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THE EMULSION POLYMERIZATION
OF ISOPRENE
BY CUMEME HYDROPEROXIDE.

by

Warren L. Reynolds.

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ABSTRACT

The emulsion polymerization of isoprene by means of cumene hydroperoxide was found to yield polymers of irreproducible intrinsic viscosities. The cause was found to be in the procedure used which was that recommended for drying GR-S type rubbers. The temperature and drying period finally found to be satisfactory were 35° C. and 48 hours.

The formula recommended for the production of GR-S rubber by means of cumene hydroperoxide when applied to isoprene gave a rubber with too low a molecular weight. By studying the effect of varying the concentration of each of the components, and also the temperature, conditions have been established for the production of a satisfactory polymer.

ACKNOWLEDGEMENT.

I wish to acknowledge the keen interest, enthusiasm and helpful guidance of Dr. R.H. Clark under whose direction this research was carried out.

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HISTORY.

Attempts to prepare rubber by polymerizing isoprene date back to about 1862 when isoprene was first recognized as the fundamental building unit of natural rubber. Little progress in rubber research was made, however, until two decades later when Ipatieff and Wittorf gave the final proof of the structure of isoprene. It was soon found that isoprene on prolonged standing formed rubber-like products. Harries greatly extended the knowledge of the chemistry of rubber by means of ozone degradation. Staudinger proposed an open chain structure for the rubber molecule on the basis of his work on the hydrogenation of rubber. Paralleling this study of the structure of rubber were many attempts to synthesize artificial rubber from isoprene. Wallach in 1887 found that light would convert isoprene to a rubber-like product. Hofmann is credited with the polymerization of isoprene in 1909 by the aid of heat. In 1910, Harries obtained an artificial rubber by a process using isoprene and an equal volume of acetic acid which required heating on a water bath in a closed tube for eight days. He also prepared, in 1913, a rubber-like polymer in small amounts by the action of ultra-violet light upon isoprene. A high molecular weight rubber was prepared by Holt by prolonged shaking of isoprene with sodium wire in a completely dry atmosphere of carbon dioxide. The process required a period of three weeks

and a temperature of 60°C . Other attempts to polymerize isoprene have involved pressures of 50 to 600 atmospheres, copolymerization with butadiene in emulsions in the presence of an oxygen evolving compound, the shaking of isoprene at 60°C in the presence of casein and potassium cinnamate or the magnesium salt of isobutyl naphthalene sulphonic acid or protein and sodium stearate, and vapor phase polymerization with aluminum chloride. None of these methods achieved importance because of the quality of the product.

Polymerization of isoprene has been achieved at this University through the use of the enzymes peroxidase and catalase and through the use of different oxidizing agents. Peroxidase and catalase gave erratic results and poor yields. Since the ferrousion-hydrogen peroxide system acts similarly to the enzyme-hydrogen peroxide system it was tried next. The resulting polymer had about the same rebound as natural rubber but only about ^{three quarters} as great a tensile strength. The use of anodic oxidation was suggested next by Dr. R.H. Clark. The physical properties of the polymer resulting from this method were almost identical with those of the polymer resulting from the previously described method. There was this difference between the methods however. It was found possible to vary the intrinsic viscosity up to about 4.4 by the anodic oxidation method whereas with the hydrogen peroxide method a maximum of 2.6 is reached. Dr. Clark then suggested the use of air

oxidation. It was also found possible to obtain a range of intrinsic viscosities up to 4.5 by this method. This polymer was not tested. Since cumene hydroperoxide was being used successfully in the manufacture of GR-S rubbers it was used next as the oxidizing agent here. As for the hydrogen peroxide polymers a maximum intrinsic viscosity of 2.6 is obtainable although the period required for polymerization has been greatly reduced.

INTRODUCTION.

The work covered by this thesis is divided into two parts. The first part of the work is concerned with the establishment of a drying procedure for the polyisoprene obtained by cumene hydroperoxide initiation. The establishment of a drying procedure became necessary when it was found that the method previously used was causing irreproducible results. The second part of the work is concerned with increasing the molecular weight of the polymer.

P A R T 1.THEORY.

By the "true" gel content of a polymer is meant the fraction of the polymer which will not form a "true" solution in benzene at room temperature, that is, the gel fraction is that portion which does not possess the thermodynamical requirements for going into solution as given by Flory (6,7,8) and which, therefore, will not dissolve except by the acquisition of an electric charge.

