and the hydrolysis was allowed to proceed for twenty-four hours. Another drop of β-amylase was then added and the mixture was allowed to remain at room temperature for another twenty-four hours. The reducing value was then determined by oxidation with ferricyanide[9,10] and calculated as maltose.

The amount of polysaccharide originally present in the sample was found by determining the glucose obtained when a 2-ml. aliquot portion was treated with 1 *N* sulfuric acid for two and one-half hours at 100°. On this basis, the extent of the amylopectin hydrolyzed with β-amylase to maltose was estimated to be 63.5%. The limit of amylose hydrolysis with this enzyme was 90%.

Acknowledgment.—The authors are grateful to the Corn Industries Research Foundation for their support of this work, and to Dr. A. K. Balls for the crystalline β-amylase.

Summary

Apple starch was separated into amylose and amylopectin, the amylose content being 24.8% of the total. Osmotic pressure measurements of the acetylated fractions gave a number-average molecular weight of 160,000 (560 glucose residues) for the acetylated amylose and 1,200,000 (4200 glucose residues) for the acetylated amylopectin.

End-group determination by periodate oxidation showed an average of 24 glucose residues per end-group for the amylopectin and a chain-length of 530 glucose residues for the amylose. Since the end-group value for amylose is in fair agreement with the value of 560 obtained from osmotic pressure measurements, it is assumed that a single chain represents one amylose molecule.

The data indicate that apple starch is similar in structure to the cereal and tuber starches, with the difference that the molecular weights of its components are smaller.

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[9] W. Z. Hassid, *Ind. Eng. Chem., Anal. Ed.*, **9**, 228 (1937).

[10] W. Z. Hassid, R. M. McCready and R. S. Rosenfels, *ibid.*, **12**, 142 (1940).

[CONTRIBUTION NO. 96 FROM THE GENERAL LABORATORIES OF THE UNITED STATES RUBBER COMPANY]

Chain Initiation in Styrene Emulsion Polymerization[1]

BY WENDELL V. SMITH

Introduction

The chain length and rate of polymerization in emulsion are controlled principally by the relationship between two quantities, the rate of chain initiation and the rate of chain propagation. In contrast with bulk polymerization, the rate constant for the termination step does not play a significant role in the mechanism of emulsion polymerization.[1a] The rate of chain propagation in styrene polymerization has already been considered[1a] and this paper discusses the rate of the initiation step in styrene polymerization.

Three methods are used for investigating the rate of initiation. The first is based on the observation that fragments of the chain initiator, persulfate, are chemically combined with the polymer.[2] It consists in determining how rapidly these fragments become combined by measuring the rate of polymerization and the radioactivity of polystyrene prepared using radioactive persulfate as initiator. The second consists in determining the initial rate of polymer particle formation from measurements of the size of the particles and the rates of growth of the particles, making use of a previously developed theory relating these.[1a] The third consists in determining the rate of molecule formation from the molecular weight of polymer and the rate of polymerization.

Experimental Procedures

Radioactive Potassium Persulfate.—The radioactive S^{35} was received as a trace constituent of potassium chloride from Clinton Laboratories (now Oak Ridge National Laboratory) on allocation by the U. S. Atomic Energy Commission.

The active sulfur in the irradiated unit was isolated as barium sulfate by boiling with bromine in water solution then precipitating with barium ion. The barium sulfate (1.3 mg.) was converted to sulfate free potassium persulfate by dissolving in concentrated sulfuric acid, adding potassium sulfate and electrolyzing cold. The precipitated potassium persulfate after washing and drying (0.35 g.) contained 12% of the total sulfur; it was made up to a 1.81% solution. After the preliminary measurements the persulfate was regenerated by a new electrolysis at which time it was further diluted with inactive sulfur.

Determination of Sulfur Content of Polystyrene from its Radioactivity.—All radioactivities were determined using a Radiation Counter Laboratories thin mica window Geiger–Müller counter tube and scaling circuit.

The resolving time[3] of 2.5×10^{-4} sec. requires a correction of only 0.25% for a counting rate of 10 per sec.

The range of the β-radiation from S^{35} is quite

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[1] Presented at the North Jersey Section Meeting-in-Miniature, January 10, 1949, Newark, N. J.

