

Emulsion Polymerization of Ethylene. IV. Effect of Recipe and Polymerization Conditions on Polymer Properties

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Synopsis

Some physical, chemical, and solution properties of polyethylene prepared by emulsion polymerization are described and compared with those of conventional high-pressure polymer. The emulsion polymers contain an unusually large amount of low molecular weight material for the solution viscosities they exhibit. It is this low molecular weight material that contributes to the characteristic low elongation of the emulsion polymer, as well as to its wide distribution of molecular weights. The effect of changes in recipe and in conditions of polymerization on these properties is discussed. It is shown that some of the emulsifier present during polymerization becomes part of the polymer chain.

INTRODUCTION

In recent papers we presented a method for preparing stable latexes by the emulsion polymerization of ethylene,¹ described the size and distribution of the latex particles,² and discussed the factors affecting the stability of polyethylene latexes.³ In this paper we discuss the properties of the polymer contained in these latexes and the effect on the properties of changes in recipe and in conditions of polymerization.

EXPERIMENTAL

Preparation of Latexes

The latexes were produced by the process of emulsion polymerization of ethylene described by Helin et al. in the first paper of this series.¹ The statistically designed experiment from which the data in Table IX were derived is described in experiment I of the second paper.² In all references to quantities of ingredients used in polymerization recipes, the term "parts" indicates parts per 100 parts of aqueous medium (water or water plus solvent).

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Separation of Polymer

About 100 g. of the latex at 40% solids in a liter beaker was mixed well with 500 ml. of acetone containing 5 ml. of concentrated hydrochloric acid. While being stirred, the mixture was brought to a boil and then cooled to 20°C. in an ice bath. The polymer was separated and successively stirred in 500 ml. of acetone, in 400 ml. of distilled water, and finally in 400 ml. of boiling acetone. Before filtering, the acetone was cooled to 20°C. The polymer was dried under a pressure of 20 mm. Hg at 50°C. for 1 hr. and then at room temperature for several days to a constant weight. Small portions of the polymers listed in Table VI were further purified by leaching in methanol for two weeks.

Inherent Viscosity

The inherent viscosity is based on the viscosity at 135°C. of a 0.2% solution of polymer in tetrahydronaphthalene in a Stabin modified Ubbelohde viscometer (ASTM D 1601-58T). The equation used in the calculation is:

$$\text{Inherent viscosity} = \frac{\ln \left[\frac{t(\text{solution})}{t(\text{solvent})} \right]}{\text{g. polymer/dl.}}$$

where t is the time required for a given volume to pass through the viscometer. The inherent viscosity of samples of fractionated polymer was measured in the same manner, except that they were dissolved in *p*-xylene at 100°C.

Molecular Weight Distribution

The polymers were dissolved in *para*-xylene at 100°C. and were fractionated⁴ on a sand column with Cellosolve as the nonsolvent. The polymer was isolated and redissolved for the inherent viscosity determination. The molecular weight of the polymer was estimated from the correlation with intrinsic viscosity given by Trementozzi.⁵ (Some error was introduced by making the calculation with the inherent viscosity; but, because the inherent viscosity does not change much as the polymer concentration is reduced, the errors are of little consequence.)

Melt Index

Inasmuch as the polymer was isolated as a powder that was difficult to use without bubbles appearing in the extrudate, the polymer was first compression-molded at a temperature slightly above its melting point into strips $\frac{1}{16} \times 1 \times 3$ in. These were then diced for use in the melt viscometer according to ASTM D 1238-62T condition A. The melt viscosities were reported as grams extruded in 10 min. at 190°C. under a load of 325 g.

Crystalline Melting Point

A sample was placed between crossed Nicols in a polarizing microscope and heated at a rate giving a temperature rise of 1°C./min. The temperature at the disappearance of the spherulites was taken as the melting point.

Crystallinity

The polymer was molded into a $1/16 \times 1$ in. disk at a gage pressure of 6 tons and a temperature slightly above the melting point of the polymer. The disk was annealed in nitrogen for 1 hr. at a temperature 10°C. below the melting point of the polymer. The heating bath and the disk were allowed to cool overnight to room temperature. The crystallinity was measured on the annealed disk by the x-ray integrated area method based on the work of Bunn.⁶

Density

The density of the polymer was measured in a gradient column according to ASTM D 1505-57T or by difference in weight of a sample in air and in *n*-butyl alcohol, the disk prepared for the crystallinity determination being used as the sample.

Tensile Properties

Tensile strength and per cent elongation at the point of break were obtained according to ASTM D-638-60T on samples cut from strips molded for melt viscosity.

Infrared Analyses

The polymer powder was molded at a temperature slightly above its melting point and at a pressure of 6 tons into a $11/16$ -in. diameter disk between sheets of Mylar separated by a 5-mil Mylar shim. The actual thickness of the disk was measured with a micrometer. The spectra were obtained on an Infracord IR-137 instrument.