Kolthoff and Medalia⁽¹³⁾ outlined a procedure for the determination of the "true" gel content in GR-S which required drying the polymer in a vacuum oven at 80°C for 12 hours. Bardwell and Winkler⁽²⁾ found that mechanical mixing of the coagulum prior to heating does not appear to have any significant effect on the values obtained for gel content or intrinsic viscosity.

As stated by Baker⁽¹⁾, heating at a sufficiently high temperature causes "coagulation" of the microgel as a result of collisions prompted by thermal diffusion with van der Waal's forces causing the particles to adhere upon collision. Although the polymer after the heat treatment still does not contain macrogel (in the structural sense of a macroscopic network held together by primary valence bonds), the van der Waal's forces are sufficiently strong to prevent colloidal dispersion of the macrogel particles in the absence of agitation during the process of solution.

It is to be expected, though, that the purely physical means by which the van der Waal's forces are induced between the microgel molecules may be reversed, for example, by peptization from an electric charge on the microgel. According to Baker⁽¹⁾ such a charge can be formed if there are present in the solvent traces of antioxidant, soap, water, alcohol, oxygen or other polar substances.

Kolthoff and Medalia⁽¹³⁾ have presented two other causes for the agglomerating effects of heating and milling. First it appears possible that primary valence bonds may be formed between microgel particles when they collide in the same manner as the bonds are formed during polymerization and their formation might be catalyzed by traces of oxidant or mercaptan left in the polymer. Secondly, oxygen vulcanization may be essential for the gelation of polymers which are very close to the "gel-point". Polymers may not contain microgel before heating and milling but only highly branched molecules which are not of themselves insoluble in benzene but which readily undergo vulcanization by traces of oxygen to form a macrogel structure held together partly by C-C bonds and partly by C-O bonds. These two methods of macrogel formation would be irreversible. However, the presence of an antioxidant such as P.B.N.A. should largely prevent macrogel formation by these two means.

EXPERIMENTAL PROCEDURES

The experimental procedures outlined here will be the same for both parts 1 and 2.

A. Preparation of the Model.

The reagents were used in the following proportions:

Water	195.0	grams
R.R.C. soap	4.2	"
Glucose	1.0	"
Fe SO ₄ . 7H ₂ O	0.1	"
Na ₄ P ₂ O ₇ . 10H ₂ O	1.0	"
Cumene hydroperoxide	0.2	"
M.T.M. #4	0.45	"
Isoprene	100.0	"

The R.R.C. soap was dissolved in 180.0 mls. of boiling distilled water and the solution was cooled to 25°C. To this soap solution was added 5 mls. of a boiled glucose solution containing 1 gm. of glucose. The 16 oz. bottle containing the soap solution was then shaken to distribute the glucose solution throughout the soap solution. 10 mls. of a solution containing 1 gm. of Na₄P₂O₇.10H₂O and 0.1 gm of FeSO₄.7H₂O was then added and the bottle reshaken. The cumene hydroperoxide and the M.T.M. were then added separately with the mixture being reshaken after each addition. 147 mls. of isoprene freshly distilled from metallic sodium were then added and the bottle shaken to obtain a fine

emulsion. The bottle was immediately placed in the polymerizer which contained water at 45°C and which rotated the bottle end over end 18 times per minute. At the end of a specified reaction period the bottle was removed, cooled to reduce the vapor pressure of the unreacted isoprene, and 3 mls. of a saturated hydroquinone solution added by means of a hypodermic needle to shortstop the reaction.

B. Determination of Percentage Conversion.

Approximately 20 gms. of latex was poured from the bottle into a previously weighed weighing bottle containing a stirring rod and ground glass top and weighed quickly to the nearest milligram. The latex sample was placed in an oven until dried to a constant weight. The percentage conversion was calculated on the basis of the amount of solids initially present in the reaction mixture.

C. Preparation of the Polymer for Viscosity and Gel Determinations.

The latex was poured from the 16 oz. bottle used into a beaker and stirred with a mechanical stirrer while first P.B.N.A. emulsion and then brine acid solution were added. Enough P.B.N.A. emulsion was added to give a P.B.N.A. content of approximately 1.25% of the dry polymer weight.

The P.B.N.A. emulsion was prepared by mixing 100 mls. of water, 3 gms. of R.R.C. soap, and 20 gms. of P.B.N.A. in a Waring Blendor for 3 - 5 minutes to obtain a stable emulsion.

The brine acid solution used for coagulating the latex had the following composition:

Water	6 liters
NaCl	367 gms.
Conc. H_2SO_4	10.5 mls.

