

Emulsion Polymerization of Ethylene. V. Kinetics and Mechanism

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Synopsis

The solubility of ethylene was measured in water, water-*tert*-butyl alcohol, water-emulsifier, water-*tert*-butyl alcohol-emulsifier, and water-*tert*-butyl alcohol-emulsifier-polyethylene. The polymerization of ethylene in an emulsion system differs from that of other vinyl monomers in several ways: the rate of polymer formation is inversely proportional to the emulsifier concentration and to the number of particles, the molecular weight of the polymer increases as the particle size increases, the polymer contains bound emulsifier whose concentration depends inversely on the particle diameter. These peculiarities are attributed to a transfer reaction between polymer radicals and emulsifier adsorbed on the surface of the polymer particle. In the presence of a fatty-acid soap, the transfer probably occurs primarily at the carbon α to the carboxyl group.

INTRODUCTION

The Smith-Ewart equation appears to describe satisfactorily many aspects of the emulsion polymerization of vinyl monomers. There are, however, frequent reports of departure from theory which appear to be linked to specific properties of the monomers.¹ The exponent of rate dependence on emulsifier concentration, for example, decreases as the solubility of the monomer in the aqueous phase increases. Owing to the observed transfer reaction obtained when vinyl acetate was polymerized in a solution containing poly(ethylene oxide) dodecyl ether, Okamura and Motoyama² tried to relate differences in kinetic behavior in emulsion polymerization between styrene and vinyl acetate to differences in radical reactivity. Comparative studies with vinyl caproate, however, showed that the differences were due to solubility rather than to radical reactivity.

Although ethylene resembles vinyl acetate in solubility, its radical reactivity is much greater. Indeed, the high reactivity of the radical gives rise to intramolecular transfer leading to short-chain branching^{3,4} and to telomerization with compounds containing active hydrogens.^{5,6} This paper undertakes to explain the unusual behavior of ethylene in emulsion polymerization by the high reactivity of the ethylene radical.

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EXPERIMENTAL

Materials

A typical analysis of ethylene used in this work is: ethylene, 99.68; carbon dioxide, 0.156; nitrogen, 0.009; oxygen, 0.001; ethane, 0.132; and methane, 0.018 mole-%.

Lauric and myristic acids were obtained from Matheson, Coleman and Bell and stearic acid (U.S.P. powder) from Mallinckrodt at calculated acid contents of 96.6, 97.3, and 105.9%, respectively, based on titration with standard solutions of sodium hydroxide.

The polyethoxylated alkylphenol and sodium lauryl sulfate emulsifiers were obtained from Rohm & Haas and duPont, respectively.

Potassium persulfate, potassium phosphate, and potassium hydroxide were materials of analytical reagent grade from Mallinckrodt.

The technical grade *tert*-butyl alcohol, which contained small amounts of water and isobutylene, was obtained in 99+ % purity from Shell Chemical Company.

Distilled water was used to prepare all recipes and solutions.

All materials were used without further purification.

Preparation of Latexes

The polyethylene latexes were made by the procedure for the emulsion polymerization of ethylene described by Helin et al.⁷ Most of the experiments were carried out with 2 kg. of materials in a 1-gal. stainless steel Magne-Dash autoclave weighing nearly 100 lb. and having a wall thickness of about 1.5 in. Owing to the mass of the autoclave, the amount of reactants, and the high heat of polymerization, the reaction temperature was difficult to control and generally varied through a range of 8°C. Other experiments, particularly those in which the solubility of ethylene in the polymer was measured, were carried out in a stirred, 18-gal. stainless steel autoclave.

The concentrations in the recipe are given as parts of an ingredient per 100 parts of aqueous phase, which can be either water or water plus *tert*-butyl alcohol. The concentrations in the latex of monomer and polymer are also given in this manner. The expression "parts of polymer" is useful as a substitute for the concept of per cent conversion, which is meaningless in this system because ethylene is supplied at a constant pressure.

Sampling

The amount of ethylene dissolved in the latex at operating conditions was determined by withdrawing a 200-g. sample of the unagitated latex through a dip-tube extending to the bottom of the reactor. (Because the ethylene was above its critical temperature, a foam, rather than an emulsion formed. Although the foam contained about 15–20 wt.-% ethylene, a latex phase separated as soon as agitation was stopped.) The latex was caught in a 3-liter, tared flask connected to a wet test meter through an ice-cooled

condenser. When the sample was collected at a rate limiting the flow of ethylene through the wet test meter to 180 l./min., the one condenser was adequate, as in preliminary experiments a Dry Ice-cooled trap downstream from the condenser collected only 0.5 g. of material. The amount of latex collected was obtained by reweighing the flask, the volume of ethylene measured by the wet test meter was reduced to standard conditions (dry), and the solids content of the latex was determined by evaporating a sample on a moisture balance. If only the solids were to be measured as a check on the progress of the polymerization, the sample was limited to a weight of 10–20 g.

The polymer was isolated and analyzed as described in an earlier paper.⁸ Its concentration in the latex was calculated from the solids content corrected for nonpolymeric solids as measured before polymerization or as calculated from the recipe. The amount of ethylene dissolved in the polymer was obtained by correcting the measured volume (S.T.P., dry) by the volume equivalent to the amount of ethylene dissolved in the associated aqueous phase as measured at reaction conditions prior to polymerization.

Carbonyl Absorbance

The emulsion polymers of ethylene prepared with potassium myristate as the emulsifier contained bound emulsifier whose concentration was measured quantitatively by infrared absorption of the carbonyl band at 5.85 μ . The absorbance per mil of polymer A is related to the number of carbonyl groups per gram of polymer E by eq. (1):

$$A = kE \quad (1)$$

The cell constant k was determined on mulls of Nujol and myristic acid, whose absorbance over the concentrations studied obeyed the Beer-Lambert law, and was found to have a value of 5.29×10^{-21} g./molecule/mil of film.

Particle Diameter and Number

A modification⁹ of Maron's method¹⁰ was used to measure the amount of soap that was adsorbed by the latexes and to determine the average surface-to-volume diameter D . The number of particles per milliliter of aqueous phase N_w was calculated from the polymer content of the latex and the average particle diameter as determined by soap adsorption. The samples that contained *tert*-butyl alcohol were first evaporated to one-half volume in a rotating flask to remove the alcohol and then diluted with water to their original volume. The surface tension of the latexes was measured with a ring tensiometer.