[1a] W. V. Smith and R. H. Ewart, *J. Chem. Phys.*, **16**, 592 (1948); W. V. Smith, THIS JOURNAL, **70**, 3695 (1948).

[2] W. V. Smith and H. N. Campbell, *J. Chem. Phys.*, **15**, 338 (1947); W. E. Mochel and J. H. Peterson, THIS JOURNAL, **71**, 1426 (1949).

[3] A. F. Reid, A. S. Weil and J. R. Dunning, *Anal. Chem.*, **10**, 824 (1947).

short; Libby[4] gives the aluminum range as 13.5 mg./sq. cm. Thus for active samples which are appreciably thicker than this, the radiation escaping from unit surface is independent of the thickness of the sample and, for a given concentration, depends only on the absorption characteristics of the material comprising the sample.

For this investigation the absorption characteristics of the materials comprising the samples are characterized sufficiently when a relationship is determined between the radiation from an infinitely thick sample (*i. e.*, thickness greater than the range) and that from a sample thin enough that absorption of radiation within the sample can be neglected. Thus, if I_0 is the radiation from a mass, m, of sample thin enough that self-absorption can be neglected, and if I_∞ is the radiation from an area, A, of the sample which has a thickness greater than the range of the radiation in the sample, then there exists a relation

$$I_0/m = \alpha I_\infty/A$$

where α is a characteristic of the absorption of the material.

The value of α for water as defined by the above equation was determined as follows: A water solution of the active persulfate (0.02 mg./ml.) was placed in an aluminum dish 1 inch in diameter giving a sample thickness of 300 mg./sq. cm. The radiation intensity from the surface of the sample escaping through a circular window 1 cm. in radius was

$$I_\infty/A = (3.176 - 0.394)/\pi = 0.886 \text{ cm.}^{-2} \text{ sec.}^{-1}$$

where 3.176 sec.$^{-1}$ was the rate of reception of impulses by the counter when the sample was in place and 0.394 sec.$^{-1}$ was the background rate. Next a sample of the solution was evaporated to dryness in an aluminum dish, giving a film of thickness 0.02 mg./sq. cm., which was thin enough to neglect self-absorption. The intensity of radiation obtained from this gave

$$I_0/m = (15.5 - 0.4)/100 = 0.151 \text{ mg.}^{-1} \text{ sec.}^{-1}$$

Thus for water

$$\alpha_w = 0.151/0.886 = 0.170 \text{ cm.}^2/\text{mg.}$$

To compare the absorption of polystyrene with that of water a sample of polystyrene was prepared in emulsion using radioactive potassium persulfate. This active sample, polymer A was mixed with 32 parts of a low molecular weight inactive polystyrene. A portion of the mixed benzene solution was evaporated to dryness in an aluminum dish to give a polystyrene film of thickness 56 mg./sq. cm. The intensity of radiation from this film measured through a 1-cm. radius window gave for the undiluted polymer A

$$I_\infty/A = 33(1.337 - 0.338)/\pi = 10.5 \text{ cm.}^{-2} \text{ sec.}^{-1}$$

For measuring the radiation from a thin film of the polymer a film containing 0.853 mg. of the undiluted polymer A was used. Since the thickness of this film was 0.17 mg./sq. cm. it was necessary to apply a small correction for self-absorption. This was done assuming exponential absorption so that the intensity I from area A of a film of thickness l is given by

$$I/A = (I_0/m) \int_0^l e^{-\alpha l}\, dl$$

For sufficiently small values of αl this gives

$$I_0/m = (I/m)\,(1 + \alpha l/2)$$

For

$$\alpha = 0.17 \text{ cm.}^2/\text{mg.}$$

and

$$l = 0.17 \text{ mg./cm.}^2$$

the correction factor is 1.015 so

$$I_0/m = 1.015\,(1.826 - 0.338)/0.853 = 1.77 \text{ mg.}^{-1} \text{ sec.}^{-1}$$

Thus

$$\alpha_p = 1.77/10.5 = 0.169 \text{ cm.}^2/\text{mg.}$$

which is practically the same as that found for water.

The value of the "absorption coefficient," α, found for water and polystyrene in this investigation is considerably smaller than the value of 0.32 sq. cm./mg. reported by Henriques[5] and co-workers for absorption in benzidine sulfate. It is believed that this difference reflects largely the different techniques used in determining the "absorption coefficient" rather than different absorption characteristics of the polystyrene or water and benzidine sulfate.