The coagulated polymer was rinsed with warm water. Portions of it were cut into pieces of about a cubic millimeter in size and placed in a vacuum oven where they were dried at a specified temperature for a specified length of time.

D. Determination of Gel Content.

An approximately 0.2 gm. sample of the dried polymer was placed in an accurately weighed Harris cage and reweighed accurately. The cage was then suspended in a 250 ml. beaker so that it touched neither the bottom nor the sides. An amount of C.P. toluene sufficient to cover the cage was then pipetted in. The beaker was then placed in a desiccator containing toluene in place of desiccant. This prevented evaporation of toluene from the beaker. The desiccator was placed in the dark and allowed to stand without disturbance at room temperature for a minimum of 45 hrs.

The placing of the desiccator in the dark prevented any peptization by light. At the end of this time the cage was lifted slowly from the beaker and allowed to drain for a short time before suspending it in an oven at 80°C to dry the gel. The percentage gel in the polymer was calculated from:

$$\frac{\text{Weight of gel in cage}}{\text{Weight of sample used}} \times 100 = \text{Percent gel.}$$

$$\text{Percent sol} = 100 - \text{Percent gel.}$$

E. Determination of Intrinsic Viscosity.

The equation used for the evaluation of intrinsic viscosity was that proposed by Cragg, Rogers, and Henderson⁽⁵⁾ as being most suitable for G.R-S type polymers. It is:

$$[\eta] = \frac{8[(tr)^{\frac{1}{2}} - 1]}{C}$$

The concentration, C, in grams of polymer per 100 cc. of solution was calculated from the percentage sol and the volume of toluene used in the gel determination as the polymer solution resulting from the gel determination was used in evaluating viscosity.

The viscometers used were Ostwald-Cannon Fenske capillary viscometers A.S.T.M. No. 50. They were charged with 10.0 mls of liquid, the same pipette being used for each charging, and suspended in a water bath kept at 25°C ± 0.01. Time was allowed for the viscometer and contained liquid to come to the temperature of the water

bath. The flow time of the liquid was then taken, using a stop watch, until readings coinciding within 0.1 sec. were obtained.

After the flow time of each polymer solution taken, the viscometer was flushed twice with hot toluene and the viscometer filled with toluene and allowed to stand until the next time it was used. The flow time of toluene was frequently taken to ensure that the viscometer remained in proper working condition.

The difficulty, caused by bits of gel partially plugging the capillary tubes, that was experienced in last year's work was not experienced this year. This is believed to be due to the lower drying temperature used this year.

VARIATIONS OF EXPERIMENTAL PROCEDURES.

Four bottles of latex were prepared and shortstopped at different percentage conversions. Only 0.23 gms. of M.T.M. were used and all bottles were taken well beyond the gel point. The resulting polymers were then subjected to the following experimental variations:

- | | |
|-----------------------|-----------|
| 1. Drying temperature | 25° C. |
| Extraction period | 45 hours. |
| (a) Drying period | 15 hours. |
| (b) " " | 22.5 " |
| (c) " " | 48 " |
| (d) " " | 72 " |
| | |
| 2. Drying temperature | 35° C. |
| Extraction period | 45 hours. |
| (a) Drying period | 16 hours. |
| (b) " " | 24 " |
| (c) " " | 48 " |
| (d) " " | 72 " |
| | |
| 3. Drying temperature | 40° C. |
| Extraction period | 45 hours. |
| (a) Drying period | 18 hours. |
| (b) " " | 24 " |
| (c) " " | 48 " |
| (d) " " | 72 " |
| | |
| 4. Drying temperature | 35° C. |
| Extraction period | 72 hours. |
| (a) Drying period | 48 hours. |
| (b) " " | 72 " |
| | |
| 5. Drying temperature | 40° C. |
| Extraction period | 72 hours. |
| (a) Drying period | 48 hours. |
| (b) " " | 72 " |

RESULTS.

The results are tabulated for convenient comparison.

