present).

Now the rate of polymer formation under typical conditions is substantially constant and the rate of reaction of the persulfate may be expected to be substantially constant since only a relatively small fraction of it reacts during polymerization,[2] so the ratio of sulfur to polymer in the polymer should be just equal to the ratio of the rate of chain initiation to the rate of polymerization. Thus, measurements of the rate of polymerization and sulfur content of the polymer should be sufficient to determine the rate of the initial persulfate reaction leading to chain initiation.

Such data have been obtained at two different temperatures. Charges were made using water containing 0.5% soap (S.F. Flakes) and about 0.171% potassium persulfate prepared from radioactive sulfur. The rate of polymerization of styrene added to this solution was measured and the ratio of the radioactivity of the polymer produced to that of the total latex was determined. The results obtained, together with the rates of the initiation reaction calculated from them, are given in Table VII.

TABLE VII

RATE OF CHAIN INITIATION IN EMULSION POLYMERIZATION OF STYRENE

Rates are given per cc. of water solution; *i. e.*, water plus soap plus persulfate.

Temp., °C.	Polymerization rate, g./cc. × sec.	Moles sulfur per g. pol.	Initiation rate, moles/cc. × sec.
70	1.56×10^{-4}	1.62×10^{-6}	2.52×10^{-10}
90	4.03×10^{-4}	6.95×10^{-6}	2.80×10^{-9}

Extrapolation of these data to 50° gives 1.4×10^{13} free radicals per sec. per cc. of water solution for the rate of production of free radicals assuming one free radical produced for each atom of sulfur in the polymer.

Number of Particles

Having investigated the factors which determine the rate of polymer formation in a single swollen polymer particle, the next and final step in working out the kinetics of the polymerization is to investigate the laws governing how many polymer particles are formed. In view of the importance of the soap micelles in forming polymer particles, the effect of soap concentration on the number of particles formed was first investigated.

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(7) W. V. Smith and H. N. Campbell, *J. Chem. Phys.*, **15**, 339 (1947).

In most of the runs, the persulfate concentration was 0.175% (based on the water). The amount of styrene used was such as to give an emulsion containing 35% styrene. The polymerization temperature was 50°. Polymerization was carried to about 90–95% conversion of the styrene to polystyrene. The number of particles formed was obtained by determining the polymer content of the latex and the average volume of the polystyrene latex particles. The results are shown in Fig. 3, where the number of particles formed per gram of soap is plotted against the concentration of soap in the water solution used for preparing the emulsion. The straight line in the figure having a slope of $-{}^2/_5$ths will be referred to in the Discussion. From this figure, it is evident that a given weight of soap is more effective in forming particles in a dilute than in a concentrated solution.

The effect of persulfate concentration on the number of particles produced by a 1% soap solution emulsifying styrene is given in Table VIII. Also in the table are the number of particles produced relative to those produced by the concentration of persulfate normally used (0.175%); the last row gives the relative number calculated from a simple theory of particle formation (see Discussion).

TABLE VIII

EFFECT OF INITIATOR CONCENTRATION ON NUMBER OF PARTICLES PRODUCED BY A GRAM OF SOAP AT 50°

Persulfate concentration, %	0.70	0.175	0.044
Particles/g. soap × 10^{-17}	1.37	0.805	.498
Relative number	1.70	1	.62
Theoretical relative number	1.74	1	.58

Increase in temperature increases the number of particles formed, as is shown by the data in Table IX for two different soap concentrations.

TABLE IX

EFFECT OF TEMPERATURE ON NUMBER OF PARTICLES

Soap concentration, %	Particles per g. soap 30°	50°	Ratio 50/30
1	3.8×10^{16}	8.1×10^{16}	2.1
1	2.3×10^{16}	6.8×10^{16}	3.0
0.333	4.2×10^{16}	10.2×10^{16}	2.4

For the 1% soap concentration two different comparisons between 30 and 50° are given. Usually in these particle size investigations experiments run simultaneously give better comparisons than those run at different times, due no doubt to unintentional lack of proper control of some important variables.

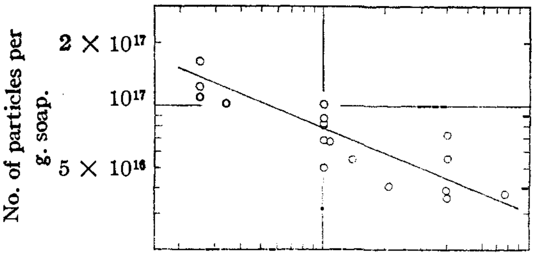

Fig. 3.—Effect of soap concentration on number of polystyrene particles formed in emulsion polymerization.