Molecular Weight

The number-average molecular weight \bar{M}_n was calculated from the relation

$$\bar{M}_n = 3.1 \times 10^4 \eta - 6300 \quad (2)$$

TABLE I
Effect of Recipe Composition on the Properties of Polymer and Latex Produced
by the Emulsion Polymerization of Ethylene at 80°C. and 3000 psig

Run	Composition, parts ^a				Polymer- ization rate, parts/hr.	Polymer surface, cm. ² /g. × 10 ⁻⁵	Average particle diameter, cm. × 10 ⁸	Number of particles/ ml. of aqueous phase × 10 ⁻¹³	Polymer inherent viscosity, dl./g.
	Fatty acid soap ^{b,c}	Potassium persulfate	<i>tert</i> - Butyl alcohol	Polymer concn., parts					
416	1.46L	0.2	5	35.0	12.0	12.8	510	5.5	0.80
410	2.21L	0.2	5	29.3	6.2	21.8	300	22.5	0.53
418	1.46L	0.3	5	31.8	8.2	13.3	490	5.5	0.64
395	2.21L	0.3	5	29.3	10.4	20.2	330	17.4	0.53
384	1.46L	0.2	10	31.0	21.7	16.1	410	9.6	0.84
391	2.21L	0.2	10	29.8	7.8	17.6	370	12.1	0.62
394	1.46L	0.3	10	29.1	18.4	10.8	610	2.6	0.84
408	2.21L	0.3	10	32.8	13.9	13.6	480	6.1	0.76
417	1.66M	0.2	5	31.2	4.7	13.2	490	5.4	0.63
385	2.49M	0.2	5	31.1	13.4	14.6	450	7.2	0.45
388	1.66M	0.3	5	29.6	21.6	16.8	390	10.6	0.49

415	2.49M	0.3	5	29.8	9.0	19.2	340	15.9	0.52
404	1.66M	0.2	10	31.8	11.6	12.5	520	4.6	0.64
411	2.49M	0.2	10	28.8	7.1	16.8	390	10.1	0.64
387	1.66M	0.3	10	33.2	34.6	12.0	540	4.3	0.66
419	2.49M	0.3	10	28.7	12.1	16.8	380	11.2	0.59
402	2.00S	0.2	5	33.0	11.2	13.3	490	5.8	0.54
407	3.00S	0.2	5	30.1	8.1	17.1	380	11.6	0.43
396	2.00S	0.3	5	28.3	5.0	13.5	480	5.2	0.40
406	3.00S	0.3	5	30.7	15.1	15.0	440	7.7	0.50
386	2.00S	0.2	10	29.1	16.9	9.2	710	1.7	0.58
412	3.00S	0.2	10	30.4	10.5	14.7	440	7.1	0.45
405	2.00S	0.3	10	35.5	17.3	9.0	730	1.9	0.61
401	3.00S	0.3	10	30.7	19.7	14.5	450	7.0	0.50
383	2.07M	0.25	7.5	31.9	25.9	13.4	460	6.3	0.56
392	2.07M	0.25	7.5	27.3	21.2	19.4	340	14.9	0.51
403	2.07M	0.25	7.5	30.2	10.7	15.0	430	7.6	0.37
414	2.07M	0.25	7.5	33.6	7.9	13.1	500	5.7	0.62

^a Parts/100 parts of aqueous phase (water plus *tert*-butyl alcohol). Each recipe also contained 0.5 part of tripotassium phosphate.

^b The low concentrations are equivalent to 0.062 mole/l. and the high to 0.093 mole/l. The soaps were made with potassium hydroxide.

^c Abbreviations: L = lauric; M = myristic; S = stearic.

where η is the relative viscosity determined on 2.0 g. of polymer/l. in tetralin at 135°C. and the constants are based on ebulliometrically measured values of \bar{M}_n .

Experimental Design

The effects of various components of the recipe on polymer inherent viscosity, polymerization rate, and particle number were measured in a statistically designed experiment¹¹ consisting of a randomized block of 28 combinations comprised of a 3×2^3 arrangement of factors: three fatty acid soaps and two concentrations each of emulsifier, *tert*-butyl alcohol, and initiator, regularly interspersed with four "center-point" combinations. These data are given in Table I, where the variables, except for the center-point replicates, are listed in conventional order under each emulsifier. In this form, the data do not divulge their maximum information, especially in view of the wide variation appearing in the replicate determinations; therefore, statements and values derived from Table I are based on average values. In Table III, for example, the average rate of polymerization obtained with 2 parts of emulsifier is 14.7 parts of polymer per hour, which is $1/12$ of the sum ($12.0 + 8.2 + \dots + 17.3$). The limits attached to those averages are based on a measure of experimental error as established by the pooled variances of the center-point replicates and the three- and four-factor interactions and indicate the range within which the true average has a 0.95 probability of falling. All experiments of this series were carried out at 80°C. and 3000 psig.

DATA AND DISCUSSION

Solubility of Ethylene

The solubility of ethylene at 4500 psig. in various solvents is shown in Figures 1 and 2, which represent the amount of ethylene that can dissolve in the aqueous phase at various stages of polymerization. As Figure 1 shows, the solubility of ethylene in water at 80°C. is about 9 g./kg. of solution (0.3 molal) and can be increased to about 15 g./kg. by the addition of potassium myristate. The solubility, however, increases abruptly between emulsifier concentrations of 0.3–0.5 parts, but thereafter remains relatively constant. Hence the increase is probably associated less with ethylene dissolving in micelles than with the aqueous phase forming a stable foam that persisted into the sampling period.

