THE EFFECT OF MECHANICAL AGITATION ON THE EMULSION POLYMERIZATION OF STYRENE CATALYZED BY POTASSIUM PERSULFATE

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THE EFFECT OF MECHANICAL AGITATION ON THE EMULSION POLYMERIZATION OF STYRENE CATALYZED BY POTASSIUM PERSULFATE

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INTRODUCTION

Many factors influencing the emulsion polymerization of styrene have been thoroughly studied and extensive data are available concerning them.

The effect of mechanical agitation on the emulsion polymerization has been mentioned but not studied. The lack of information about this variable, we believe, has made comparison between data obtained by different workers difficult or meaningless.

This work is an attempt to show the possible importance of controlled type and rate of mechanical agitation in the emulsion polymerization field.

HISTORICAL

The polymerization of styrene was first observed in 1839 and since that time its polymerization has been studied more extensively than any other single monomer. Today, styrene is still one of the most important monomers and polystyrene in various forms, as well as the copolymers of styrene are of wide commercial importance. Extensive literature exists on polymerization of styrene in bulk and in solution by light, heat, and other catalysts.

In 1915 a patent by Fikentscher[1] described for the first time a method of polymerizing unsaturated monomers when suspended in aqueous emulsion. This method, due to certain features, namely the ease of temperature control, the high molecular weights of the products formed, and the introduction of a number of new controlling factors in the polymerization reaction, became of widespread use in the production of polymers.

Emulsion polymerization due to the heterogenity of the system and the many variables affecting rate and molecular weight of the polymers formed presents a complex problem. Extensive work has been carried out on the process by commercial concerns in the production of marketable products. Considerable theoretical and experimental work has also been reported but many of the variables that affect the reaction have only been mentioned. It still remains impossible to predict the reaction rate and molecular weights of the polymers from system to system or within a given system when one of the many variables is changed.

Mark and Raff[2] give a list of ingredients necessary for the emulsion polymerization as: Basic phase or emulsion medium, the main monomer, additional monomers, emulsifying agent or agents, stabilizer, regulator of surface tension, catalyst, chain regulator. The more important of these are monomer, catalyst and emulsifying agent.

The catalysts in emulsion polymerization are usually of the water soluble type such as hydrogen peroxide or salts of the peracids. Of the latter type potassium persulfate is most widely used.

Price and Kolthoff[3] have shown that the rate of polymerization is dependent on the square root of the persulfate concentration and that the concentration of persulfate decreases slightly towards the end of the reaction,[4] but the mechanism of the decomposition of the persulfate catalyst and its combination with the monomer to produce an active nucleus in an emulsion polymerization is not clearly understood.

The emulsifying agents are usually soaps or sulfonated aliphatic alcohols.

The polymers formed can be coagulated by the nonsolvents such as alcohol, ether, etc.

Hohenstein, Mark and collaborators[5] reported that emulsion polymerization of styrene takes place in the aqueous phase. If a layer of styrene, approximately 1 c.m. thick is placed in a test tube on the top of a dilute potassium persulfate or hydrogen peroxide solution and allowed to stand for several days, the aqueous phase slowly becomes cloudy.

Substances more soluble in water such as, methacrylic esters, vinylacetate etc., cause cloudiness more rapidly. These facts indicate that the polymerization takes place in the aqueous phase. Active centers produced by the interaction of the monomer and the potassium persulfate catalyst in water, can grow in the aqueous phase without being in direct contact with the liquid monomer.

In 1944, Vinogard and his collaborators[6] observed the behavior of small droplets of styrene in the aqueous solution of peroxides under the microscope. They found that the radius of these globules decreases roughly in proportion to the time of immersion and that further the polymer in the absence of soap is slowly formed in the aqueous phase outside of the droplet.

If soap solutions are used instead of pure water this situation changes significantly. Fryling and Harrington[7] reported that acrylonitrile polymerizes rapidly if it is in direct contact with water containing soap and catalyst.

An important observation made, by Kolthoff, Bovey and Dale[8] was that at a given oxygen concentration the length of the induction period and the disappearance of oxygen in the system is essentially independent of the soap concentration. This indicates that the activation reaction during the inhibition period, takes place preponderantly in the "truly" dissolved styrene and not in the solubilized fractions.

The extensive studies of Harkins, MacBain and their collaborators[9-13] on the solubilization of hydrocarbons in soap solutions in the absence and presence of peroxidic initiators provided a great deal of clarifying information and helped to develop the present picture of the course of an emulsion polymerization.