DATA AND DISCUSSION

General Properties

The properties of polyethylene made by emulsion polymerization differ from those of polyethylene made by bulk polymerization in several respects. (In this paper, bulk polymer refers to conventional high-pressure polyethylene.) A comparison of the properties of the two types of polyethylene is presented in Table I. Values for properties of emulsion polyethylene will fall usually in the ranges given in the first column. These ranges are based on properties of polymers prepared at 20–100°C. and 2500–15,000 psi by recipes containing 0–5.5 parts of emulsifier, 0–25 parts of *tert*-butyl alcohol or other organic solvents, and 0.08–0.65 part of initiator.

TABLE I
Comparison of Properties of Bulk and Emulsion Polyethylene

Property	Range of values for emulsion polymer	Specific emulsion polymer	Specific bulk polymer
Intrinsic viscosity, dl./g.	0.15-1.20	0.90	0.966
Crystalline melting point, °C.	77-120	98-102	102-05
Density, g./cc.	0.908-0.958	0.921	0.916
Crystallinity by x-ray, %	60-75	67	66
Melt index	45-17,000	45	3
Methyl content/100 C atoms	0.7-4.7	3.0	3.1
Tensile strength, psi	400-3500	1264	1313
Yield point, psi	400-3500	1264	1127
Elongation at yield, %	<100	12	18
Elongation at break, %	<100	12	165
Carbonyl, absorbance/mil	0.02-0.30	0.04	0
Sulfate, %	<0.1	0.02	0

The values given in the second column are for a specific emulsion polymer having an inherent viscosity of 0.90 and those in the third column are for a bulk polymer of similar solution viscosity. The emulsion polymer was made in an 18-gal. stainless steel autoclave according to the recipe and conditions given in Table II.

TABLE II
Recipe and Conditions

Water, parts	85
<i>tert</i> -Butyl alcohol, parts	15
Myristic acid, parts	2.06
Potassium hydroxide, part	0.44
Potassium phosphate (hydrate), part	0.50
Potassium persulfate, part	0.08
Ethylene pressure, psig	2500
Temperature, °C.	80
Final solids, %	23.4

The bulk polymer was a commercial product prepared at a pressure and temperature above 15,000 psig and 150°C.

Tensile Properties

Corresponding values for most of the physical properties of the emulsion and bulk polymers agree satisfactorily, but those of melt index and of elongation at break show that the emulsion polymer has a higher melt index and cannot be cold-drawn. Actually, a high melt index and lack of elongation are not found exclusively in emulsion polyethylene, inasmuch as Vincent⁷ showed that cold-draw in bulk polyethylene is almost absent at a melt index of 70. They are, however, characteristic of emulsion polyethylene; for we seldom have made any having a melt index below 70, and we have never made one having an elongation exceeding 100%.

Polymer Composition

An outstanding difference in the infrared spectrum between emulsion polyethylene prepared in the presence of a fatty-acid emulsifier and conventional high-pressure polyethylene is the strong absorbance of the emulsion polymer at 5.85μ (Fig. 1), the wavelength at which the acid carbonyl

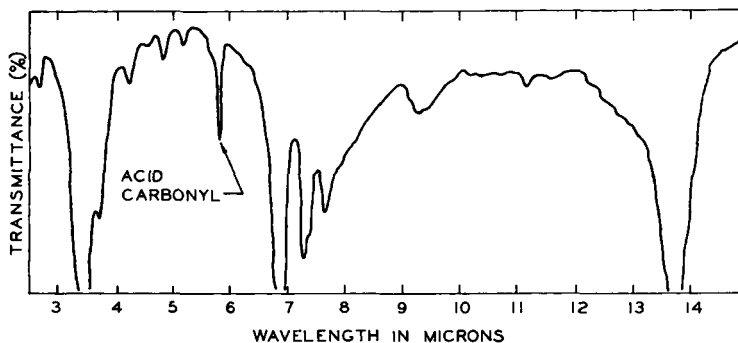


Fig. 1. Infrared spectrum of emulsion polyethylene precipitated in the presence of acetone.

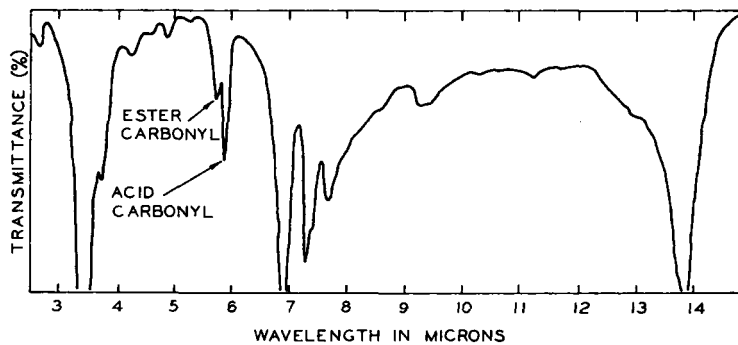


Fig. 2. Infrared spectrum of emulsion polyethylene precipitated in the presence of methanol.