Figure 2 shows that the solubility of ethylene at 54°C. in an aqueous phase containing 20% *tert*-butyl alcohol is similar to that in water at 80°C., but the rise in solubility as emulsifier concentration increases is less abrupt. At 80°C., however, the jump in solubility with increased emulsifier concentration disappears in favor of a steady increase that is in keeping with the results expected when the solubility depends on the presence of micelles. The amount of dissolved ethylene, whether in micelles or not, is at best doubled by the addition of 3 parts of emulsifier. Because the

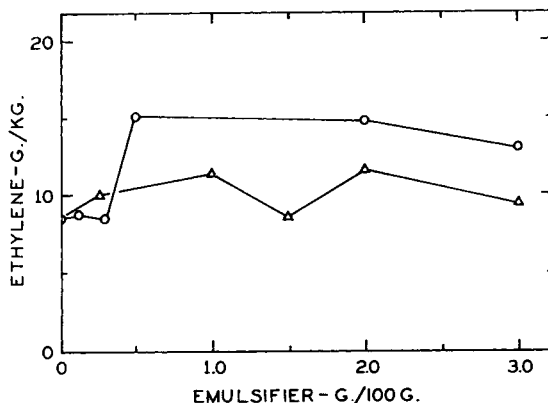


Fig. 1. Effect of emulsifier concentration on the solubility of ethylene at 4500 psig. in water at 80°C.: (O) potassium myristate; (Δ) polyethoxylated (9.5) octylphenol.

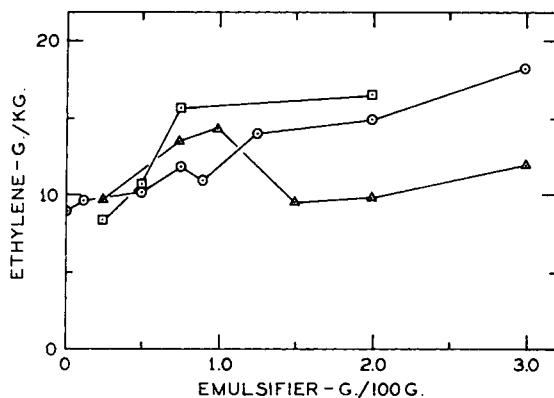


Fig. 2. Effect of emulsifier concentration on the solubility of ethylene at 4500 psig in an 80/20 solution of water and *tert*-butyl alcohol: (□) potassium myristate at 54°C. (O) potassium myristate at 80°C.; (Δ) polyethoxylated (9.5) octylphenol at 80°C.

emulsifier is removed from solution by adsorption on the polymer surface during the course of polymerization, the solubility of ethylene in the aqueous phase must revert to $<1.0\%$ as the polymerization progresses.

During polymerization, the solubility of ethylene in the latex increases owing to the additional amount that dissolves in the growing polymer phase. The data in Table II, which are corrected for ethylene dissolved in the aqueous phase prior to polymer formation, show the monomer solubility in the polymer during polymerizations made at two pressures and with various emulsifiers. Except for a few values associated generally with low polymer concentrations, the ethylene/polymer ratios within a run are substantially constant. Although the variation in solubility assignable to differences among emulsifiers is not significant compared with the standard error in the measurements of 0.016 g. of ethylene/g. of polymer,

the difference between the average solubility of 0.17 g./g. at 2500 psig and of 0.21 g./g. at 3300 psig is significant and, when extrapolated, indicates that the solubility at 4500 psig is 0.27 g./g. According to a pressure-enthalpy diagram for ethylene, 0.27 g. of ethylene at 80°C. and 4500 psig

TABLE II
Solubility^a of Ethylene in Polyethylene Latex Particles During Polymerization^b

Emulsifier	Ethylene pressure, psig	Emulsifier concentration, parts ^c	Polymer concentration, parts ^c	Ethylene concentration, g./g. of polymer
Sodium lauryl sulfate	2500	1.2	2.9	0.17
			6.2	0.16
			8.4	0.17
			11.1	0.16
			14.4	0.17
Sodium lauryl sulfate	2500	2.0	17.2	0.17
			3.8	0.16
			8.3	0.14
			11.9	0.17
			15.2	0.16
Potassium stearate	2500	3.4	17.0	0.18
			18.4	0.18
			0.9	0.11
			3.7	0.19
			6.0	0.18
			8.0	0.18
			9.7	0.19
Polyethoxylated (9.5) octylphenol	3300	3.0	10.9	0.21
			14.2	0.18
			16.7	0.18
			2.6	0.27
			6.0	0.22
			9.0	0.23
			11.3	0.17
			13.2	0.12
			14.3	0.22
15.6	0.21			
15.9	0.23			
			18.0	0.19

^a Solubility corrected for ethylene dissolved in the aqueous phase.

^b At 80°C. in an aqueous phase consisting of 85 parts of water and 15 parts of *tert*-butyl alcohol.

^c Per 100 parts of aqueous phase.

occupies a volume of about 0.78 ml. which, when added to the 1.1 ml. volume of 1 g. of polymer, yields a monomer concentration in the growing particles of 5 mole/l. This value places the solubility of ethylene in its polymer well within the concentration range of 4-9 mole/l. reported¹ for seven vinyl monomers commonly used in emulsion polymerization.

Surface Tension

The variation of surface tension during the emulsion polymerization of ethylene is given in Figure 3 for two concentrations of potassium myristate in the presence and absence of *tert*-butyl alcohol. (The *tert*-butyl alcohol was, of course, removed from the samples before the surface tension was measured; otherwise, there would have been substantially no variation from sample to sample.) Initially, the surface tension was that associated with the critical micelle concentration (CMC) of the emulsifier. Although

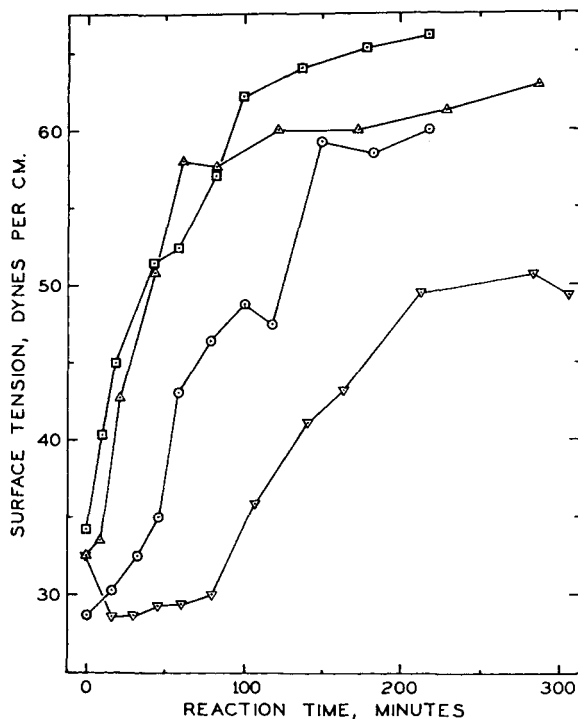


Fig. 3. Effect of reaction time on surface tension: (O) (run 716) 3.72 parts potassium myristate and 10 parts *tert*-butyl alcohol; (□) (run 718) 3.72 parts potassium myristate and no *tert*-butyl alcohol; (▽) (run 719) 5.58 parts potassium myristate and 10 parts *tert*-butyl alcohol; (△) (run 720), 5.58 parts potassium myristate and no *tert*-butyl alcohol.