Variation	Sample No.	1	2	3	4
1 (a)	Gel [t]	26% 1.91	28% 1.84	25% 1.58	28% 1.81
1 (b)	Gel [t]	76% 0.98	78% 0.86	67% 1.03	81% 0.96
1 (c)	Gel [t]	74% 0.96	75% 0.92	72% 0.76	74% 0.97
1 (d)	Gel [t]	73% 1.09	77% 0.86	72% 0.80	74% 0.91
2 (a)	Gel [t]	60% 1.41	68% 1.37	69% 0.91	74% 0.90
2 (b)	Gel [t]	71% 1.03	70% 0.91	74% 0.75	74% 0.75
2 (c)	Gel [t]	71% 0.88	71% 0.88	73% 0.74	74% 0.75
2 (d)	Gel [t]	70% 0.87	73% 0.85	73% 0.77	77% 0.78
3 (a)	Gel [t]	70% 0.90	72% 0.91	72% 0.87	78% 0.78
3 (b)	Gel [t]	73% 0.94	74% 0.90	76% 0.76	77% 0.78
3 (c)	Gel [t]	71% 0.88	72% 0.87	71% 0.77	73% 0.76

Variation	Sample No.	1.	2	3	4
3 (a)	Gel [t]	72% 0.91	75% 0.88	70% 0.75	73% 0.75
4 (a)	Gel [t]	73% 0.86	70% 0.89	73% 0.76	72% 0.77
4 (b)	Gel [t]	70% 0.89	74% 0.85	71% 0.74	75% 0.75
5 (a)	Gel [t]	70% 0.90	71% 0.86	73% 0.74	70% 0.75
5 (b)	Gel [t]	72% 0.87	73% 0.89	70% 0.77	74% 0.74

DISCUSSION

In preliminary work it was found that values obtained for the intrinsic viscosities were quite irreproducible. A search for the cause of this irreproducibility lead to the testing of the drying procedure. The procedure used previously employed drying in a vacuum oven at 80°C for a period of 12 hrs. A gel-free sample was subjected to different drying temperatures for varying lengths of time. The values obtained for the intrinsic viscosity of the sample varied in an irregular manner with length of drying period at temperatures above 45°C. A prolonged drying period of 2 - 3 days at 60°C showed a definite melting and running of the polymer. Clearly a lower temperature was required. From the results given in the table it can be seen that a period of 48 hrs. at 35°C or a period of 24 hrs. at 40°C is required to obtain a reproducible viscosity. Also it can be seen that an extraction period of 45 hrs. is sufficiently long to extract all of the soluble portion since no change in the gel or viscosity values resulted when the extraction period was increased to 72 hrs. This was to be expected. Kolthoff and Medalia⁽¹³⁾ and Winkler⁽²⁾ found 40 hrs. to be a safe extraction period. There is no reason to believe that the lowered drying temperature should require a longer extraction period.

A drying period of 48 hrs. in the vacuum oven at 35°C was chosen as this temperature was further from 45°C, the temperature at which variations had been observed to start.

P A R T 2.

THEORY

A. Emulsion Polymerization.

The monomers are dispersed in water with an emulsifying reagent prior to polymerization. The product is a latex, i.e., an emulsion of polymer particles.

B. Locl of Reaction.

It has been found that, in general, most of the soap dissolved in water is present as aggregates each of which contains a large number of soap molecules. McBain⁽¹²⁾ designated these aggregates as micelles. The general structure that has been assigned to soap micelles is illustrated in Fig. 1 in which the molecules of soap are associated into double layers with the polar groups toward the water and the oil groups toward each other.

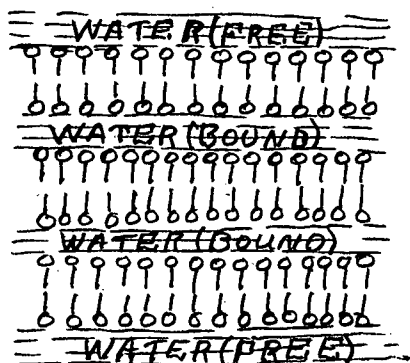


FIGURE 1.

The physical effects of the soap are:

1. The soap emulsifies the monomer.
2. The soap micelles dissolve monomer and mercaptan between the hydrocarbon ends of the oriented soap molecules.
3. The soap micelles serve as the initial locus for formation of polymer particles. The monomers, together with some of the mercaptan and peroxide, may be considered as present initially in the form of emulsion droplets but they diffuse through the aqueous phase into the micelles. The oil layers of the micelle contain the mercaptan, peroxide and monomer. The bound water layers are sufficiently thick to allow ions of the catalyst and activator to diffuse through them. X-ray evidence also indicates that the layers of soap have a liquid structure and thus contain many "holes" so they should allow water and catalyst, present in the water, to diffuse through them.

The soap micelle is, then, the most prominent initial locus. However, the polymer particle formed adsorbs a monolayer of soap molecules and causes the disappearance of the soap, and hence of the micelles. The monomer, mercaptan and peroxide may also diffuse into the polymer-adsorbed soap particle as well as into the micelle. Thus the main locus of reaction is changed upon the disappearance

ance of the micelles to the polymer-monomer particles.