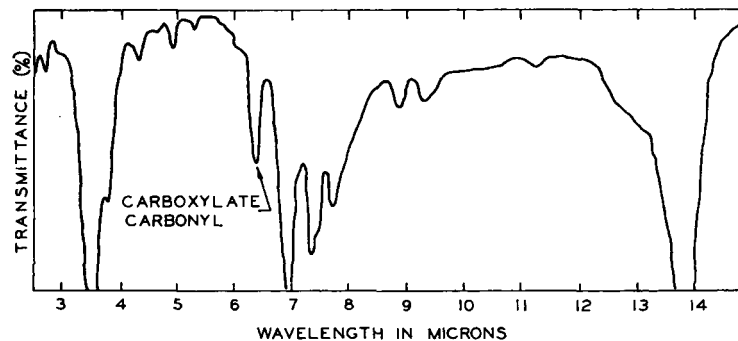


Fig. 3. Infrared spectrum of emulsion polyethylene precipitated in methanol and boiled in alcoholic potassium hydroxide.

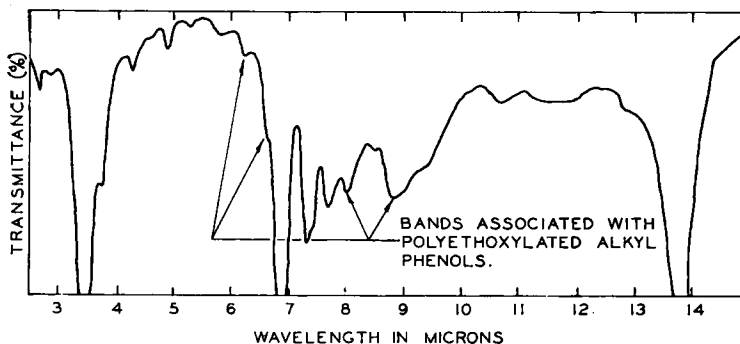


Fig. 4. Infrared spectrum of emulsion polyethylene prepared with a polyethoxylated alkylphenol.

group absorbs. We initially attributed it to the presence in the polymer of occluded emulsifier, but repeated extractions with ethanol failed to reduce substantially the intensity of the absorbance. While trying to remove this emulsifier by altering the method of coagulating the latex, we observed that polymer precipitated with methanol instead of acetone displayed a new band at 5.75μ , the absorbance band for the ester carbonyl group (Fig. 2). We were able, moreover, to shift both bands to 6.4μ , the absorbance band for the carboxylate group, by boiling the polymer with alcoholic potassium hydroxide (Fig. 3). It was quite obvious after these experiments that some of the fatty-acid emulsifier had become an integral part of the polymer chain.⁸

This combined emulsifier is distributed throughout the molecular weight range of the polymer. A sample of emulsion polymer prepared with potassium myristate was fractionated according to molecular weight, and the inherent viscosity of each fraction was determined. Infrared spectra were obtained on some of the fractions and the absorbance per mil thickness at 5.85μ (carbonyl absorbance) was calculated. The results are listed in Table III. Owing to the small amount of material recovered from some of the fractions, the data are incomplete, but the

TABLE III
Dependence of Carbonyl Absorbance on Inherent Viscosity

Fraction no.	Carbonyl absorbance, absorbance/mil thickness	Inherent viscosity, dl./g.
B	—	0.14
C	—	0.17
D	2.88	0.20
E	—	0.22
F	1.47	0.25
H	—	0.32
J	0.39	0.47
Q	0.28	—

TABLE IV
Dependence of Bound Nonionic Emulsifier on Inherent Viscosity

Sample no.	Bound emulsifier, %	Inherent viscosity, dl./g.
1	1.65	0.87
2	3.90	0.83
3	5.28	0.44
4	5.62	0.40
5	6.02	0.34
6	14.51	0.19

presence of the carbonyl band in all fractions examined shows that the emulsifier is incorporated in the polymer chains of all lengths. In addition, emulsion polyethylene made in the presence of a polyethoxylated nonylphenol emulsifier contained some emulsifier that resisted all efforts to remove it from the polymer, as indicated in Figure 4 by aromatic bands at 6.2 and 6.6 μ and by an ether band at 9.0 μ . The concentration of nonionic emulsifier bound in some of these polymers is given in Table IV along with their inherent viscosities. Although these data were obtained on whole polymer rather than on fractions, the same effect was observed, that is, the amount of bound nonionic emulsifier declines as the molecular weight of the polymer rises. The binding of the emulsifier as well as the decline of its concentration with increasing molecular weight of the polymer is explained by a transfer reaction between growing polymer chains and emulsifier adsorbed on the surface of the polymer particles.⁸

Fragments of potassium persulfate used to initiate the emulsion polymerization of a vinyl monomer appear as endgroups in the polymer. If the degree of polymerization is high, these groups form a very small part of the polymer. But as the degree of polymerization decreases, they become an increasingly large part of the polymer, provided, of course, that the amount of chain transfer remains the same. The emulsion polyethylene made by Hopff⁹ was rich in sulfur, owing to his use of high concentrations of persulfate initiator. Our polymer contains these sulfate groups, but to a much lesser extent. Hopff's polyethylene contained 1.2% sulfur, whereas ours contained generally less than 0.1%. We have, however, separated a low molecular weight fraction from our polymer that contained 0.40% sulfur. This fraction amounted to 0.2% of the whole polymer and had a number-average molecular weight by ebulliometry of 700. The concentration of the sulfate groups, as well as the concentration of the carbonyl groups, increases as the molecular weight of the polymer decreases.