the expected increase with time occurred, two aspects of the curves require comment. First, in the absence of alcohol, the early and precipitous rise reflects the rapid formation of many small particles whose total surface area is large. Secondly, in the presence of alcohol, the rise is slower, especially at the higher emulsifier concentration. Indeed, the drop in surface tension followed by a rise suggests the existence of competing polymerization processes. One is the process of solution polymerization that can result in the formation of alkyl sulfate oligomers capable of lower-

ing the surface tension through their surfactant properties. The other, whose full appearance coincides with the rise in surface tension, is the normal emulsion process resulting in polymer surface on which emulsifier is adsorbed from the aqueous phase.

Particle Number

Average values for the number of particles per milliliter of aqueous phase N_w are given in Table III for latexes prepared at the given concentrations (parts per 100 parts of aqueous phase) of emulsifier C_E , initiator C_I , and *tert*-butyl alcohol C_A . The polymerizations were made at 80°C. and 3000 psig and carried to a final solids concentration of 25–30%. Of the several recipe changes that altered the number of particles by amounts significantly larger than the experimental error, those associated with the emulsifier are the most pronounced. Polymerization in the absence of *tert*-butyl alcohol produced latexes⁹ in which the particle number followed the relation $N_w \propto C_E^{1.1}$. When *tert*-butyl alcohol was present, however, the dependence of particle number on emulsifier concentration changed according to the amount of alcohol. When C_A was held constant at 5 parts, $N_w \propto C_E^{2.8}$; but when C_A was fixed at 10 parts, $N_w \propto C_E^{1.8}$. Depending

TABLE III
Average Effect of Recipe Composition on Polymerization Rate and Particle Number
Produced in the Emulsion Polymerization of Ethylene at 80°C. and 3000 psig^a

Recipe component	Component concentration, parts	Polymerization rate, parts/hr.	Number of particles/ml. of aqueous phase $\times 10^{-15}$	
<i>tert</i> -Butyl alcohol	5	10.0 \pm 5.7	9.2 \pm 2.9	
	10	15.3 \pm 5.7	6.5 \pm 2.9	
Emulsifier ^b	2	14.7 \pm 5.7	4.4 \pm 1.9	
	3	10.6 \pm 5.7	11.3 \pm 2.9	
	Potassium laurate	2,3	11.8 \pm 7.0	10.2 \pm 3.5
	Potassium myristate ^c	2,3	13.5 \pm 7.0	7.5 \pm 3.5
	Potassium stearate	2,3	12.5 \pm 7.0	6.0 \pm 3.5
Potassium persulfate	0.2	10.4 \pm 5.7	8.6 \pm 2.9	
	0.3	14.9 \pm 5.7	7.2 \pm 2.9	
<i>tert</i> -Butyl alcohol	5	10.0 \pm 8.1	4.8 \pm 4.1	
				Emulsifier
<i>tert</i> -Butyl alcohol	5	10.0 \pm 8.1	13.7 \pm 4.1	
				Emulsifier
<i>tert</i> -Butyl alcohol	10	19.2 \pm 8.1	4.3 \pm 4.1	
				Emulsifier
<i>tert</i> -Butyl alcohol	10	11.4 \pm 8.1	8.9 \pm 4.1	
				Emulsifier

^a The appropriate values from Table I were averaged in sets of 6, 8, or 12 to obtain these entries. The ranges represent the 95% confidence interval.

^b The concentration is measured in parts of potassium stearate equivalent to whichever acid was used.

^c The center-point data were not used to obtain the listed averages.

on the amount of alcohol, the exponent α in the relation $N_w \propto C_w^\alpha$ appears to assume values of 1-3.

As a corollary, $N_w \propto C_A^{0.0}$ when C_E was fixed at 2 parts, and $N_w \propto C_A^{-1.0}$ when C , was fixed at 3 parts. The ability of *tert*-butyl alcohol to reduce particle number was also evident at emulsifier concentrations of 3.4 and 5.1 parts, especially during the initial period of polymerization.⁹ At these emulsifier concentrations in the absence of alcohol, N_w was initially about 10^{18} , which agrees well with the 10^{18} micelles/ml. of aqueous phase expected from that amount of emulsifier. The initial average particle diameters, moreover, were micellar in size, as they were in the range 30-90 Å. (The determination of particle diameters less than 100 Å. contains many uncertainties, and the real diameter could well be larger. The rapid rise in surface tension shown for runs 718 and 720 in Figure 3, however, coincides with the formation of so little polymer that the particles could reasonably have diameters of micellar dimensions.) If 10 parts of *tert*-butyl alcohol were added to the recipe, N_w would be initially about 10^{16} . The ability of

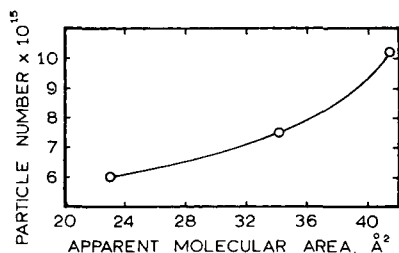


Fig. 4. Effect of apparent molecular area of fatty-acid soaps on the final number of latex particles/ml. of aqueous phase.

the alcohol to reduce the number of latex particles produced by a given amount of fatty-acid soap could be explained if the alcohol were to increase considerably the CMC of the soap. Such an increase in CMC would require, however, an inversion at 80-85°C. of the depression of CMC observed by Shinoda¹² on adding alcohols to solutions of potassium soaps at 10-18°C.