Discussion

The fact that the rate of polymerization of styrene per polymer particle is so nearly independent of the main variables (except temperature) is a very strong indication that the styrene emulsion polymerization system is an example of the Case 2 of emulsion polymerization discussed by Smith and Ewart.[6] Thus, the simple situation exists in which one-half the polymer particles present possess a single growing free radical while the remainder possess none. The rate of polymerization per particle should be simply one-half the chain propagation constant times the concentration of monomer in the particle. The chain propagation constant is the specific reaction rate constant for the reaction

$$M_n^{\cdot} + M \xrightarrow{k_p} M_{n+1}^{\cdot}$$

where $M_n^{\cdot}$ is a growing polymer free radical containing n monomer units and M is the monomer. From Fig. 1, it is seen that the rate of polymerization per particle in the region in which this rate is substantially constant is 2.0×10^{-19} g. of styrene per second. This corresponds to 2300 molecules of styrene per second per free radical at 50°. The concentration of the styrene in a swollen polymer particle can be estimated from the studies on solubility of styrene in polystyrene latex discussed above. A monomer polymer ratio of 1.6 g. of styrene per g. of polystyrene corresponds to a styrene concentration of 5.9 moles per liter. It is probable that, in the region of particle concentration of Fig. 1 in which the rate of polymerization is constant, the polymer particles approach saturation with respect to styrene; however, in the region of higher concentration where the rate per particle becomes less, it is probable that the particles are not saturated, thus accounting for the lower rate. This chain propagation constant calculated from the rate per free radical and the saturation styrene concentration is 2300/5.9 = 390 l. mole⁻¹ sec.⁻¹ at 50°. Combining this value with the activation energy found from the data of Table III, the expression for the chain propagation constant is

$$k_p = 3.5 \times 10^{10} e^{-11{,}700/RT} \text{ l. mole}^{-1}\text{ sec.}^{-1}$$

The frequency factor is within about a factor of 10 of that expected from collision theory. This is in contrast to the propagation constant for vinyl acetate obtained by Burnett and Melville[8] from photopolymerization studies; they report a frequency factor which is 10^{-5} times that expected

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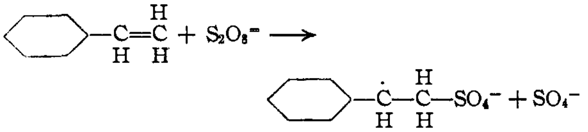
(8) G. M. Burnett and H. W. Melville, *Proc. Roy. Soc. (London)*, **189**, 456 (1947).

from collision theory. M. S. Matheson[9] from photopolymerization studies reports $k_p = 36$ at 30° and 173 at 60°, giving an activation energy of 10.5 kcal. This activation energy is in satisfactory agreement with that obtained in this investigation though his value of the chain propagation constant at 30° is about a factor of 3 smaller than that obtained here. Bamford and Dewar[10] report an even smaller value, 4.5 at 25° for the propagation constant; however, from the same data they obtain a transfer constant of 3×10^{-4} for styrene radical transferring with styrene monomer; from the molecular weights obtainable in styrene polymerization, particularly in emulsion, this transfer constant is unreasonably high.

In making the calculation of the propagation constant the concentration of styrene, rather than its activity, was used. This is in accord with the statistical considerations of Flory[11] rather than the suggestion of Walling, *et al.*,[12] though using the activity would give better agreement with values for the propagation constant obtained by the other methods.

The initiation step is still under investigation. At present, it appears to involve both the persulfate and the styrene. A possible reaction is



The probable locus of this reaction is the water solution.