C. Mechanism of Polymerization.

Our whole knowledge of simple chemical reactions excludes the possibility that a large number of individual molecules all collide at one moment and that a macromolecule is suddenly formed in one single collision. If⁽¹⁰⁾ one considers a polymerization reaction as a chain reaction, one can resolve the total reaction into individual processes as chain reactions are mostly composed of a relatively slow process of nucleus formation, a subsequent rapid growth reaction, and some kind of cessation process. These three processes are popularly termed initiation, propagation, and termination.

1. Initiation.

Wall and Swoboda⁽¹⁴⁾ studied the system benzoyl peroxide, sorbose, ferrous ion, pyrophosphate ion, and sodium stearate and advanced the following theory to explain the function of each of the reagents.

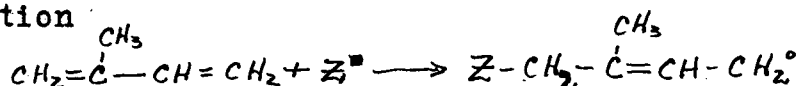
Peroxide decomposition supplies the free radicals for chain initiation and this decomposition is strongly catalysed by Fe^{++} but not by Fe^{+++} ions. High Fe^{++} concentration causes an almost instantaneous decomposition of peroxide which would be useless for polymerization. In this system the rate of decomposition is controlled by:

1. The peroxide is in the oil phase and the Fe^{++} ion is in

of polymerization at the temperatures normally used.

is an efficient initiator, its decomposition
Therefore, since cumene hydroperoxide is probably catalyzed
by the ferrous ion and the rate of decomposition controlled
by the four factors given above as was the case for the
benzoyl peroxide.

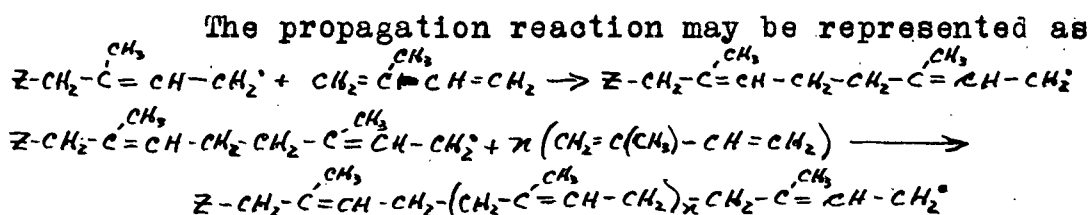
The initiation process may be represented by the
equation



2. Propagation.

The propagation reaction is the growth of a
polymer chain by the addition of the active radical formed
in the initiation step to successive monomer molecules.

Bawn⁽³⁾ considers the propagation reaction to be of very
short duration and the polymer particle once formed to be
inert towards further initiation and propagation possibil-
ities.

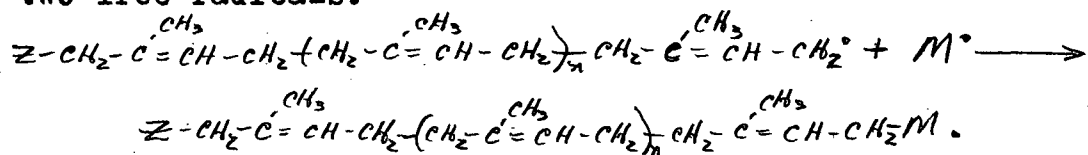


The resulting chain need not be the simple
head-to-tail arrangement given here. It is known from
recent investigations of Marvel⁽¹⁾ and his collaborators
that in some cases the substituents
on ethylene derivatives are arranged head-to-tail, while
in other cases they are arranged head-to-head, and are,
perhaps, sometimes irregularly distributed according to

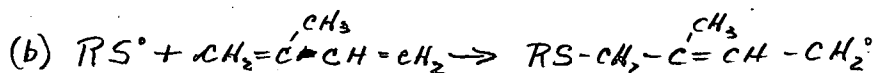
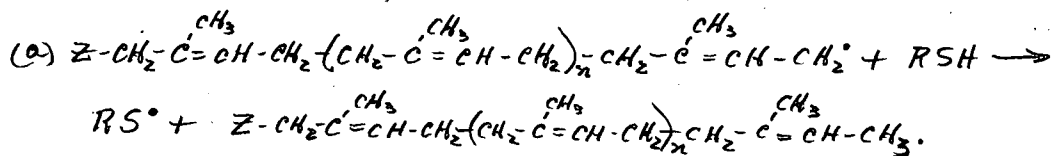
the laws of probability.