The differences among the emulsifiers are also of importance, especially the increase in particle number obtained by using potassium laurate. Although the myristate soap formed more particles than the stearate, the difference is not much larger than that which could occur through experimental variation. As shown in Figure 4, however, the number of particles produced does increase in accord with the apparent molecular area of the soap.

The data included in Table III also show that particle number is independent of initiator concentration. Although the range of initiator concentration studied is narrow (0.2-0.3 part), another study⁹ over the range of 0.016-0.32 part also demonstrated that particle number does not depend on initiator concentration.

Polymerization Rates

The conventional method of following an emulsion polymerization consists of plotting monomer conversion against time. Because the emulsion polymerization of ethylene was carried out at a constant pressure, the extent of reaction was measured in parts of polymer produced rather than in per cent of monomer converted. Typical plots of parts of polymer versus time are shown in Figure 5. The rate during the batch polymerization of a vinyl monomer generally passes through three well-defined stages: an initial stage of increasing rate during which particles are formed; a second stage of constant rate beginning with the disappearance of micelles and ending with the depletion of the emulsified monomer phase; and a final stage of declining rate accompanying the consumption of the remaining monomer dissolved in the polymer particles. Although the rate in the emulsion polymerization of ethylene generally exhibits these three stages, the first and last are not well defined, and the stage of constant rate is occasionally missing. The initial stage is often characterized by an induction period during which very little polymer forms, especially in runs made with less than about 1 part of emulsifier, but the middle period then shows a rapid rate of polymerization. A poorly defined terminal period is under-

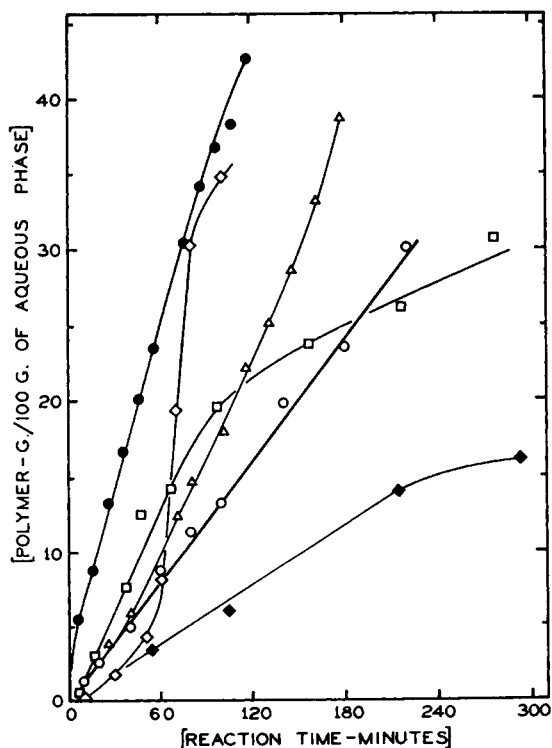


Fig. 5. Typical polymer-time curves at 85°C. and 4500 psig: (O) (run 718); (□) (run 720); (◇) (run 724); (Δ) (run 732); (●) (run 733); (▲) (run 735).

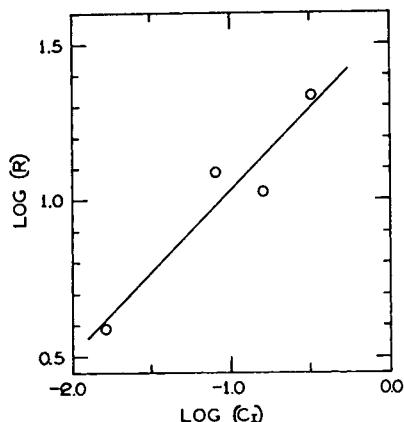


Fig. 6. Effect of initiator concentration (parts) on rate of polymer formation (parts/hr.) at 85°C. and 4500 psig.

standable, because the concentration of ethylene in the particles is constant throughout the run and does not decline so long as the pressure is maintained. Any decline in rate that does occur, therefore, must arise from factors other than a decrease of monomer concentration in the particles. The rates R presented here were taken from the linear part of the plots and are expressed in parts of polymer produced per hour. In the few plots lacking a linear portion, the rates were taken from a tangent near the midpoint of the plot.

The effect of temperature and pressure on the rate of polymerization was not studied extensively enough to establish quantitative relationships. Qualitatively, however, an increase in either causes the rate to rise. A recipe yielding solids of 25% after a polymerization of 3 hr. at 85°C. and 4500 psig, for example, required 10 hr. or more to reach 10% solids at a polymerization temperature of 50°C., even with a redox initiator system; or, if the pressure were raised to 15,000 psig, the rate of polymerization at 85°C. became so rapid that the temperature rose beyond control and the latex coagulated.

Table II includes data which show the average rate of polymerization at 80°C. and 3000 psig obtained at the indicated concentrations of *tert*-butyl alcohol, potassium persulfate initiator, and fatty-acid soap emulsifier. By comparison with the experimental error, the only rate change large enough to be statistically significant is the increase obtained by raising the concentration of *tert*-butyl alcohol. This increase in rate, however, appears to occur primarily at the lower emulsifier concentration. The average influence of these components of the recipe indicates that $R \propto C_A^{0.8} C_I^{0.9} C_E^{-0.8}$.

The rate of polymerization of ethylene at 85°C. and 4500 psig was measured over a wide range of initiator concentration in the absence of *tert*-butyl alcohol. The data appear in Figure 6 as a plot of logarithm R versus logarithm C_I . The slope of the line indicates that $R \propto C_I^{0.5}$.

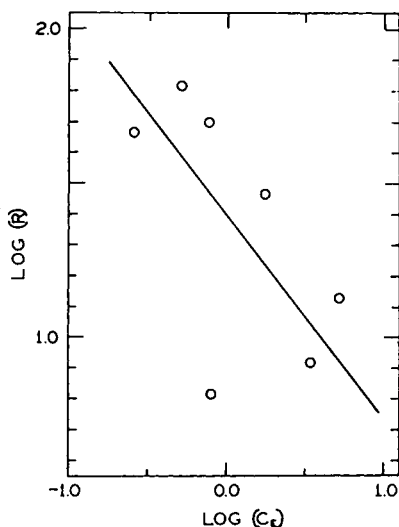


Fig. 7. Effect of emulsifier concentration (parts) on rate of polymer formation (parts/hr.) at 85°C. and 4500 psig.