Molecular Weight Distribution

These differences between properties of emulsion and bulk polyethylenes having equal solution viscosities reflect the broader molecular weight distribution of the emulsion polymer. In Table V are presented inherent viscosity and molecular weight values determined on fractions obtained from an emulsion polyethylene having a melt index of 1700. The cumu-

TABLE V
Distribution of Molecular Weight in an Emulsion Polyethylene

Fraction weight, g.	Inherent viscosity, dl./g.	$\bar{M}_n \times 10^{-3}$
Whole polymer	0.956	50.0
0.05987	0.11	1.6
0.11574	0.12	1.9
0.09106	0.13	2.0
0.12618	0.218	4.8
0.14184	0.274	6.9
0.17573	0.285	7.4
0.13663	0.377	11.5
0.24815	0.428	14.0
0.36261	0.508	18.5
0.15029	0.699	30.5
0.04428	0.728	32.5
0.12274	1.644	185
0.58758	1.391	110
0.26289	b	—
0.08118	b	—
0.02218	b	—
0.02020	b	—

2.74915 g. total recovered, or 91.6%.

^a Computed from Trementozzi's equation.⁵

^b Small gelled particles were observed in these samples when they were dissolved for the inherent viscosity determination.

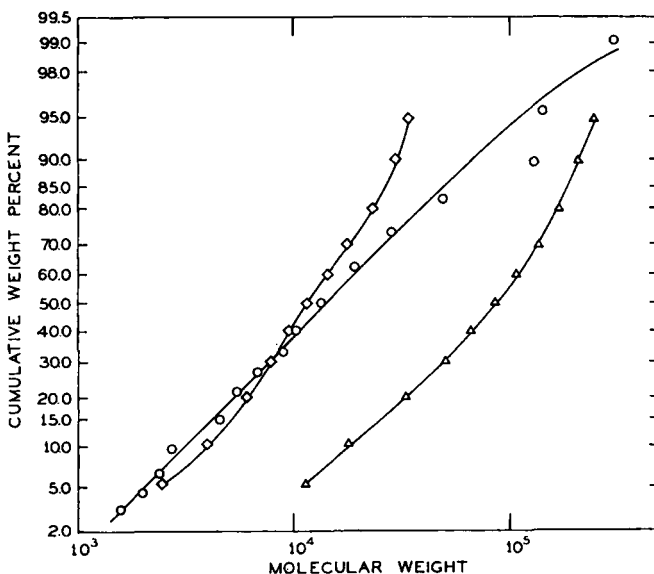


Fig. 5. Molecular weight distribution in bulk and emulsion polyethylene: (O) emulsion polymer, melt index = 1700; (◇) bulk polymer, melt index = 1700; (Δ) bulk polymer, melt index = 0.24. (Molecular weight plotted on log scale.)

TABLE VI
Melt Index and Solution Viscosity of Emulsion Polyethylene

Sample no.	Melt index ^a	Inherent viscosity, dl./g. ^b
356	17000	0.22
365	13000	0.20
371	8900	0.18
369	6200	0.18
368	6200	0.21
374	2800	0.35
401	2100	0.50
415	1900	0.52
388	1800	0.49
411	1650	0.64
375	1600	0.49
403	1550	0.37
402	1550	0.54
412	1525	0.45
354	1300	0.38
395	1280	0.53
386	1250	0.58
378	1200	0.59
364	1150	0.72
350	1100	0.56
383	1100	0.56
370	1100	0.62
417	1060	0.63
349	1050	0.52
414	840	0.62
387	800	0.66
416	580	0.80
384	240	0.84
3-33	45	0.90

^a ASTM D-1238-57T.

^b Determined on a 0.2% solution in tetralin at 135°C.

lative weight fractions and molecular weights are plotted on log-probability coordinates in Figure 5. Also included in the plot are curves for similar data reported by Mussa¹⁰ for two bulk polyethylenes having melt indexes of 0.24 and 1700. The distribution of molecular weights is definitely broader in the emulsion polymer as is demonstrated by the fact that its range covers the combined ranges of the two bulk polymers. Less direct evidence of the broader distribution is implicit in the values of melt index and inherent viscosity given in Table VI for emulsion polyethylenes prepared at 85°C. and 3500 psi. Most of these melt indexes are high, especially by comparison with values of the usual bulk polyethylene; yet the inherent viscosities, particularly those corresponding to melt indexes less than 2000, are relatively normal by bulk standards. The difference in the behavior of the two types of polyethylene is more apparent in Figure 6, which shows the plot of logarithm of melt index versus inherent viscosity [η] for the data