3. Termination.

Termination is the deactivation of the polymeric radical by a reaction which converts it into an inactive molecule. Termination may take place by the reaction of two free radicals.



where M may be one of the initiating free radicals or a growing polymer chain radical. Termination may also take place by chain transfer with a modifier molecule as shown below:



VARIATIONS OF EXPERIMENTAL PROCEDURES

The formula used in the preparation of the various polymer samples was essentially that outlined in A of Experimental Procedures in Part 1. The variations that were made in the formula in order to prepare different polymer samples are given in the following experimental procedures.

- A. The M.T.M. content and the polymerization time were varied so as to give the highest intrinsic viscosity possible with low gel content.

Amt. of cumene hydroperoxide used = 0.2 gms.

Amt. of R.R.C. soap used = 4.2 gms.

- B. R.R.C. soap - 4.2 gms.

Cumene Hydroperoxide - 0.2 gms.

An excess of M.T.M. was used and the polymerization period extended.

- C. R.R.C. soap - 4.2 gms.

M.T.M. - 0.56 gms.

An excess of cumene hydroperoxide was used and the polymerization period extended.

- D. R.R.C. soap - 3.0 gms.

Cumene Hydroperoxide - 0.2 gms.

The soap concentration was reduced to reduce the number of reaction loci. The length of the polymer-

ization period and the amount of M.T.M. were adjusted to give a product with the highest intrinsic viscosity possible and low gel content.

E. Same as D except that the soap concentration was still further reduced to 2 gms.

F. R.R.C. soap - 4.2 gms.

Cumene hydroperoxide - 0.1 gms.

The cumene hydroperoxide content was reduced to reduce the number of reaction loci. The length of the polymerization period and the amount of M.T.M. were adjusted to give a product with the highest intrinsic viscosity possible and low gel content.

G. R.R.C. soap - 3.0 gms.

M.T.M. - 0.45 gms.

Cumene hydroperoxide - 0.2 gms.

Dr. J.S. Tapp of the Polymer Corporation advised us to try an increase in the amount of catalyst as they had used this method with success in GR-S rubbers.

This was accordingly done in this part.

H. R.R.C. soap - 3.0 gms.

M.T.M. - 0.45 gms.

Cumene Hydroperoxide - 0.2 gms.

The polymerization temperature was decreased to 25°C.

RESULTS.

A.

Sample	P'z'n Time	Yield	Gel	$[\eta]$	M.T.M.
1	2.5 hrs.		80%	0.80	0
2	2.5 "		1%	1.30	0.23 gms.
3	2.5 "		2%	0.96	0.45 "
4	2.5 "		0	-	0.68 "
5	2.5 "		0	-	0.90 "
6	2.5 "		0	-	1.13 "
7	4.5 hrs.		80	0.76	0.23 "
8	4.5 "		60	0.87	0.34 "
9	4.5 "		55	1.18	0.45 "
10	4.5 "		1%	1.30	0.56 "
11	4.5 "		1%	1.00	0.68 "
12	5.0 hrs.	81%	77%	1.18	0.45 gms.
13	5.0 "	82%	1%	1.48	0.56 "
14	5.0 "	82%	1%	1.19	0.68 "
15	5.5 hrs.	84%	80%	1.21	0.45 gms.
16	5.5 "	86%	1%	1.65	0.56 "
17	5.5 "	85%	1%	1.35	0.68 "
18	6.0 "	93%	77%	1.12	0.45 "
19	6.0 "	93%	1%	2.29	0.56 "
20	6.0 "	91%	1%	1.82	0.68 "
21	6.5 hrs.	96%	85%	1.17	0.45 gms.
22	6.5 "	90%	1%	2.12	0.56 "
23	6.5 "	93%	1%	1.76	0.68 "

B.

Sample	P'z'n Time	Yield	Gel	$[\eta]$	M.T.M.
1	6.0 hrs.	92%	1%	1.46	0.80 gms.
2	24.0 "	96%	1%	1.39	0.80 "
3	31.0 "	94%	1%	1.49	0.80 "
4	48.0 "	94%	1%	1.60	0.80 "

C.

Sample	P'z'n Time	Yield	Gel	$[\eta]$	Cumene Hydroperoxide
1	12 hrs.	93%	1%	1.27	0.4 gms.
2	24 "	89%	1%	1.36	0.4 "
3	32 "	88%	1%	1.35	0.4 "
4	48 "	91%	1%	1.38	0.4 "
5	55 "	92%	1%	1.30	0.4 "

D.