Hess[11] and his coworkers obtained a number of remarkable diffraction patterns from concentrated soap solutions, which indicate the presence of lamellar micelles. In order to explain the accelerating influence of soap on the rate of the polymerization, it is now assumed that lamellar micelles not only exist in concentrated (10%-30%) soap solution but also in the dilute (1%-3%) soap solutions. These micelles contain solubilized monomers and, because of the low soap to water ratio, are highly swollen with water. They permit, therefore, a free diffusion of water soluble initiator. It is thus concluded that these micelles are the principal loci for the formation of active centers.[11,14,15]

As the activation energy of the initiation of styrene in the emulsion polymerization by potassium persulfate was found to be 17,000 Cals., per mole[5,6,16] which is about 8,000 calories less than that in bulk or solution polymerization, it is apparent that the activation of the double bond by potassium persulfate inside of a soap micelle requires less energy than in the bulk and solution polymerization. It is assumed that the orientation and polymerization of the monomer molecules within the soap micelles are (at least partly) responsible for this drop of activation energy and at the same time responsible for an increase in the average degree of polymerization by decreasing the accessibility of the growing chains for chain terminators.[17]

Rainard[18] reported that there is a maximum potential which is due to the interaction between soap and persulfate, and since the yield maxima occurs in approximately the same region, he concluded that the reaction product of soap and persulfate is capable of initiating polymerization. In the emulsion polymerization, soap not only brings the monomer into the aqueous phase to establish a close contact with the activating radical, but also stabilizes the latex to prevent polymer particles from coalescing.

The molecular weights of the polymer at different stages of the reaction is significant in the study of mechanism and rate of reaction. The relation of rate of conversion to the average molecular weight was studied by Siggia, Hohenstein and Mark.[5] It was found that the molecular weight of the polymer formed, during the period immediately after the beginning of the polymerization is comparatively low. This is due to the deactivation by inhibitor. Following the initial phase, the molecular weight increases at a steady rate to reach a maximum. Finally the molecular weight decreases due to a decrease in monomer concentration and an increase of chain breaking decomposition products.

Many methods have been used to determine the molecular weight of the polymer, the most important being 'Osmotic', 'Viscoscimetric', 'Ultracentrifugal', and 'Light Scattering'. Use of any of these methods results in average molecular weights rather than absolute values. The 'Viscoscimetric' method for reasons of simplicity of equipment and operation is widely used.

Staudinger[12] developed an expression for molecular weight based on viscosity which has generally been employed in calculating average molecular weights. There is a great deal of controversy as to the validity of the Staudinger's equation and many correction factors have been applied to it.[19,20]

The average molecular weight of the polymer at any stage is fairly constant, a fact that has been explained by Schulz as being due to a constant ratio of chain propagations to chain terminations throughout the course of the polymerization. Smith[21] has shown that the average molecular weight of a polymer is related to the ratio of monomer to regulator.

Emulsion polymerizations generally have an induction period. This is the interval during which the activated monomers are reacting with inhibiting components in the system until the latter are substantially neutralized. After that, the chain propagation reaction becomes the major reaction. One type of inhibition is due to the traces of stabilizers left in the monomer. When the emulsion is agitated these stabilizers in the monomer diffuse into the aqueous phase and react with the activated monomers.[22,23,24] This goes on until their concentration (stabilizers) reaches a low value, after which the formation of long chain polymers begins. The rate of polymerization increases as the inhibitor decreases.

Another type of inhibition is due to traces of oxygen.[25]

Vinogard,[6] Frilette,[16] and Price[26] have pointed out that the exclusion of oxygen reduces an induction period. The inhibition period is the time necessary to build up a concentration of active nuclei sufficient to establish a steady-state radical concentration.

Breitenbach[27] polymerized styrene using a nitrogen atmosphere to prevent oxygen inhibition, and in this laboratory use of a nitrogen atmosphere, or lack of oxygen, has been found essential for the duplication of results.

EXPERIMENTAL

Reagents:

1. Styrene
2. Potassium persulfate
3. Hydrogen peroxide
4. "Colloidal" iodine
5. Sodium bisulfite
6. Dodecyl Mercaptan
7. Duponol-C
8. Ethanol (95%)
9. Aluminum Chloride

Styrene: The styrene was obtained from Dow Chemical Company. It was purified by vacuum distillation from a three-neck flask with ground glass joints under a nitrogen atmosphere, after the air in the distillation flask had been removed by flushing the system with nitrogen gas. The fraction boiling at 43°C/17 m.m. and having an index of refraction of 1.5420 was used.

The styrene was used immediately or stored under an atmosphere of nitrogen gas in a refrigerator for no longer than a week before use.