Now if free radicals are entering polymer particles as rapidly as they are being formed, *i. e.*, $\sim 10^{13}$ per sec. per cc. of water, and if there are 10^{14} polymer particles per cc. of water, then on the average there will be an interval of ten seconds between successive entrances of free radicals in a given particle. Consequently, it is pertinent to ask whether 2 or more free radicals can exist together in the same particle for times of the order of ten seconds. By assuming that free radicals in a swollen polymer particle will terminate at a rate comparable to that in the bulk polymerization of styrene, one can estimate the average lifetime for two radicals in the same particle. If there are m molecules of monomer and r free radicals present in a bulk polymerizing system which gives polymer with a degree of polymerization P, then the ratio of the propagation constant, k_p, to the termination constant, k_t, is given by (assuming no transfer)

$$k_p/k_t = Pr/m$$

But the over-all rate of polymerization is

$$\mathrm{d}m/\mathrm{d}t = r\sigma$$

where σ is the rate of polymerization per free radical; so

$$k_p/k_t = (P/\sigma)(\mathrm{d}\ln m/\mathrm{d}t)$$

Gregg[13] has determined values for P and $\mathrm{d}\ln m/\mathrm{d}t$ for several concentrations of benzoyl peroxide as initiator in bulk styrene polymerization and the product $P \times \mathrm{d}\ln m/\mathrm{d}t$ is quite constant when a small correction for chain transfer is made; the product has a value of 7.7×10^{-3} sec.$^{-1}$ at 60°. The value of σ can be estimated from the value for the chain propagation constant discussed above; thus one obtains $k_p/k_t = 1.3 \times 10^{-6}$ at 60°. Using this to estimate the termination constant, the average lifetime for two free radicals in the same polymer particle is estimated to be of the order of 0.5×10^{-3} sec. This estimate is probably too large because it is based on data for termination of two relatively large free radicals. Actually, since the average time between successive additions of monomer units to a free radical is of the same order of magnitude, when a second free radical enters a polymerizing particle it cannot react with many styrene units before it terminates with the radical already present. Thus, termination probably involves reaction between a large free radical and a small one containing no more than one or two styrene units.

It is somewhat more difficult to discuss the situation in the water solution outside of the particles but a few qualitative considerations are probably instructive. It has been shown above that free radicals enter polymer particles at the rate of about 10^{13} per second per cc. of water solution. Professor P. Debye has pointed out to the author that if their rate of entrance is simply a diffusion process, then the diffusion current, I, into a particle of radius r is

$$I = 4\pi r D n_0$$

where D is the diffusion constant of the free radical through the water and n_0 is the concentration of free radicals in the water. Letting $r = 3 \times 10^{-6}$ cm., $D = 10^{-5}$ cm.^{2}/sec. and $I = 10^{-1}$ radicals per second, and solving for n_0 gives $n_0 \cong 10^8$ free radicals per cc. of water solution. Actually, the concentration will probably be higher since both the particles and the free radicals are negatively charged, but, in any case, it is quite probable that when there are of the order of 10^{14} polymer particles present per cc. of water solution there are many more free radicals in polymer particles than in the water solution.

Assuming a steady state concentration of 10^8 free radicals per cc. of water solution and a rate of entrance into polymer particles of 10^{13} sec.$^{-1}$, a given free radical will exist in the water solution for only 10^{-5} seconds, which is much too short a time for it to react with one of the styrene molecules dissolved in the water. Also, it is very much too short a time for it to react with another of the free radicals in the water solution. Therefore, sub-

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[9] M. S. Matheson, unpublished data obtained in these laboratories.

[10] C. H. Bamford and M. J. S. Dewar, *Nature*, **157**, 845 (1946).

[11] P. J. Flory, *J. Chem. Phys.*, **12**, 425 (1944).

[12] C. T. Walling, E. R. Briggs and F. R. Mayo, THIS JOURNAL, **68**, 1145 (1946).

[13] R. A. Gregg, unpublished data obtained in these laboratories.

stantially none of the free radicals produced in the water will be terminated there but practically all will enter polymer particles; moreover, they will enter them while the free radicals are still small, containing not more than one or two styrene units.

It is evident that increasing the rate of free radical formation in the aqueous solution without changing the number of particles will decrease the interval between successive entrances of free radicals into a particle. While this will not affect the rate of polymerization, it will decrease the degree of polymerization. Also, if the rate of free radical formation is kept constant while the number of particles is increased, for example, by using a high soap concentration, then the degree of polymerization will be increased, as also will the rate. This possibility of simultaneous increases in rate and degree of polymerization is the most striking difference between emulsion and bulk polymerization.

The process of formation of new polymer particles by the diffusion of free radicals from the water solution into styrene dissolved in micelles has been discussed by Smith and Ewart.[6] They show that the total number of particles formed per cc. of water up to the time that all of the soap has become adsorbed on polymer particles should be given by a law of the type

$$N = k(\rho/\mu)^{2/5}(a_s S)^{3/5}$$

where k is a numerical constant with a value between 0.37 and 0.53, ρ is the rate of formation of free radicals, μ is the average rate of increase in volume of a particle due to polymerization, a_s is the interfacial area occupied by one gram of soap, and S is the total amount of soap associated with one cc. of water.