The comparison between water and polystyrene in this investigation was made using a continuous film of the polymer in the radiation measurements. However, for the subsequent measurements of the activities of different polymer samples it was more convenient to determine the activity of the polymer when it was in the form of a fine powder, as that is the condition in which it was isolated from the latex. Consequently a series of comparisons was made of the intensity of radiation from the same polystyrene in a continuous film and in powder form. These comparisons consistently showed that the radiation from the film was less than that from the powder, giving the relation: activity of film = 0.965 × activity of powder. This correction factor was used in all calculations.

The sulfur contents of the active polymers were determined by making a direct comparison between the activity of the purified polymer and that of the over-all latex. Since the total sulfur content of the latex was known from the ingredients comprising the charge, the sulfur content of the polymer was calculated from the ratio of the activities. Errors due to fluctuations in the sensitivity of the counting mechanism were minimized by counting the polymer and latex with a minimum time interval between measure-

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(4) W. F. Libby, *Anal. Chem.*, **19**, 2 (1947).

(5) F. C. Henriques, Jr., G. B. Kistiakowsky, C. Margnetti and W. G. Schneider, *Ind. Eng. Chem.*, *Anal. Ed.*, **18**, 349 (1946).

ments. With the very low activity polymer produced at 30.5° the counting rate with the sample in the counter was only slightly greater than the background, so a long series of alternate counting with and without the sample in place was made.

Polymerization.—The polymers used for the radioactivity determinations were made separately from those used for polymer yield and molecular weight determinations to avoid unnecessary manipulations with active polymer. A typical charge was made up by adding to a test-tube: 3.00 ml. of a 0.55% (by weight) S. F. Flakes soap solution, 0.300 ml. of a 1.81% radioactive potassium persulfate solution and 2.00 ml. of distilled styrene. The test-tube and charge were cooled with ice and the vapor space swept out with nitrogen, after which the test-tube was sealed. The charge was then placed on a rotating carriage in a water-bath thermostated at the desired temperatures until substantially complete polymerization had taken place. The test-tube was opened and a 1-ml. portion of latex was diluted with 100 ml. of water, then flocculated by addition of hydrochloric acid. After warming, filtering and washing with water and methanol, the polymer was dried on the filter by radiation with an infrared lamp while air was simultaneously sucked through it. It was then ready for comparing its radioactivity with that of a sample of the original latex as described above.

The method of purification proved to be quite important for obtaining significant results. Thus the first procedure investigated consisted in coagulating by adding the latex to a large amount of methanol, then dissolving the precipitated polymer in benzene and reprecipitating with methanol. However, when this method was tested on latex prepared from inactive potassium persulfate, but to which active persulfate was added after polymerization, the polymer was found to be active and no amount of subsequent purification would render it appreciably less active. In contrast, when this same experiment was done using the method of purification finally adopted as described above the dried polymer was inactive.

The charges used for rate of polymerization and molecular weight determination were made up practically the same as those described above. However, they were coagulated by transferring the entire charge to 100 ml. of methanol containing 2 ml. of a 5% aqueous solution of hydroquinone as a short-stop. The precipitated polystyrene was filtered, washed twice with boiling methanol, then dried overnight on a vacuum line. Representative data on polymerization time and polymer yield for the series used in comparing with the radioactivity measurements are given in Table I. The last time in each sequence corresponds with the time used for polymerizing the samples with radioactive persulfate.

TABLE I

RATES OF STYRENE EMULSION POLYMERIZATIONS

30.5°; 0.5% soap; 0.172% persulfate

Time, min.	60	120	180	240	300	330
G. polymer per ml. water	0.0177	0.0357	0.0807	0.120	0.164	0.182
Intrinsic viscosity	8.39	11.9	15.6	16.1	17.4	17.3

50°

Time, min.	30	60	90	120	150	180	240
G. polymer per ml. water	0.0314	0.0854	0.194	0.269	0.366	0.440	0.482
Intrinsic viscosity	5.82	7.60	8.83	9.23	9.72	9.63	9.01

70°

Time, min.	10	20	30	40	50	60	90
G. polymer per ml. water	0.074	0.175	0.273	0.357	0.452	0.48	0.51
Intrinsic viscosity	4.28	4.80	5.38	5.05	5.29	5.07	3.86

90°

Time, min.	5	10	15	20	25	30
G. polymer per ml. water	0.095	0.244	0.364	0.458	0.497	0.505
Intrinsic viscosity	1.25	1.36	1.43	1.42	1.39	1.42

From the last charge of each sequence a small quantity of latex was saved for particle size determination, which was done by means of electron microscope photographs of the particles. For each latex examined the diameters of 100 particles were measured. From these diameters the average volume of the particles was calculated and used with the polymer yield to calculate the number of particles per ml. of water solution.