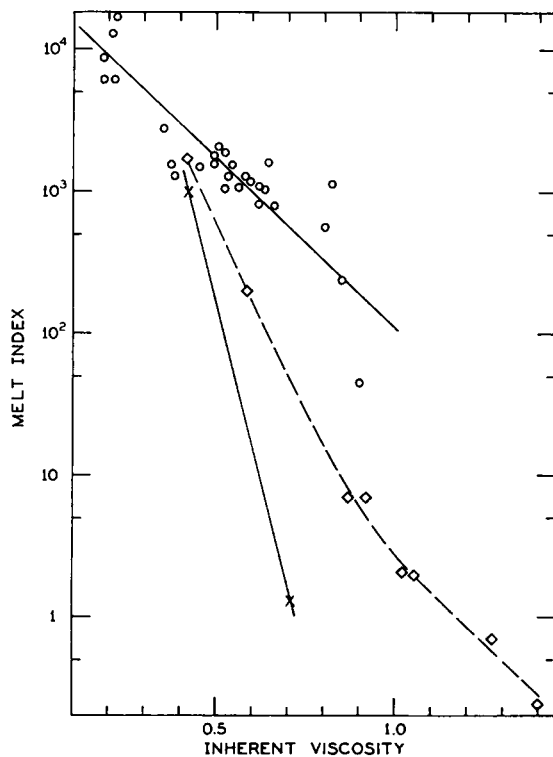


Fig. 6. Relation between melt index and inherent viscosity for bulk and emulsion polyethylene: (O) emulsion polymer; (X) bulk polymer, data of Sperati et al.;¹¹ (◇) bulk polymer, data of Mussa.¹⁰

in Table VI and the same relationship for bulk polyethylene described by Mussa¹⁰ and by Sperati et al.¹¹ The Sperati relation, $\log(\text{melt index}) = 5.09 - 1.53 \times 10^{-4} \bar{M}_n$, was combined through number-average molecular weight \bar{M}_n with Trementozzi's equation⁵ $[\eta] = 1.05 \times 10^{-3} \bar{M}_n^{0.63}$ to obtain the given plot. If the same dependence between inherent viscosity and molecular weight holds for both emulsion and bulk polyethylene, it is then obvious that the emulsion polymer not only contains more low molecular weight material than bulk polyethylene of the same solution viscosity, but also more high molecular weight polymer than does bulk polyethylene at the same melt index. Below melt index values of about 2000, for example, the curve for the emulsion polymer falls in the area of high melt index-high inherent viscosity, which lies above and to the right of the curves for the bulk polymer.

Density and Branching

The polymerization recipes, operating conditions, and test results obtained from a series of experiments planned to investigate density and branching are presented in Table VII. The data for density and methyl

TABLE VII
Summarized Charge, Polymerization, and Polymer Property Data for Study of Effect of Temperature on Molecular Structure

Run no.	Emulsifier		Ingredients, parts					Conditions				Polymer properties					
	Kind	Parts	KOH	H ₂ O	<i>tert</i> -BuOH	K ₃ PO ₄	K ₂ S ₂ O ₈	FeSO ₄	Na ₂ P ₂ O ₇	Na ₂ SO ₃	Temp., °C.	Operating pressure, ×10 ² , psig	Total solids, %	Reaction time, hr.	Inherent viscosity, dl./g. ^a	Methyl groups/100	
652	Stearic acid	2.21	0.53	85	15	0.5	0.75 ^b	—	—	—	130–160	45–48	15.2	6.0	0.142	0.9088	6.14
489	Lauric acid	1.23	0.41	80	20	0.5	0.13	—	—	—	108–125	45–48	19.2	3.4	0.853	0.9239	3.80
344	Myristic acid	2.14	0.52	100	0	0.5	0.25	—	—	—	98–101	28–30	16.4	2.0	0.215	0.9161	4.60
362	Stearic acid	2.08	0.41	85	15	0.5	0.25	—	—	—	80–86	28–30	21.0	1.37	0.503	0.9224	3.47
644	Nonionic ^c	3.0	—	77.5	22.5	—	0.25	—	—	—	120	45–48	13.8	5.5	0.759 ^d	0.9169	4.30
423	Nonionic ^c	3.0	—	80	20	—	0.25	—	—	—	80–93	45–48	23.4	7.5	0.848 ^d	0.9272	2.63
580 ^e	Lauric acid	1.23	0.41	80	20	—	1.00	0.28	0.44	0.10	22	45–48	6.4	43.0	0.389	0.9572	0.75
576	Lauric acid	1.23	0.41	80	20	—	0.25	0.07	0.11	0.10	50	45–48	10.2	19.5	0.589	0.9448	0.72
562	Lauric acid	1.23	0.41	80	20	0.5	0.25	—	—	—	47–62	45–48	9.0	20.9	0.750	0.9410	0.80
587 ^e	Lauric acid	1.23	0.41	80	20	—	1.50	0.42	0.66	0.10	10–22	45–48	8.6	9.9	0.352	0.9563	0.94
591 ^e	Lauric acid	1.23	0.41	80	20	—	1.50	0.42	0.66	0.10	47–52	45–48	7.0	8.0	0.380	0.9584	1.28
658	Lauric acid	1.55	0.53	85	15	0.5	0.25	—	—	—	160	45–48	8.0	4.0	0.157	0.9080	3.95
512	Nonionic ^c	3.0	—	85	15	—	0.60	—	—	—	85	45–48	19.6	2.87	0.840	0.9313	2.38
532	Nonionic ^c	4.0	—	85	15	—	0.30	—	—	—	95	45–48	19.0	2.55	0.861	0.9699	2.65

^a Inherent viscosity measured on a 0.2% solution in tetralin at 135°C.