Potassium persulfate: The potassium persulfate used as a catalyst was Merck C. P. grade, which was recrystallized from water and the same lot of recrystallized material was used throughout this work.

Hydrogen peroxide: Hydrogen peroxide used was Baker and Adamson C. P. grade.

"Colloidal" iodine: The catalyst "Colloidal" iodine was prepared by dissolving 1 gm. of iodine crystals in 20 ml. of aqueous sodium hydroxide solution containing 0.36 gm. of the alkali and the sodium hydroxide was then neutralized to litmus by 36% hydrochloric acid. The solution was made up to the mark in a 100 ml. volumetric flask.

Sodium bisulfite: C. P. grade was used.

Mercaptan: Dodecyl Mercaptan from Sharples Chemical Company. Grade 3B.

Duponol-G: The Duponol-G used as an emulsifying agent was a sulfonated derivative of lauryl alcohol produced by Du Pont Company.

Ethanol: The ethanol used to coagulate the polymer was commercial 95% grade.

Aluminum chloride: The aluminum chloride used to coagulate the polymer was a technical grade.

Water: All water used was distilled under a nitrogen atmosphere from an alkaline permanganate solution as follows: Fifty ml. of alkaline potassium permanganate solution (300 gm. potassium hydroxide, 8 gm. potassium permanganate per liter of solution) and 2000 ml. of distilled water were refluxed under a nitrogen atmosphere for 30 minutes. The water was then distilled under a nitrogen atmosphere, the first 200 ml. discarded and the freshly distilled water collected was kept under a nitrogen atmosphere until used.

EQUIPMENT

The experimental emulsion polymerizations were carried out in a four neck flask, equipped with glass joints. The flask was fitted with a thermometer, a nitrogen inlet tube, a vacuum sampler, and a mercury sealed stirrer operated by a variable speed motor. The flask was immersed in a constant temperature water bath kept at 40°C ± 1.0°C. The same stirrer, flask, and fittings were used throughout these experiments.

The nitrogen used in these experiments was cylinder nitrogen, passed through two 500 ml. bottles containing 5% solution of pyrogallic acid in 10% aqueous potassium hydroxide, to remove traces of oxygen. The purified gas was passed into the reaction flask above the polymerizing reaction material.

The latter part of the experiments were carried out in a copper tank constant temperature water bath kept at 40°C ± 1.0°C. A rocking motor was used to shake the reaction bottle under water. The speed of shaking was also adjustable. The reaction flask was a 450 ml. bottle having a pharmaceutical rubber closure. The polymerization in the reaction bottle was carried out under a nitrogen atmosphere and samples were taken out by means of a hypodermic syringe through the rubber closure.

A Cannon - Fenske - Ostwald viscosity pipette was used to determine the specific viscosity of all polymer solutions.

PROCEDURES

Part I The Effect of Stirring on the Emulsion Polymerization of Styrene under a Nitrogen Atmosphere Catalyzed by Potassium Persulfate

Experiment 1

The reaction flask was flushed with purified nitrogen gas. To the reaction flask immersed in a water bath at 40°C ± 1.0°C were added six hundred and forty ml. of deoxygenated and distilled water and 6.4 gm. of Duponol-G.

The contents were stirred by the mechanical stirrer until the temperature of the mixture in the reaction flask was 40°C ± 1.0°C. The stirring was continued and 0.178 gm. of potassium persulfate was added. After five minutes 80 grams of styrene were added and the time of addition was recorded. The stirring was continued for another five minutes to complete the emulsion and then discontinued. In the so called"non-stirred" reactions stirring was always discontinued at this point but in studying stirred systems it was maintained throughout the reaction at a constant rate.

The beginning of the polymerization was determined by vacuum sampling very small amounts of the reaction mixture into alcohol every ten minutes. As soon as a cloudiness was observed, the reaction mixture was vacuum sampled at known time intervals into previously weighed (0.1 gm.) Erlenmeyer flasks containing 50 ml. of 95% alcohol and 0.001 gm. of aluminum chloride. The amount of sample was determined by weight difference and sampling was continued until the reaction was nearly complete.

The polymer in each sample was coagulated by the addition of three times the sample volume of 95% ethyl alcohol. The precipitated mixture was centrifuged and the clear supernatant liquid was removed by decantation. The polymer was washed several times with alcohol to remove traces of emulsifier and then dried in a drying room at 100°F. The dried polymer was weighed and the percentage polymerization (percent polymer formed) was calculated as follows:

$$\% \text{ polymerization} = 100 \times \frac{\text{Weight of Polymer in Sample}}{\text{Weight of Sample}} \times \frac{\text{Total Weight of Reaction Mixture}}{\text{Weight of Styrene Used}}$$

Experiment 2

The reaction was carried out under the same conditions and in a manner identical with that used in experiment 1 with the exception that the reaction was stirred at a rate of 360 revolutions per minute throughout the entire polymerization.