Molecular Weight.—The molecular weights were estimated from intrinsic viscosities which were determined in benzene, using a Fenske viscometer. A single concentration of polystyrene was used and the intrinsic viscosity was calculated from the relation

$$\eta_{sp}/c_v = [\eta] + 0.375[\eta]^2 c_v$$

where c_v is the concentration of the polymer in grams per 100 ml. of solution.

The relationship between intrinsic viscosity and molecular weight for polystyrene prepared in oil phase[6] has been established over a molecular weight range from 10^4 to 6×10^5. Since most of the polymers in the present investigation had molecular weights above this range, extrapolation of the relationship was carried out using Debye's theory of solution viscosities.[7] In Debye's theory the relationship between intrinsic viscosity and molecular weight can be represented by the conventional equation

$$[\eta] = KM^a$$

where the exponent, a, is substantially constant over a limited molecular weight range but decreases slowly to a value of $^1/_2$ as the molecular weight increases. Debye has established the nature of the relation between a and molecular weight. Thus, the procedure used was to fit the above equation to the experimental data,[6] then to extrapolate using Debye's calculated relationship between a and molecular weight. While leaving much to be desired, this method of estimating the molecular weight appeared to be the best available. The low molecular weight polystyrene prepared in emulsion at 90° had the same relationship between intrinsic viscosity and osmotic molecular weight as the polymers referred to above[6]; thus, the emulsion process of polymerization does not produce any particularly unusual molecular weight distribution.

Results

The first step in the investigation consisted in determining how many atoms of sulfur are com-

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(6) Mayo, Gregg and Matheson, to be published; also see R. H. Ewart and H. C. Tingey, paper presented at 111th meeting of A. C. S., April, 1947.

(7) P. Debye, *J. Chem. Phys.*, **14**, 636 (1946); P. Debye and A. M. Bueche, *ibid.*, **16**, 573 (1948).

bined with one molecule of polymer. The results are given in Table II.

TABLE II

SULFUR CONTENTS OF POLYSTYRENE POLYMERIZED WITH RADIOACTIVE PERSULFATE

Temp., °C.	Activity of pol., % of that of latex	G. polymer per mole sulfur	Mol. weight	Atoms of sulfur per polymer molecule
		0.5% soap; 0.165% persulfate		
30.5	0.281	43.5 × 10^6	20 × 10^6	0.46
50	2.70	4.52 × 10^6	6.2 × 10^6	1.4
70	19.9	0.62 × 10^6	1.4 × 10^6	2.3
90	85.1	0.144 × 10^6	0.274 × 10^6	1.9
		0.5% soap; 0.511% persulfate		
70	12.4	0.33 × 10^6	0.53 × 10^6	1.6
		2.0% soap; 0.165% persulfate		
70	11.7	1.05 × 10^6	2.1 × 10^6	2.0

The sulfur content in column 3 is obtained from the radioactivity of the polymer as discussed above. The molecular weight is obtained from the intrinsic viscosity of the last sample in each sequence of Table I. This intrinsic viscosity was converted to number average molecular weight as described above. The last column giving the atoms of sulfur per polymer molecule is, of course, the quotient of the two preceding columns. This quotient approximates two for the higher temperature polymers but is much less than that for the polymer prepared at 30°.

The number of particles produced in the emulsion polymerization of styrene depends primarily on the rate of particle formation, the rate of particle growth and the amount of soap available. A previous approximate discussion of this problem[1a] indicates that the number N, of polymer particles produced per ml. of water solution up to the time that all the soap becomes adsorbed on polymer particles should be given by a law of the type

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

where k is a numerical constant with a value between 0.37 and 0.53, ρ is the initial rate of formation of polymer particles per ml. of water solution, μ is the rate of increase in volume of a polymerizing polymer particle, and (a_sS) is the interfacial area of the initial soap micelles per ml. of water solution. Thus measurements of the number of particles and rate of polymerization should yield information on the initial rate of formation of polymer particles. The second column of Table III gives the average volumes of the polymer particles produced in the last sample of each sequence of runs listed in Table I.