Although the exponent of rate dependence is in good agreement with the 0.5 value required by Medvedev's¹³ theory, the variation in the data is such that the Smith-Ewart value of 0.4 is equally reasonable.

The polymerization rate of ethylene at 85°C. and 4500 psig at an initiator concentration of 0.16 part of potassium persulfate was measured at seven different concentrations of potassium myristate. These data appear in Figure 7 as a log-log plot which suggests that $R \propto C_E^{-0.6}$. Because $N_w \propto C_E^{1.1}$, the rate of polymerization also appears to depend inversely on the 0.5–0.6 power of the particle number. The high correlation between N_w and C_E , however, obscures their independent behavior.

The variation in the rate data is admittedly too large to give a reliable numerical value to the exponent of rate dependence α on the concentration of alcohol, initiator, or emulsifier. The data do support, however, that $R \propto C_A^{\alpha > 0} C_I^{\alpha > 0} C_E^{\alpha < 0}$. The strong, inverse dependence of rate on concentration of potassium soap that is consistently observed in the emulsion polymerization of ethylene sets its behavior apart from that of substituted vinyl monomers.

Transfer with Emulsifier

Emulsion polyethylene made in the presence of a fatty-acid soap contains carbonyl groups that are an integral part of the polymer owing to chain transfer with the emulsifier. Such transfer results from the high reactivity of the polymer radical and is unusual in emulsion polymerization. Infrared spectrograms of emulsion polystyrene prepared with potassium myristate or oleate as emulsifier did not absorb at the frequencies assigned to the carbonyl group. Vinyl acetate, whose radical activity lies

between that of the ethylene and styrene, is reported² to chain transfer with polyethoxylated dodecylphenol in bulk polymerization, but not in emulsion polymerization when this phenol is used as the emulsifier. The absence of transfer in the emulsion system is interpreted to mean that the vinyl acetate radical grows within the particle away from the emulsifier. The chain transfer reaction between the growing polymer chain and the emulsifier present during the emulsion polymerization of ethylene appears, therefore, to be unique among the vinyl monomers.

Locus of Transfer

The number of carbonyl groups contained in m grams of polymer isolated from a liter of latex is given by the expression

$$mE = E_a + E_v + E_s \quad (3)$$

where E_a , E_v , and E_s are the number of transfers yielding bound emulsifier and occurring, respectively, in the aqueous phase, within the particles, and on their surfaces. Solving for E and substituting in eq. (1) gives

$$A = k(E_a + E_v + E_s)/m \quad (4)$$

However,

$$E_a = E_a^0(1000 - m/\rho) \quad (5)$$

where E_a^0 is the number of transfers per milliliter of aqueous phase and ρ is the polymer density. In addition,

$$E_v = E_v^0 m/\rho \quad (6)$$

where E_v^0 is the number of transfers per milliliter of polymer. Finally,

$$E_s = E_s^0 m a s N_0 \times 10^{-16} \quad (7)$$

where E_s^0 is the number of transfers per square centimeter of polymer surface, a is the apparent molecular area of the emulsifier in square Angstroms, s is the total moles of emulsifier per gram of polymer at surface saturation, and N_0 is Avogadro's number. Maron showed that the average particle diameter D in Angstroms is given by the expression

$$D = 6 \times 10^{24}/\rho s a N_0 \quad (8)$$

Therefore,

$$s a N_0 = 6 \times 10^{24}/\rho D \quad (9)$$

and substitution in eq. (7) gives the relation

$$E_s = 6mE_s^0 \times 10^8/\rho D \quad (10)$$

Appropriate substitution into eq. (4) of eqs. (5), (6), and (10) yields

$$A = (k/\rho)[E_a^0(1000\rho/m - 1) + E_v^0 + 6E_s^0 \times 10^8/D] \quad (11)$$

TABLE IV
Dependence of Frequency of Transfer on Inherent Viscosity and Absorbance at 5.85 μ

Run ^a	5.85- μ absorbance, mil ⁻¹	Inherent viscosity, dl./g.	Frequency of transfer, f
716-2	0.071	0.50	0.26
-3	0.068	0.49	0.23
-4	0.060	0.52	0.23
-5	0.048	0.60	0.23
-6	0.048	0.62	0.24
-7	0.043	0.70	0.26
-8	0.049	0.79	0.39
-9	0.048	0.79	0.38
-10	0.040	0.85	0.34
718-2	0.227	0.25	0.12
-3	0.288	0.29	0.32
-4	0.216	0.33	0.36
-5	0.135	0.34	0.22
-6	0.149	0.37	0.32
-7	0.118	0.43	0.35
-8	0.123	0.37	0.25
-9	0.125	0.37	0.25

^a Conducted at 85°C. and 4500 psig.

which relates carbonyl absorbance to the number of transfers occurring at the three loci. If transfer occurs only in the aqueous phase, within the polymer, or on its surface, the logarithm of eq. (11) reduces, respectively, to

$$\log A = \log (kE_a^0/\rho) + \log (1000\rho/m - 1) \quad (12)$$

$$\log A = \log (kE_v^0/\rho) \quad (13)$$

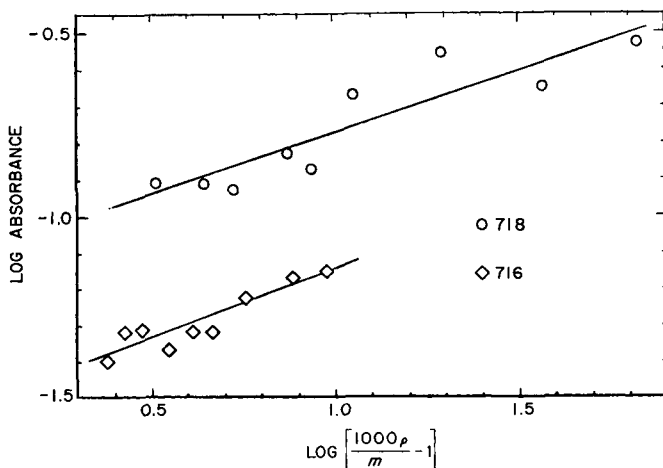


Fig. 8. Relation between absorbance at 5.85 μ and the volume of aqueous phase/g. of polymer: (\diamond) (run 716); (\circ) (run 718).