This law may be tested by calculating N from the other quantities in the equation. The value of ρ has already been given as about 1.4×10^{13} free radicals per second per cc. of water. The value of μ may be estimated from the rate of polymerization of a particle. The average rate is about 2.0×10^{-19} g. per second, but each gram of polystyrene produced will dissolve about 1.6 g. of styrene, so the rate of increase in volume of a particle will be $\mu = 2.0 \times 10^{-19} \times 2.6 = 5.2 \times 10^{-19}$ cc. per second (assuming a density of 1). The value of a_s may be taken as that given by X-ray evidence in the soap micelle.[5] This value is 28 sq. Å. per molecule or 6×10^6 sq. cm./g. Using the lower value for k (0.37) and a soap concentration of 1%, the calculated number of particles is

$$N = 0.37\left(\frac{1.4 \times 10^{13}}{5.2 \times 10^{-19}}\right)^{2/5}(6 \times 10^6 \times 10^{-2})^{3/5}$$
$$= 10^{15} \text{ particles per cc. of water}$$

or the number of particles per gram of soap at 1% soap concentration is 10^{17}. Comparison with the data shown in Fig. 3 shows this calculated value to be in good agreement with the experimental number.

Regarding the effect of the principal variables, this law predicts that the number of particles produced per gram of soap should be inversely proportional to the $^2/_5$ths power of the soap concentration as signified by the line in Fig. 3, which has a slope of $-^2/_5$.

Assuming that the rate of formation of free radicals, ρ, is proportional to the persulfate concentration, this law predicts that the number of particles should vary as the $^2/_5$ths power of the persulfate concentration. The last row in Table VIII gives the predicted $^2/_5$ths power variation in terms of the number of particles relative to the number produced by the normal (intermediate) concentration.

In conclusion, it may be well to review the important factors which permit such high rates of polymerization in emulsion. We have seen that the rate of formation of free radicals under typical conditions in styrene emulsion is of the order of 10^{13} per second per cc. of water. Now, if the termination of these took place as in bulk styrene polymerization with a specific reaction rate constant of 10^{-12} cc. molecule^{-1} sec.$^{-1}$, the concentration of free radicals under steady state conditions would be limited to about 10^{12} free radicals per cc., whereas actually the concentration of polymer particles and hence of free radicals may be as high as 10^{15} per cc. These can exist together without terminating because they are in isolated particles. In the early stages of the polymerization, the micelles serve this important function of supplying isolated loci for free radicals to cause polymerization. Thus, the polymer particles and soap micelles serve as very effective traps for catching and holding free radicals. They also keep the free radicals supplied with a relatively high concentration of monomer compared with the water solution. This effect of emulsifying agent in interfering with termination of growing free radicals has been pointed out by Evans and co-workers[14] who state "increasing the concentration of emulsifying agent increased the rate of reaction; this was traced to the effect of emulsifying agent upon $(k_p/k_t)^{1/2}$ and is consistent with a decrease in the coagulation constant k_t." However, the suggestion which has frequently been made that the high viscosity of the locus of reaction (polymer particle) results in a decrease in the termination reaction is probably not even true and certainly it has practically no bearing on the high reaction rate and high molecular weight obtainable in emulsion. While the termination constant plays an integral role in determining the kinetics of bulk polymerization, the kinetics of emulsion polymerization does not involve the termination constant at all, providing it is large enough, as it is in the case of styrene.

Summary

In aqueous emulsions containing relatively few

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[14] J. H. Baxendale, M. G. Evans and J. K. Kilham, *J. Polymer Sci.*, **1**, 466 (1946).

polymer particles the rate of polymerization of styrene is proportional to the number of polymer particles present and is in dependent of the persulfate concentration. This can best be interpreted as indicating that the average number of free radicals per particle is a constant and equal to one-half. Thus from the rate of polymerization per particle and the concentration of monomer in the particle reported herein, the chain propagation constant for styrene has been calculated to be $3.5 \times 10^{10} \exp(-11{,}700/RT)$ l. mole^{-1} sec.$^{-1}$.