^b *tert*-Butyl hydroperoxide.

^c Ethoxylated nonylphenol.

^d Part of the polymer was insoluble.

^e These polymers were additionally purified by dissolving in xylene, filtering, and precipitating with methanol.

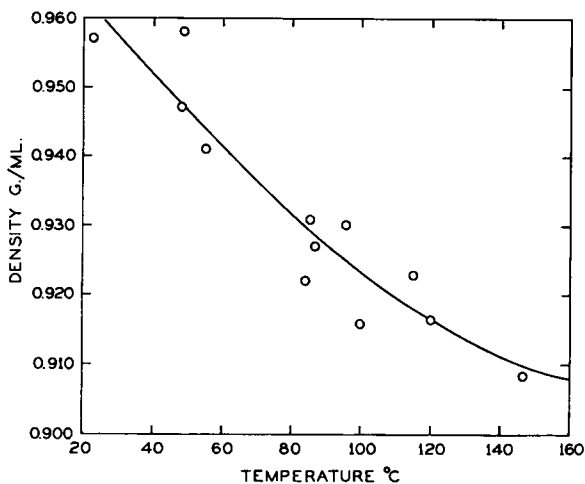


Fig. 7. Effect of polymerization temperature on the density of emulsion polyethylene.

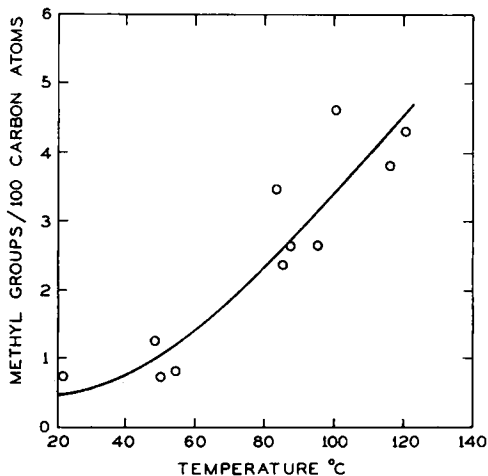


Fig. 8. Effect of polymerization temperature on the number of methyl groups in emulsion polyethylene.

content, which is taken as a measure of the branching, show that in emulsion polyethylene, as in bulk polyethylene, these properties depend primarily upon the temperature of polymerization. Moreover, their qualitative response to temperature is the same; for when the temperature of polymerization is increased, the density of the polymer decreases (Fig. 7) and the number of methyl groups increases (Fig. 8). Because both density and methyl content reflect the degree of branching of the polymer, one would expect to find a well-defined correlation between the properties. Figure 9 shows this relationship for emulsion polyethylene as well as for conventional high-pressure polyethylene described by Sperati et al.¹¹ and

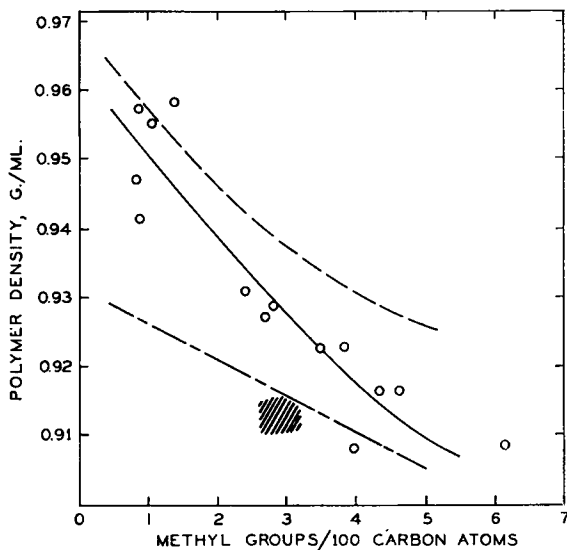


Fig. 9. Relationships between density and methyl group content of various polyethylenes: (O) emulsion polyethylene; (--) data of Smith et al.;¹³ (---) Sperati et al.;¹¹ (ZZZ) data of Marker et al.¹²

by Marker et al.¹² and also for some Ziegler copolymers of ethylene and propylene described by Smith et al.¹³ The curve for emulsion polymer lies between the other two; hence at equal methyl content, the emulsion polyethylene is denser than conventional high-pressure polyethylene, but not as dense as the Ziegler copolymers.

Methods of Controlling Polymer Properties

The molecular weight, as measured by inherent viscosity, can be controlled in emulsion polymerization of ethylene by adjusting the recipe and conditions of polymerization. We found, as the data in Table VIII show, that the molecular weight of the polymer can be raised merely by increasing the parts of *tert*-butyl alcohol used in the recipe. This effect was also reported in the patent literature¹⁴ and was stated to be unique with *tert*-butyl

TABLE VIII
Effect of *tert*-Butyl Alcohol on Inherent Viscosity

Run no.*	<i>tert</i> -Butyl alcohol, parts	Inherent viscosity, dl./g.
426	0	0.22
422	7.5	0.44
370	15	0.62
423	22.5	0.72
425	30	0.82

* Conditions: temperature = 80–90°C.; pressure = 3000 psig; ethoxylated nonylphenol = 3.0 parts; potassium persulfate = 0.25 part.