Sample	P'z'n Time	Yield	Gel	$[\eta]$	M.T.M.
1	6.0 hrs.	93%	74%	1.00	0.23 gms.
2	7.0 "	94%	74%	1.08	0.23 "
3	8.0 "	94%	74%	0.96	0.23 "
4	24.0 "	95%	74%	0.87	0.23 "
5	32.0 "	94%	74%	0.84	0.23 "
6	5.0 "	82%	74%	1.48	0.30 gms.
7	6.0 "	90%	73%	1.40	0.30 "
8	5.5 hrs.	86%	74%	1.12	0.34 gms.
9	6.0 "	90%	72%	1.03	0.34 "

Sample	P'z'n Time	Yield	Gel	[η]	M.T.M.
10	6.5 hrs.	92%	73%	0.90	0.34 gms.
11	5.0 hrs.	82%	63%	0.87	0.38 "
12	6.0 "	89%	63%	0.94	0.38 "
13	8.0 "	95%	62%	1.02	0.38 "
14	5.5 "	86%	2%	2.51	0.45 "
15	6.0 "	90%	3.5%	2.63	0.45 gms.
16	6.5 "	92%	5%	2.60	0.45 "

E.

Sample	P'z'n Time	Yield	Gel	[η]	M.T.M.
1	5.0 hrs.	70%	1%	2.38	0.34 gms.
2	6.0 "	82%	0	1.34	"
3	7.0 "	86%	72%	1.04	"
4	5.0 hrs.	70%	Very low	M.W.	0.45 gms.
5	6.0 "	80%	1%	2.43	"
6	7.0 "	86%	1%	2.36	"

F.

Sample	P'z'n Time	Yield	Gel	[η]	M.T.M.
1	5.0 hrs.		75%	0.87	0.23 gms.
2	5.5 "		73%	0.72	"
3	6.0 "		67%	0.98	"
4	6.0 "	72%	72%	1.12	"
5	7.0 "	76%	75%	1.19	"

Sample	P'z'n Time	Yield	Gel	$[\eta]$	M.T.M.
6	8.0 hrs.	74%	72%	1.06	0.23 gms.
7	24.0 "	81%	73%	1.00	"
8	5.0 "	69%	52%	1.19	0.28 gms.
9	6.0 "	72%	55%	1.12	"
10	5.0 hrs.	69%			0.34 gms.
11	6.0 "	72%	35%	1.36	"
12	7.0 "	76%			"
13	5.0 "	68%	39%	2.35	"
14	5.5 "	70%	71%	1.20	"
15	6.0 "	71%	54%	2.04	"
16	5.0 "	79%	40%	1.09	0.39 gms.
17	6.0 "	80%	69%	0.87	"
18	7.0 "	82%	72%	1.07	"
19	5.0 hrs.	81%	35%	2.28	0.45 gms.
20	6.0 "	82%	1.5%	2.33	"
21	7.0 "	79%	3%	2.22	"

G.

Sample	P'z'n Time	Yield	Gel	$[\eta]$	FeSO ₄	Na ₄ P ₂ O ₇	Glucose
1	6.0 hrs.	91%	2%	2.66	.05 gms.	.5 gms.	0.5 gms.
2	"	95%	3%	2.59	.1 "	1.0 "	1.0 "
3	"	94%	3.5%	2.06	.2 "	2.0 "	2.0 "
4	7.0 hrs.	93%	3.5%	2.40	.2 "	2.0 "	2.0 "
5	6.0 hrs.	85%	3.5%	1.69	.3 "	3.0 "	3.0 "

H.

Sample	P'z'n Time	Yield	Gel	$[\eta]$
1	6 hrs.	Very low	-	-
2	24 "	65%	0	2.24
3	32 "	75%	0	2.61
4	48 "	80%	0	1.83

DISCUSSION

From table A it can be seen that by increasing the M.T.M. content and increasing the polymerization period the intrinsic viscosity could be increased up to the limiting value of 2.3 obtained with the use of 0.56 gms. M.T.M., 0.2 gms. cumene hydroperoxide, 4.2 gms. of R.R.C. soap and 6 hrs. polymerization. For smaller amounts of M.T.M. the gel point occurred at lower values of the percentage conversion and of the intrinsic viscosity. The intrinsic viscosity could not be increased above 2.30 by addition of larger quantities of M.T.M. and longer polymerization periods because the maximum percentage conversion occurred at six hours and made the attainment of higher percentage conversions impossible. The results listed in Table B bear this out. Additional amounts of M.T.M. only serve to decrease the intrinsic viscosity as is to be expected.