Experiment 3

This experiment was carried out under the same conditions and in a manner identical with that used in experiment 1 with the exception that the reaction was stirred at a rate of 720 revolutions per minute throughout the entire polymerization.

Duplicates were carried out for experiments 1 and 2.

Part II The Effect of Shaking on the Emulsion Polymerization under Nitrogen Atmosphere of Styrene Catalyzed by Potassium Persulfate

Experiment 4

To the reaction bottle (a 450 ml. bottle having a pharmaceutical rubber closure) were added 320 ml of deoxygenated distilled water, 3.2 gm. of Duponol-G and 0.09 gm. of potassium persulfate. Deoxygenated nitrogen gas was bubbled through the reaction mixture and then 40 gm. of styrene were added while the bubbling of nitrogen through the reaction mixture was continued. Then the bottle was quickly closed and the time recorded. The reaction flask was immediately placed in the shaker mounted in the copper tank constant temperature water bath kept at 40°C and shaken at a rate of 50 shakes per minute.

A similar sampling technique to that described in experiment 1 was employed for all bottle experiments except that sampling was by syringe through the rubber closure. It was necessary to stop the shaking and remove the bottle during the time necessary for sampling. The so called "non-shaken" reactions were sometimes carried out for convenience in the reaction flask described in experiment 1. In this case stirring was used to prepare the emulsion but stirring was discontinued within five minutes after adding the styrene. When a bottle technique was employed the bottle was shaken vigorously for five minutes after adding the styrene in order to prepare a suitable emulsion of the monomer in the aqueous phase.

Experiment 5

A polymerization reaction was carried out keeping all the conditions the same as in experiment 4 except the rate of shaking was increased to 340 shakes per minute.

Experiment 6

A polymerization reaction was carried out under the same conditions used in experiment 4 except the rate of shaking was 600 shakes per minute.

Duplicates were carried out for experiments 4 and 5.

Part III The Effect of Shaking on the Emulsion Polymerization under a Nitrogen Atmosphere of Styrene Catalyzed by a Redox System - Iodine-Sodium Bisulfite

Experiment 7

A polymerization was attempted under similar conditions (not stirred) to experiment 1 but with the potassium persulfate catalyst replaced by 0.001 M "colloidal" iodine.

No polymerization was observed after 46 hours so the attempt to polymerize under these conditions was discontinued.

Experiment 8

A polymerization was carried out under similar conditions to experiment 7 but with 0.001 M sodium bisulfite in addition to 0.001 M "colloidal" iodine.

Experiment 9

A polymerization was carried out under similar conditions to experiment 8 except that the bottle technique was employed and the reaction bottle was shaken at the rate of 340 shakes per minute.

Part IV The Effect of Shaking on the Emulsion Polymerization of Styrene under Nitrogen Atmosphere Catalyzed by Potassium Persulfate and in the Presence of a Chain Transfer Agent - Dodecyl Mercaptan

Experiment 10

A polymerization reaction similar to experiment 1 was carried out except that it contained 0.001 M dodecyl mercaptan.

Experiment 11

A polymerization was carried out under similar conditions to experiment 10 except that the bottle technique was employed and the reaction bottle was shaken at the rate of 340 shakes per minute.

Part V The Effect of Oxygen on the Emulsion Polymerization of Styrene Catalyzed by Potassium Persulfate

Experiment 12

A polymerization reaction similar to experiment 1 was carried out but a nitrogen atmosphere was used only for the first three hours and then an oxygen atmosphere was used for the rest of the reaction.

Experiment 13

A polymerization reaction similar to experiment 1 was carried out but 0.001 M hydrogen peroxide was used in addition to the 0.001 M potassium persulfate.

Part VI Average Molecular Weight Determinations

The average molecular weights of the polymers were determined by viscosity methods.

Into 100 ml. volumetric flasks were placed 0.10 gm. of polystyrene samples. Ten milliliters of toluene were added to these flasks which were placed in a hot room (44°C) overnight to dissolve the polymers.

Then the flasks were cooled to 20°C and the solutions were made up to the mark by adding more toluene. Ten milliliters of the solutions were transferred into the viscosity pipette and the efflux time of the solutions measured at 20°C.