TABLE IX
Effect of Solvents on Inherent Viscosity

Run no. ^a	Emulsifier type ^b	<i>tert</i> -Butyl alcohol, parts	Other solvent		Inherent viscosity, dl./g.
			Name	Parts	
370	Anionic	15	—	—	0.62
364	Anionic	15	—	—	0.72
350	Anionic	15	Acetone	0.59	0.56
378	Anionic	15	Acetone	0.59	0.59
338	Anionic	15	Hexane	17.5	0.18
379	Anionic	15	Hexane	17.5	0.21
349	Anionic	15	Cyclohexene	0.04	0.52
375	Anionic	15	Cyclohexene	0.04	0.49
354	Anionic	15	Acetone	0.59	0.38
			Cyclohexene	0.04	
374	Anionic	15	Acetone	0.59	0.35
			Cyclohexene	0.04	
476	Anionic	0	Dimethyl sulfoxide	5.0	0.26
765	Nonionic	12	—	—	0.89
773	Nonionic	15	2-Ethyl hexaldehyde	7.9	0.24
767	Nonionic	15	Carbon tetrachloride	1.0	0.20
778	Nonionic	15	Isopropyl acetate	1.0	0.78

^a Conditions: temperature = 80–90°C.; pressure = 3000–4500 psig; emulsifier = 3 parts; potassium persulfate = 0.16–0.25 part.

^b Anionic emulsifier = myristic acid; nonionic emulsifier = polyethoxylated nonylphenol.

alcohol. The data in Table IX, which shows the effect of various solvents on inherent viscosity, confirm the uniqueness of *tert*-butyl alcohol in this respect, for the presence of the second material did not increase the molecular weight of the polymer.

The molecular weight can also be adjusted by changing the type and amount of emulsifier used in the recipe, as is shown in Table X. If a stable latex is to be obtained, the adjustments possible with changes in the concentration of emulsifier are small compared with those to be gained by adding *tert*-butyl alcohol. This is especially evident in Table XI, where the effect of the alcohol and soap are directly compared in runs 716, 718, 719, and 720. The molecular weight of polymer from these four runs, and generally from the others, is always higher at the low concentration of emulsifier, but the difference is small compared with the increase obtained by adding 10 parts of *tert*-butyl alcohol. If the stability of the latex is not important, one can reduce or even omit the emulsifier and obtain polymer that contains—to judge by its insolubility under the conditions used to measure solution viscosity—a large fraction of very high molecular weight polymer.

TABLE X
Effect of Type and Amount of Emulsifier on the
Inherent Viscosity of Emulsion Polyethylene^a

	Avg. inherent viscosity, dl./g.	95% Confidence interval, dl./g.
Emulsifier type		
Potassium laurate	0.69	±0.053
Potassium myristate	0.58	±0.053
Potassium stearate	0.50	±0.053
Emulsifier concentration		
2 parts ^b	0.64	±0.044
3 parts	0.54	±0.044

^a Conditions: temperature = 80°C.; pressure = 3000 psig; *tert*-butyl alcohol = 5–10 parts; potassium persulfate = 0.2–0.3 part; potassium phosphate = 0.5 part.

^b These parts are nominal: 2 parts is equivalent to 62.0 and 3 parts to 93.2 mmole of the fatty-acid salt per liter of aqueous phase.

TABLE XI
Effect of Emulsifier Concentration on Inherent Viscosity

Run no. ^a	Myristic acid, parts	<i>tert</i> -Butyl alcohol, parts	Inherent viscosity, dl./g.
728	0	0	^b
723	0.22	0	^b
724	0.43	0	^b
727	0.64	0	0.79
725	1.07	0	0.41
726	1.50	0	0.42
718	2.90	0	0.38
720	4.35	0	0.32
716	2.90	10	0.85
719	4.35	10	0.66

^a Conditions: temperature = 85°C.; pressure = 4500 psig; potassium persulfate = 0.16 part; potassium phosphate = 0.42 part.

^b The polymer was partly insoluble at the conditions used to determine inherent viscosity.

Another method commonly used in emulsion polymerization to control the molecular weight of the polymer is to change the amount of initiator used in the recipe. In the emulsion polymerization of ethylene, however, a change in initiator concentration has no apparent effect on the molecular weight of the polymer, at least over the twentyfold range reported in Table XII.