The addition of excess initiating reagent, cumene hydroperoxide, does not serve to re-initiate activity in the formed polymer particles and so produce further polymerization. This is in accordance with Bawn⁽³⁾ who says that the polymer particles, once formed, are inert towards further growth. An excess of initiating reagent only decreases the polymer particle size by supplying a greater number of initiation centers and by acting as a chain termination reagent also. This latter conclusion is

supported by the study Fordham and Williams⁽⁹⁾ made of the thermal decomposition of cumene hydroperoxide in relation to certain aspects of emulsion polymerization. They found that cumene hydroperoxide appears to enter into two phases of polymerization. The first is the initiation of polymerization by free radical production. The second is the stopping of the polymerization reaction by terminating the growing polymer chains and destroying the residual initiator or otherwise rendering it inactive. In Table C the results of polymerization with an excess of cumene hydroperoxide are listed and show a considerable decrease in intrinsic viscosity.

The soap content was reduced from 4.2 gms. to 3.0 gms. to reduce the number of reaction loci. A decrease in the number of reaction loci should lead to some increase in the polymer particle size. An intrinsic viscosity of 2.6 was obtained in 6 hrs. with the use of 0.45 gms. M.T.M. and 0.2 gms. cumene hydroperoxide. Less M.T.M. was necessary to prevent gel formation than was necessary to prevent gel formation when 4.2 gms. of soap was used. This is probably the main reason for the increase in intrinsic viscosity obtained.

A good emulsion was still obtainable and the percentage conversions proved to be quite accurately reproducible.

The results for decrease of soap content to 3.0 gms. are listed in Table D.

A further decrease of soap content to 2.0 gms. was unrewarding. The emulsion did not seem too stable and large amounts of precoagulum formed in some bottles. The reaction rate was decreased. Also there is a large discrepancy between the values obtained for the intrinsic viscosities of samples 1 and 2. The values for both were checked but the second determinations gave identically the same results. The polymer obtained for sample 4 was not in reasonable accord with the polymers obtained in samples 5 and 6; it was a very thin runny polymer. Table E lists the results of this variation.

A decrease in the amount of initiating reagent should produce fewer initiation centers and so give some increase in molecular weight. The amount of cumene hydroperoxide was accordingly reduced by one half to 0.1 gms. to see whether any significant change could be produced. The amount of soap used was 4.2 gms. No increase in viscosity was obtained; in fact, the maximum intrinsic viscosity obtained was 2.3, the same as was obtained in A with the use of 4.2 gms. soap and 0.2 gms. cumene hydroperoxide. This result is in accord with the views of Dr. J.S. Tapp of the Polymer Corporation who advised us in a letter that he did not think a decrease of initiating reagent would increase the molecular weight. As these results had been obtained prior to the receipt of the letter, they certainly serve to support his view. Furthermore, the maximum

conversion obtainable was decreased by about 10% and the conversions were not too reproducible. The results are listed in Table F.

In the letter mentioned above, Dr. Tapp advised us that we might try increasing the amount of catalyst used in order to increase the molecular weight as they had used this method successfully. This was accordingly done. 3.0 gms. of soap, 0.45 gms. of M.T.M., and 0.2 gms. of cumene hydroperoxide were used with varying quantities of catalyst. The results in Table G show a decrease in intrinsic viscosity with increasing amounts of catalyst. Results for the control bottle, sample 2, check very closely with the results obtained previously in D for identical amounts of the reagents and the same polymerization period. This testifies as to the reproducibility of the reaction using 3.0 gms. of R.R.C. soap.

Table H shows the result of a decrease in the polymerization temperature to 25°C. A decrease in the temperature might increase the molecular weight by slowing down the initiation and termination reactions. 3.0 gms. of soap, 0.45 gms. of M.T.M., and 0.2 gms. of cumene hydroperoxide were used. A maximum intrinsic viscosity of approximately 2.6 was obtained as before with the use of these quantities of reagents. It can also be seen that the reaction rate was greatly decreased, 32 hrs. being necessary to obtain 75% conversion.

It may be remarked in concluding that a maximum value of approximately 2.6 to 2.7 for the intrinsic viscosity was obtained by the hydrogen peroxide method of polymerization⁽⁴⁾. This value is also the maximum value obtained by the cumene hydroperoxide method of polymerization.

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