From this volume and the polymer content of Table I the number of particles per ml. is calculated and given in column 3. From the polymer content as a function of time given in Table I, the rate of polymerization is calculated by fitting the data (except for the high conversions) with a least-squares straight line. This rate divided by the number of particles gives the rate of polymerization per particle given in column 4. The value of the initial rate of particle formation given in the last column is calculated from the equation given above. In making the calculation the lower value of k, namely, 0.37, was used. The interfacial area for soap micelles was taken to be 6 × 10^6 cm.^{2}/g. The rate of polymerization per particle given in column four was multiplied by 2.6 to obtain the rate of volume increase, μ. The factor of 2.6 comes from the measured ratio between volume of swollen particle and weight of polymer found for polystyrene latex particles swollen to equilibrium with liquid styrene at 50°.[1a] These values for the initial rate of particle formation cannot be considered to be at all accurate since small errors in the particle size measurements become greatly magnified in calculating ρ due to raising to the power 15/2.

TABLE III

TOTAL NUMBER AND INITIAL RATE OF FORMATION OF PARTICLES

Temp., °C.	Average volume of particles, cc.	Number of particles,[a] N	Rate of pol. per particle, g./sec.	Initial rate of particle formation,[a] ρ, sec.$^{-1}$
		0.5% soap; 0.172% persulfate		
30.5	1.90 × 10^{-15}	2.54 × 10^{14}	4.2 × 10^{-20}	2.6 × 10^{11}
50	8.05 × 10^{-16}	6.0 × 10^{14}	7.8 × 10^{-20}	4.2 × 10^{12}
70	4.45 × 10^{-16}	1.08 × 10^{15}	1.44 × 10^{-19}	3.3 × 10^{13}
90	3.15 × 10^{-16}	1.53 × 10^{15}	2.63 × 10^{-19}	1.5 × 10^{14}
		0.5% soap; 0.516% persulfate		
70	3.86 × 10^{-16}	1.25 × 10^{15}	1.27 × 10^{-19}	4.3 × 10^{13}
		2.0% soap; 0.172% persulfate		
70	1.95 × 10^{-16}	2.47 × 10^{15}	1.13 × 10^{-19}	2.6 × 10^{13}

[a] Per ml. of water solution (excluding polymer).

Under conditions of constant molecular weight and rate of polymerization the rate of polymer molecule formation is given by dividing the rate of polymerization by the molecular weight. The effect of concentration of polymer particles on rate of molecule formation is shown in Table IV.

TABLE IV

RATE OF POLYMER MOLECULE FORMATION—EFFECT OF NUMBER OF POLYMER PARTICLES

Soap conc., %	Number of particles[a]	Rate of polymn.,[a] g./sec.	Intrinsic viscosity	Molecular weight	Rate of molecule formation,[a] sec.$^{-1}$
		50°; 0.172% persulfate			
2.0	....	8.80 × 10^{-5}	10.6	8.2 × 10^6	6.5 × 10^{12}
0.5	6.0 × 10^{14}	4.70 × 10^{-5}	9.5	6.8 × 10^6	4.2 × 10^{12}
.67	....	4.23 × 10^{-5}	9.3	6.6 × 10^6	3.9 × 10^{12}
.22	....	2.08 × 10^{-5}	6.6	3.5 × 10^6	3.6 × 10^{12}
(Seed)[b]	5.8 × 10^{13}	8.46 × 10^{-6}	4.1	1.5 × 10^6	3.4 × 10^{12}
(Seed)[b]	2.9 × 10^{13}	4.68 × 10^{-6}	2.8	0.85 × 10^6	3.3 × 10^{12}

[a] Per ml. of water solution (excluding polymer).
[b] These charges were prepared using a small amount of previously polymerized polystyrene latex as seed but with no added soap.