The molecular weight of the emulsion polymer can also be increased by raising the polymerization pressure (Table XIII). Although the higher pressures generally produced the higher molecular weight polymers (run 768 at an ethylene pressure of 15,000 psig gave polymer having a relatively high inherent viscosity of 1.21), it is interesting to observe that the molecular weight of polymer from run 753 made with *tert*-butyl alcohol at 4500

TABLE XII
Effect of Initiator Concentration on Inherent Viscosity

Run no. ^a	Potassium persulfate, parts	Inherent viscosity, dl./g.
735	0.02	0.32
732	0.08	0.41
718	0.16	0.37
733	0.32	0.36

^a Conditions: temperature = 85°C.; pressure = 4500 psig; myristic acid = 2.90 parts; *tert*-butyl alcohol = 0 part; potassium phosphate = 0.42 part.

TABLE XIII
Effect of Ethylene Pressure on Inherent Viscosity

Run no. ^a	Pressure, psig	<i>tert</i> -Butyl alcohol, parts	Inherent viscosity, dl./g.
753	4,500	15	0.72
758	13,000	15	0.87
768	15,000	15	1.21
718	4,500	0	0.37
807	15,000	0	0.48

^a Conditions: temperature = 85°C.; myristic acid = 2.90 parts; potassium persulfate = 0.16 part; potassium phosphate = 0.42 part.

psig exceeds that of polymer from run 807 made without the alcohol at 15,000 psig.

The toughness (the area under the stress-strain curve) of emulsion polyethylene can assume a wide range of values, depending on the conditions of polymerization. The conditions that favor increased toughness are: complete omission of the emulsifier or a low concentration of one that has little or no tendency to chain transfer, the presence of *tert*-butyl alcohol, and a high pressure of ethylene. Data illustrating the effects of various combinations of these conditions are presented in Table XIV. Some of the salient points illustrated by these data are: (1) omitting the emulsifier increases the tensile strength and makes the polymer insoluble (720 versus 728); (2) raising the pressure from 4500 to 15,000 psig increases tensile strength substantially and elongation slightly (728 versus 779); (3) making either of these changes fails to increase the elongation of the polymer to a value exceeding 100%.

CONCLUSIONS

Emulsion polyethylenes prepared in the presence of an emulsifier consisting of a potassium salt of a fatty acid or an ethoxylated alkylphenol contain, in addition to initiator fragments, a portion of the emulsifier chemically bound in the polymer chain. In contrast with bulk polyethylene, an emulsion polyethylene of the same solution viscosity possesses a higher

TABLE XIV
Effect of Polymerization Conditions on Various Polymer Properties

	Run no.					
	777	720	758	768	728	779
Recipe						
Water: <i>tert</i> -butyl alcohol	85:15	100:0	85:15	85:15	100:0	100:0
Sodium lauryl sulfate, parts	3.5	—	—	—	—	—
Myristic acid, parts	—	4.35	2.90	2.90	—	—
Potassium hydroxide, part	—	1.26	0.84	0.84	—	—
Potassium phosphate, part	—	0.42	0.42	0.42	0.42	0.42
Potassium persulfate, part	0.11	0.16	0.13	0.20	0.16	0.18
Conditions						
Pressure, psig	15,000	4,250	13,000	15,000	4,250	15,000
Temperature, °C.	80–115	85	85	80–87	85	85
Time, hr.:min.	1:03	4:50	5:0	4:12	3:40	1:36
Product						
Latex, % solids	24.0	27.0	22.0	30.8	14.7	^a
Inherent viscosity, dl./g.	0.97	0.32	0.88	1.21	^b	^b
Tensile strength, psi	2250	464	1825	1170	1427	3250
Elongation, %	53	24	86	73	31	77

^a The latex coagulated at the end of the polymerization.

^b The polymer was partly insoluble at the conditions used to determine inherent viscosity.

melt index, a wider distribution of molecular weights, and generally a lower elongation.

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Résumé

Certaines propriétés physiques, chimiques et propriétés en solution d'un polyéthylène préparé par polymérisation en émulsion sont décrites et comparées aux propriétés du polymère conventionnel à haute pression. Le polymère d'émulsion contenait une quantité inhabituellement importante de matériaux de bas poids moléculaire étant donné les viscosités qu'elles manifestent en solution. C'est ce matériau de bas poids moléculaire qui contribue à l'élongation faible du polymère d'émulsion de même que la large distribution des poids moléculaires. L'effets de modification dans la recette et dans les conditions de polymérisation sur ces propriétés sont discutées. On montre qu'une certaine quantité de l'émulsifiant présent au cours de la polymérisation est incorporée dans la chaîne polymérique.

Zusammenfassung

Einige physikalische, chemische und Lösungseigenschaften von durch Emulsionspolymerisation dargestelltem Polyäthylen werden beschrieben und mit denjenigen des konventionellen Hochdruckpolymeren verglichen. Die Emulsionspolymeren enthalten im Verhältnis zu ihrer Lösungsviskosität eine ungewöhnlich grosse Menge niedermolekularen Materials. Dieses niedermolekulare Material bedingt die charakteristische, niedrige Elongation des Emulsionspolymeren sowie seine breite Molekulargewichtsverteilung. Der Einfluss einer Änderung des Polymerisationsrezepts und der Polymerisationsbedingungen auf diese Eigenschaften wird diskutiert. Es wird gezeigt, dass ein Teil des während der Polymerisation anwesenden Emulgators in das Polymere eingebaut wird.

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