A study of the number of polymer particles produced has shown that the factors favoring production of a large number of particles are high soap concentration, high persulfate concentration and high temperature. The number of particles produced agrees satisfactorily with the theoretical law.

$$N = k(\rho/\mu)^{2/5}(a_sS)^{3/5}$$

where N is the number of particles formed per cc. of water up to the time that the soap is completely adsorbed on the polymer particles, k is a numerical constant with a value between 0.37 and 0.53, ρ is the rate of formation of free radicals per cc. of water solution, μ is the rate of increase in volume of a polymerizing swollen polymer particle, a_s is the interfacial area occupied by one gram of adsorbed soap when micelles are present and S is the initial concentration of the soap in the aqueous phase.

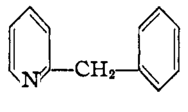
PASSAIC, NEW JERSEY RECEIVED APRIL 20, 1948

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, MASSACHUSETTS INSTITUTE OF TECHNOLOGY]

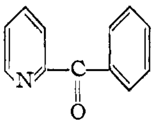
Beckmann Rearrangement of the Oximes of Phenyl 2-Pyridyl Ketone (2-Benzoylpyridine)

BY ERNEST H. HUNTRESS AND HENRY C. WALTER[1,2,3]

2-Benzoylpyridine (II), easily obtained from 2-benzylpyridine (I) by oxidation, was first oximated by Tschitschibabin,[4] who isolated different forms melting at 150–152° and 165–167°, respectively, but made no attempt to establish their configurations. From the observation that the lower melting form gave colored complexes with metal salts whereas the higher melting form did not, Tschugaeff[5] surmised that the former might be the *anti*-phenyl stereomer (III); the higher melting, the *syn*-phenyl stereomer (V).



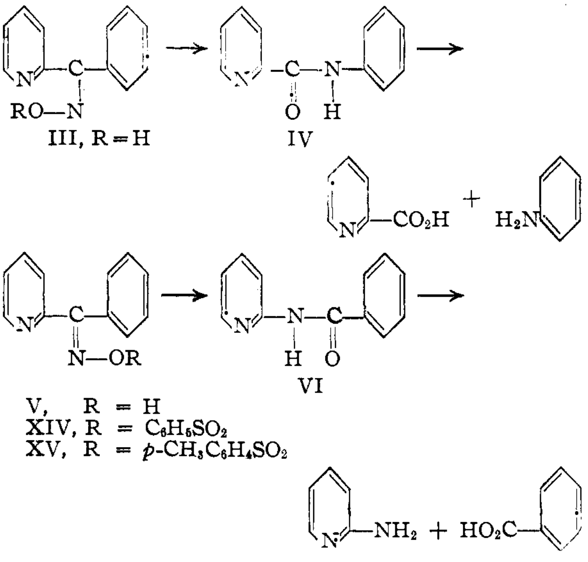
I



II

In 1930 Pfeiffer and Buchholz[6] suggested a nitrone structure for the complex salts of the lower melting form. No other work on these oximes has been reported.

In the light of modern views of the Beckmann rearrangement, including that of the *trans* interchange of radicals, a study of this reaction of these stereomers seemed of value. Rearrangement of the *syn*-phenyl stereomer (V) should yield 2-(benzoylamino)-pyridine (VI) hydrolyzable to benzoic acid and 2-aminopyridine. Similarly, the *anti*-phenylsteromer (III) should yield picolinic anilide

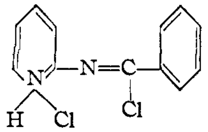


III, R = H

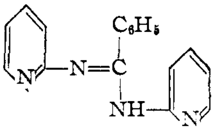
IV

VI

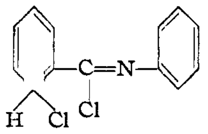
V, R = H
XIV, R = $C_6H_5SO_2$
XV, R = p-$CH_3C_6H_4SO_2$



VII



VIII



IX

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[1] This paper is constructed from part of a dissertation submitted by Henry C. Walter to the Faculty of the Massachusetts Institute of Technology in September, 1946, in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

[2] Present address: E. I. du Pont de Nemours, Jackson Laboratory, P. O. Box 525, Wilmington, Delaware.

[3] du Pont Fellow, June-December, 1943; November, 1945–June, 1946.

[4] Tschitschibabin, *J. Russ. Phys.-Chem. Soc.*, **33**, 700 (1901); *Chem. Zentr.*, **73**, I, 206 (1902).

[5] Tschugaeff, *Ber.*, **39**, 3382 (1906).

[6] Pfeiffer and Buchholz, *J. prakt. Chem.*, [2] **124**, 137 (1930).