The number of polymer particles and hence rates of polymerization were varied by varying the soap concentration and in two cases by using seed polystyrene particles with no added soap. The rates of polymerization given are from least-squares treatment of the yield data in the range in which the yield appears linear with time. The intrinsic viscosity given in column four is the average for the three or four last runs in each sequence which appear to have substantially constant intrinsic viscosities. The molecular weight was estimated from the intrinsic viscosity as discussed above. The rate of molecule formation is the rate of polymerization multiplied by Avogadro's number and divided by the molecular weight. This table indicates that the rate of molecule formation approaches a constant for the lower particle concentrations but becomes greater for the higher concentrations; in fact, the data suggest that the molecular weight may be approaching a maximum limiting value at the highest particle concentrations. The simplest interpretation is that the molecular weight is limited in the high region by chain transfer with styrene monomer and that the rate of initiation is constant. When the number of particles is small enough, free radicals enter the particles sufficiently rapidly that almost all the polymer molecules are formed by mutual termination of radicals and only a negligible fraction by self-transfer. The 50° data are consistent with the assumptions of a constant rate of initiation and a self-transfer constant of 10^{-5}. This order of magnitude is the same as that to be reported by Mayo, Gregg and Matheson[6] for transfer with the monomer in oil phase.

TABLE V

RATE OF POLYMER MOLECULE FORMATION—EFFECT OF PERSULFATE CONCENTRATION

Persulfate concn., %	Number of particles[a]	Rate of polymn.,[a] g./sec.	Intrinsic viscosity	Molecular weight	Rate of molecule formation,[a] sec.$^{-1}$
50°; 0.5% soap					
0.172	6.0×10^{14}	4.70×10^{-5}	9.5	6.8×10^{6}	4.2×10^{12}
.190	....	4.62×10^{-5}	8.2	5.1×10^{6}	5.5×10^{12}
.516	....	5.26×10^{-5}	7.13	4.0×10^{6}	8.0×10^{12}
70°; 0.5% soap					
.172	1.08×10^{15}	1.56×10^{-4}	5.2	2.3×10^{6}	4.1×10^{13}
.516	1.25×10^{15}	1.59×10^{-4}	2.56	0.73×10^{6}	1.3×10^{14}

[a] Per ml. of water solution (excluding polymer).

TABLE VI

RATE OF POLYMER MOLECULE FORMATION—EFFECT OF TEMPERATURE

(0.5% soap, 0.172% persulfate)

Temp., °C.	Number of particles[a]	Rate of polymn.,[a] g./sec.	Intrinsic viscosity	Molecular weight	Rate of molecule formation,[a] sec.$^{-1}$
30.5	2.54×10^{14}	1.06×10^{-5}	16.9	20×10^{6}	3.2×10^{11}
50	6.0×10^{14}	4.70×10^{-5}	9.5	6.8×10^{6}	4.2×10^{12}
70	1.08×10^{15}	1.56×10^{-4}	5.2	2.3×10^{6}	4.1×10^{13}
90	1.53×10^{15}	4.03×10^{-4}	1.4	0.30×10^{6}	8.1×10^{14}

[a] Per ml. of water solution (excluding polymer).

The effect of persulfate concentration on the rate of molecule formation is shown in Table V.

The various quantities in this table are obtained in the same manner as the corresponding quantities in Table IV. These data show the expected increase in rate of molecule formation with increase in concentration of persulfate. At the higher temperature, 70°, the rate of molecule formation is very nearly proportional to the persulfate concentration. At 50° this does not appear to be the case but the lack of proportionality may be due to the fact that an appreciable fraction of the molecules are formed by transfer with styrene when the persulfate concentration is low.

To obtain the temperature coefficient, studies were made at the four temperatures given in Table VI. Again the various quantities are obtained in the same manner as those in Table IV. Analysis of these data by the Arrhenius rate equation using the method of least squares gives 28 kcal. for the activation energy of molecule formation.

The rate of sulfur combination, initial rate of particle formation and rate of polymer molecule formation must all be related to the rate of chain initiation process and hence they must themselves be interrelated. They are compared in Table VII.