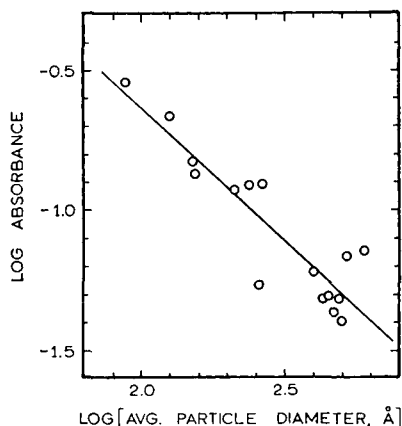


Fig. 9. Relation between absorbance at 5.85μ and average volume-surface particle diameter.

or

$$\log A = \log (6kE_s^0 \times 10^8/\rho) - \log D \quad (14)$$

If transfer were to occur in the polymer, absorbance would assume a constant value. We know from the data in Table IV, however, that absorbance decreases as the amount of polymer increases; the locus of transfer, therefore, is either the aqueous phase or the polymer surface. If transfer were to occur in the aqueous phase, a plot of $\log A$ versus $\log (1000\rho/m - 1)$ should have a slope of $+1$. Figure 8 reveals, however, two separate lines each having a slope of about $+1/3$. This obviously disqualifies the aqueous phase as the locus of transfer and suggests that $\log A$ is inversely proportional to the cube root of the polymer volume. If transfer were to occur on the surface of the polymer particle, a plot of $\log A$ versus $\log D$ should have a slope of -1 . Such a plot is shown in Figure 9. Inasmuch as the slope of the line is -0.95 , which is in excellent agreement with the -1 predicted by eq. (14), the locus of transfer appears to be the surface of the growing monomer-polymer particle.

The distribution of particle diameters, however, suggests that the mechanism of polymer formation is volume-controlled. Brodnyan¹⁴ deduced that a surface-controlled mechanism of polymerization produces particles whose radii are normally distributed, but that a volume-controlled mechanism results in radii that are log-normally distributed. Inasmuch as the emulsion polymerization of ethylene yields latex particles whose diameters are distributed log-normally,⁹ the mechanism of polymer growth appears by this criterion to be surface-controlled.

Extent and Frequency of Transfer

The ratio of bound emulsifier to total emulsifier is of value in establishing the extent of transfer. The intercept of the least-squares line (Fig. 9) of eq. (14) has a value of 1.25; hence

$$\log (6kE_s^0 \times 10^8/\rho) = 1.25 \quad (15)$$

which, for $k = 5.29 \times 10^{-21}$, gives an E_s^0 value of 4.5×10^{12} bound carbonyl groups/cm.² of polymer surface. On this basis, the bound emulsifier represents less than 1% of the recipe emulsifier.

It is also of interest to examine the bound emulsifier in terms of the frequency of transfer f in a particle during the period between successive entries of radicals. The sequence of reactions in this period or cycle is: (1) initiation by radical entry (2) propagation-transfer-propagation-etc., (3) termination by radical entry.

The number of chain ends per cycle c , which will consist of two initiator fragments I according to steps (1) and (3) and equal numbers of abstracted hydrogen atoms H and emulsifier fragments G according to step (2), can be expressed as

$$c = I + H + G \quad (16)$$

In a cycle during which p polymer molecules are formed,

$$c = 2p = I + 2G \quad (17)$$

The number of initiator fragments, of course, has a constant value of 2, which can be written as

$$I = 2p/(f + 1) \quad (18)$$

where $2p$ is the total number of chain ends and $1/(f + 1)$ is the fraction consisting of initiator fragments. Performing the indicated substitution in eq. (17) and solving for f yields

$$f = G/(p - G) \quad (19)$$

The value G for 1 g. of polymer, however, is equal to E of eq. (1). Also, the average number of chains per gram of polymer \bar{p} is given by

$$\bar{p} = N^0/\bar{M}_n \quad (20)$$

where \bar{M}_n is the number-average molecular weight defined by eq. (2). The appropriate substitutions in eq. (19) show, therefore, that

$$f = A\bar{M}_n/(3185 - A\bar{M}_n) \quad (21)$$

which is an expression for the frequency of transfer in terms of the number-average molecular weight and the carbonyl absorbance of the polymer. As shown in Table IV, the values of f calculated by eq. (21) generally fall in the range $0.30, \pm 0.08$. Such values suggest that only one cycle in three or four results in emulsifier becoming bound in the polymer, and their constancy implies a balance among the factors affecting transfer. Because of the inverse dependence of the rate of polymer formation on emulsifier concentration, the transfer reaction must occur by a mechanism that interferes with the formation of polymer. There are two ways this might happen. In one, the emulsifier radical might be slow to initiate another polymer radical. Indeed, the reactivity of the emulsifier radical toward ethylene is probably less than that of the polymer radical owing to

resonance structures similar to those contributing to the stability of the allyl radical.¹⁵ In the other, the emulsifier radical might diffuse from the particle into the aqueous phase where it could terminate, undergo a relatively slow solution polymerization, or even enter another particle. Diffusion from the particle is reasonable, as van der Hoff¹ points out that a radical having a molecular weight of several hundred can diffuse a distance of 1000 Å. in 10^{-5} sec. The observed retardation in rate, therefore, might well result from the combined effects of diffusion and low reactivity of the emulsifier radical.