The rate of sulfur combination is obtained by dividing the rate of polymerization (Tables IV, V and VI) by the grams of polymer per mole of sulfur (Table II), then multiplying by Avogadro's number. The initial rate of polymer particle formation is the same value as that given in Table III. For comparison the rates of molecule formation from Tables IV, V and VI are multiplied by 2 and inserted in Table VII. The factor of 2 is used because the formation of each molecule requires two free radicals. These three quantities agree within an order of magnitude indicating that, indeed, all three are determined principally by the rate of initiation reaction. The comparison of the rate of sulfur combination with the

TABLE VII

COMPARISON OF QUANTITIES DETERMINED CHIEFLY BY RATE OF FREE RADICAL FORMATION

Temp., °C.	30.5	50	70	90	70	70
Soap concn., %	0.5	0.5	0.5	0.5	0.5	2.0
Persulfate concn., %	.172	.172	.172	.172	.516	.172
Rate of sulfur combination[a]	1.5×10^{11}	6.3×10^{12}	1.5×10^{14}	1.7×10^{15}	2.9×10^{14}	1.6×10^{14}
Rate of particle formation[a]	2.6×10^{11}	4.2×10^{12}	3.3×10^{13}	1.5×10^{14}	4.3×10^{13}	2.6×10^{13}
2 × rate of molecule formation[a]	6.4×10^{11}	8.4×10^{12}	8×10^{13}	1.6×10^{15}	2.6×10^{14}	1.1×10^{14}

[a] Rates are given in number, atoms or molecules per second per ml. of water solution.

rate of molecule formation is really the same comparison which was made in Table II. While the initial rates of polymer particle formation are consistently lower than the rates of molecule formation, not much significance can be attached to this because of the larger error and uncertainty involved in calculating the initial rate of particle formation. Of the three methods for determining the rate of free radical formation by the initiation reaction, the rate of molecule formation is the most reliable.

Summary

The rate of persulfate combination from radioactivity measurements, the initial rate of polymer particle formation from polymer particle size measurements, and the rate of molecule formation from molecular weight measurements have been obtained for styrene emulsion polymerization, and all three quantities agree within an order of magnitude. This indicates that all three are determined principally by the rate of formation of free radicals.

The rate of free radical formation does not appear to depend on the interfacial area between organic and aqueous phases.

Passaic, N. J. Received April 27, 1949

[Contribution No. 262 from the Chemical Department, Experimental Station, E. I. du Pont de Nemours & Company]

The Structure of Neoprene. IV. Infrared Spectra and Spectral Changes with Crystallization[1]

By W. E. Mochel and M. B. Hall

Infrared spectroscopy has been valuable in elucidation of some structural features of high polymers and was therefore applied to the current examination of neoprene (polychloroprene). The infrared spectrum of neoprene has been reported previously[2] and the statement has been made that there are differences between polychloroprenes made under different conditions of polymerization.[3] However, no description of the differences has appeared. In the present study, examination of Neoprenes Type GN and Type CG and analysis of the dichroic effects in their spectra together with comparison with the infrared absorption of polybromoprene have yielded a more complete and reliable interpretation of the spectrum of neoprene than was previously available. These particular neoprenes were selected for study because they are illustrative of the effect of polymerization temperature on the rate of crystallization,[4] *i. e.*, Neoprene Type CG, made at 10°, crystallizes in a few hours at room temperature while Neoprene Type GN, made at 40° in essentially the same emulsion system, requires many days for crystallization to a comparable extent. The crystallization of neoprenes in general has been well established[5] by X-ray diffraction, dilatometry and other methods but the structural differences responsible for observed differences in crystallization rates have not been clearly demonstrated.

Experimental

Materials.—For many of the experiments commercial samples of Neoprene Type CG and Neoprene Type GN were used. To remove undesirable polymerization adjuvants from such samples, they were extracted with acetone in A.S.T.M. extractors or were dissolved in benzene and completely precipitated with methanol. Laboratory samples were also prepared using the emulsion system previously described.[4] The polymers were isolated from the alkaline latices by coagulation with large volumes of alcohol, since it was found that this procedure gave products practically free from sodium rosinate, rosin and other polymerization residues. The polymers were dried *in vacuo* at room temperature and kept under nitrogen.

To prepare films the dry polymers were dissolved in benzene to form solutions of known concentration which were used to cast films inside glass rings on a mercury surface. After the film was dry the ring could be lifted and the attached film examined directly or transferred to another specimen holder. Films were also prepared directly from the latices by filtration on porous battery cups.[6] Films 20–35 microns in thickness were generally used for infrared studies.

Instruments.—Two different instruments were used to obtain the data presented here. For most of the work in the wave length range 2–14 microns there was used a prism instrument after

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