Dependence of Polymer Properties on Transfer

The molecular weight of polymer formed during the emulsion polymerization of ethylene depends on the size of the latex particle. This dependence is evident from Figure 10, which establishes that $\eta \propto V^{0.2}$ or $D^{0.6}$. Because of this dependence, polymer formed early during polymerization when the particles are small has a low molecular weight. The presence of this low molecular weight fraction in the polymer is probably responsible for the low elongation that is characteristic of emulsion-made polyethylene.⁸

A limiting case in the dependence of molecular weight on particle diameter is reached by the "emulsion polymerization" of ethylene in the absence of added emulsifier. As shown in Table V, the average particle diameter under these circumstances is about 3000 Å. The polymer, moreover, is insoluble or forms gels rather than solutions and when heated becomes rubbery instead of fluid. Such behavior suggests that the poly-

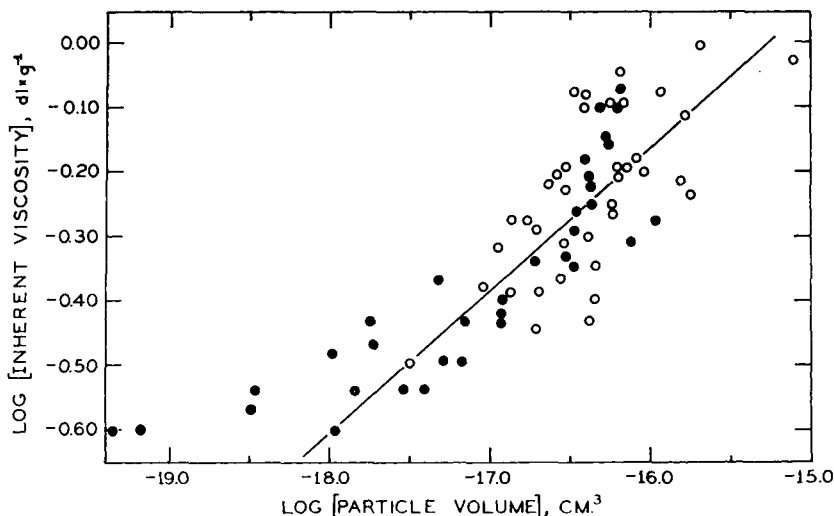


Fig. 10. Relation between polymer inherent viscosity and average particle volume: (●) polymer made at 80°C. and 3000 psig (Table I); (○) polymer made at 85°C. and 4500 psig (Table IV).

mer has a high molecular weight and is to some extent crosslinked. In addition to earlier reports of this type of polymer,¹ Kurz¹⁶ recently described some emulsion polyethylenes that had a highly ramified structure and contained high molecular weight, spherical molecules of diameters comparable with those of the latex particles. As the amount of emulsifier is increased, the particle size and molecular weight of the polymer decline. However, when an emulsifier is used which is incapable of transfer, as in run 729, the

TABLE V
Effect of Potassium Myristate Concentration on Particle Diameter
and Inherent Viscosity

Run ^a	Potassium myristate, parts	Particle diameter, cm. $\times 10^8$	Inherent viscosity, dl./g.
728	0	3000	Insoluble ^b
723	0.26	620	Insoluble ^b
724	0.50	620	Insoluble ^b
727	0.75	420	0.79
725	1.25	280	0.41
726	1.75	260	0.42
729	3.18 ^c	378	Insoluble ^b
718	3.38	285	0.37
720-9	5.07	235	0.42

^a Conducted at 85°C. and 4500 psig.

^b The polymer formed gels in tetralin at 135°C. at a concentration of 0.2 g./dl. When heated on a hotplate, the polymer softened and became rubbery.

^c The potassium myristate was replaced with an emulsifier incapable of transferring with the growing polymer radical.

polymer produced resembles that obtained with little or no emulsifier, even though the particle size is small. In the absence of chain transfer with emulsifier, the polymer radical can apparently grow without interruption by transfer when it reaches the particle surface or adsorption layer; hence the high molecular weights expected from emulsion polymerization are actually realized.

CONCLUSION

The data do not furnish a basis for a quantitative explanation of the emulsion polymerization of ethylene, but they certainly establish a qualitative picture which shows that the complexity of the system transcends that of most substituted vinyl monomers. This complexity arises from the high reactivity of the ethylene radical in comparison with that of most substituted vinyl radicals, which are to various degrees resonance stabilized. Because of the high reactivity of this simplest of vinyl radicals, emulsion polymerization of ethylene is dominated by a chain-transfer reaction with emulsifier adsorbed on the polymer surface. In essence, this transfer

reaction is a special case of telomerization of ethylene in which the chain transfer agent is the emulsifier adsorbed on the polymer surface. Recognition of the role of the reactive ethylene radical explains not only the unusual inverse dependence of rate on particle number (polymer surface) and the positive correlation between molecular weight and particle diameter, but also the presence in the polymer of bound emulsifier and the complicated molecular structure obtained in the absence of transfer with emulsifier.

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Résumé

La solubilité de l'éthylène a été mesurée dans l'eau, dans l'eau-alcool butylique tertiaire, l'eau-émulsifiant, l'eau-alcool butylique tertiaire-émulsifiant, et l'eau-alcool butylique tertiaire-émulsifiant-polyéthylène. La polymérisation de l'éthylène dans un système en émulsion diffère de celle des autres monomères vinyliques de plusieurs façons: la vitesse de formation du polymère est inversement proportionnelle à la concentration en émulsifiant et au nombre de particules, le poids moléculaire du polymère croît lorsque la grandeur des particules croît et le polymère contient de l'émulsifiant lié dont la concentration dépend inversement du diamètre de la particule. Ces particularités sont attribuées à une réaction de transfert entre les radicaux polymériques et l'émulsifiant absorbé à la surface de la particule polymérique. En présence d'un savon d'acide gras le transfert de passe probablement tout d'abord au carbone α par rapport zu groupe carboxylique.

Zusammenfassung

Die Löslichkeit von Athylen wurde in Wasser, Wasser-*tert*-Butylalkohol, Wasser-Emulgator, Wasser-*tert*-Butylalkohol-Emulgator und Wasser-*tert*-Butylalkohol-Emulgator-Polyäthylene gemessen. Die Polymerisation von Athylen in einem Emulsionssystem unterscheidet sich von der anderer Vinylmonomere auf mehrere Arten: Die Polymerbildungsgeschwindigkeit ist der Emulgatorkonzentration und der Teilchenzahl umgekehrt proportional, das Molekulargewicht des Polymeren nimmt mit steigender Teilchengröße zu und das Polymere enthält gebundenen Emulgator, dessen Konzentration dem Teilchendurchmesser umgekehrt proportional ist. Diese Besonderheiten werden einer Übertragungsreaktion zwischen Polymerradikalen und an der Oberfläche des Polymerteilchens adsorbiertem Emulgator zugeschrieben. In Anwesenheit einer Fettsäureseife findet die Übertragung wahrscheinlich primär am Kohlenstoff in α -Stellung zur Carboxylgruppe statt.

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