In a similar fashion the efflux time of the solvent was also determined. The average molecular weights were calculated from Staudinger's equation:[28]

$$M = \frac{\eta_{sp}}{K_m \times C_m}$$

$K_m = 1.8 \times 10^{-4}$

C_m = molar concentration of the polystyrene based on a recurring group - 104.

$$\eta_r = \frac{\text{Time of efflux of solution at } 20^\circ C}{\text{Time of efflux of solvent at } 20^\circ C}$$

$$\eta_{sp} = r - 1$$

The average molecular weights of the polymer samples were also calculated using the Kemp and Peter's equation.[29,30]

$$M = \frac{K \log \eta_r}{C}$$

$K = 0.73 \times 10^4$ for polystyrene in toluene.

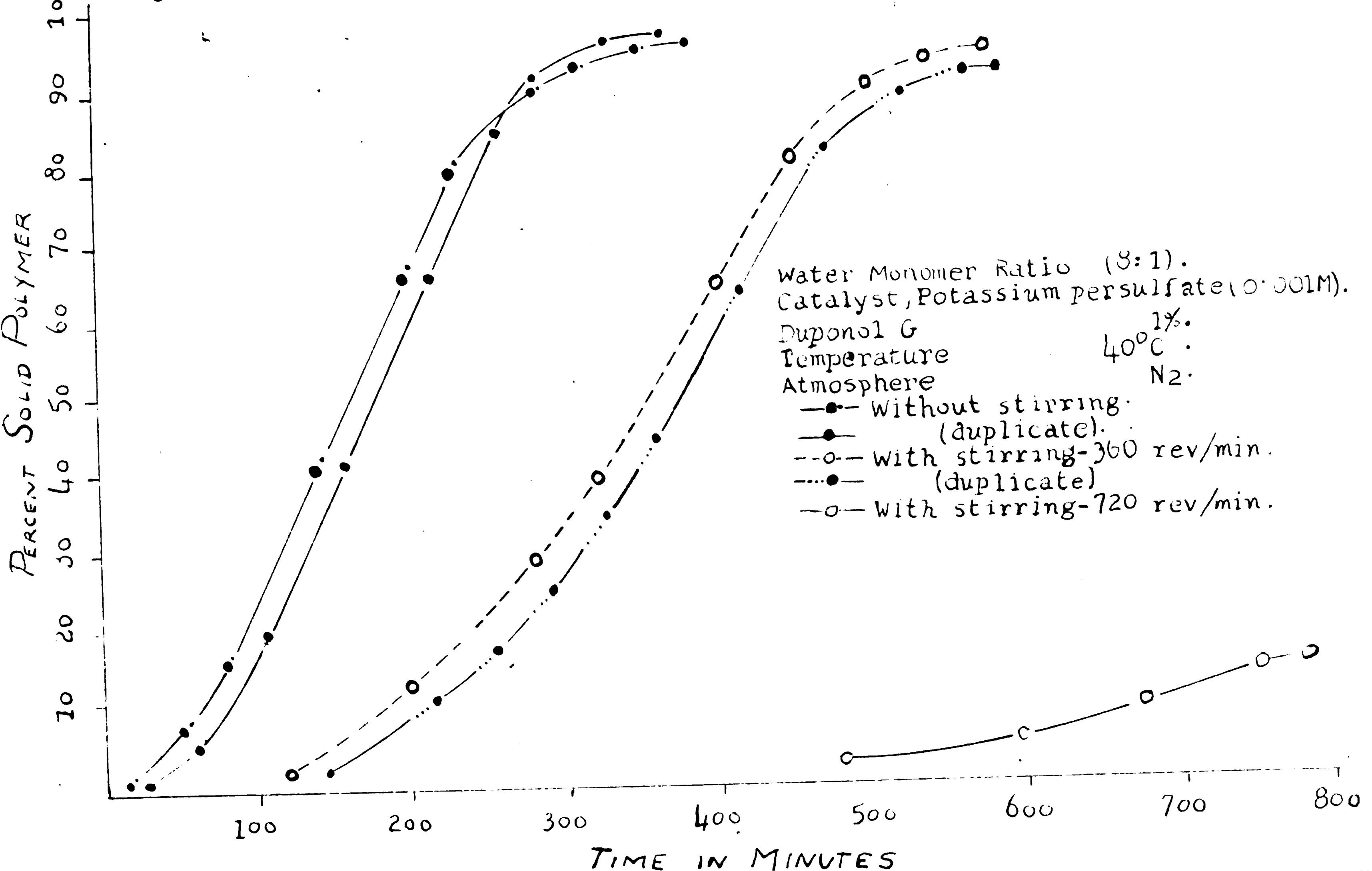
C = concentration of polymer gm./100 ml.

Average molecular weights were determined on all significant samples from the various emulsion systems investigated and the results tabulated.

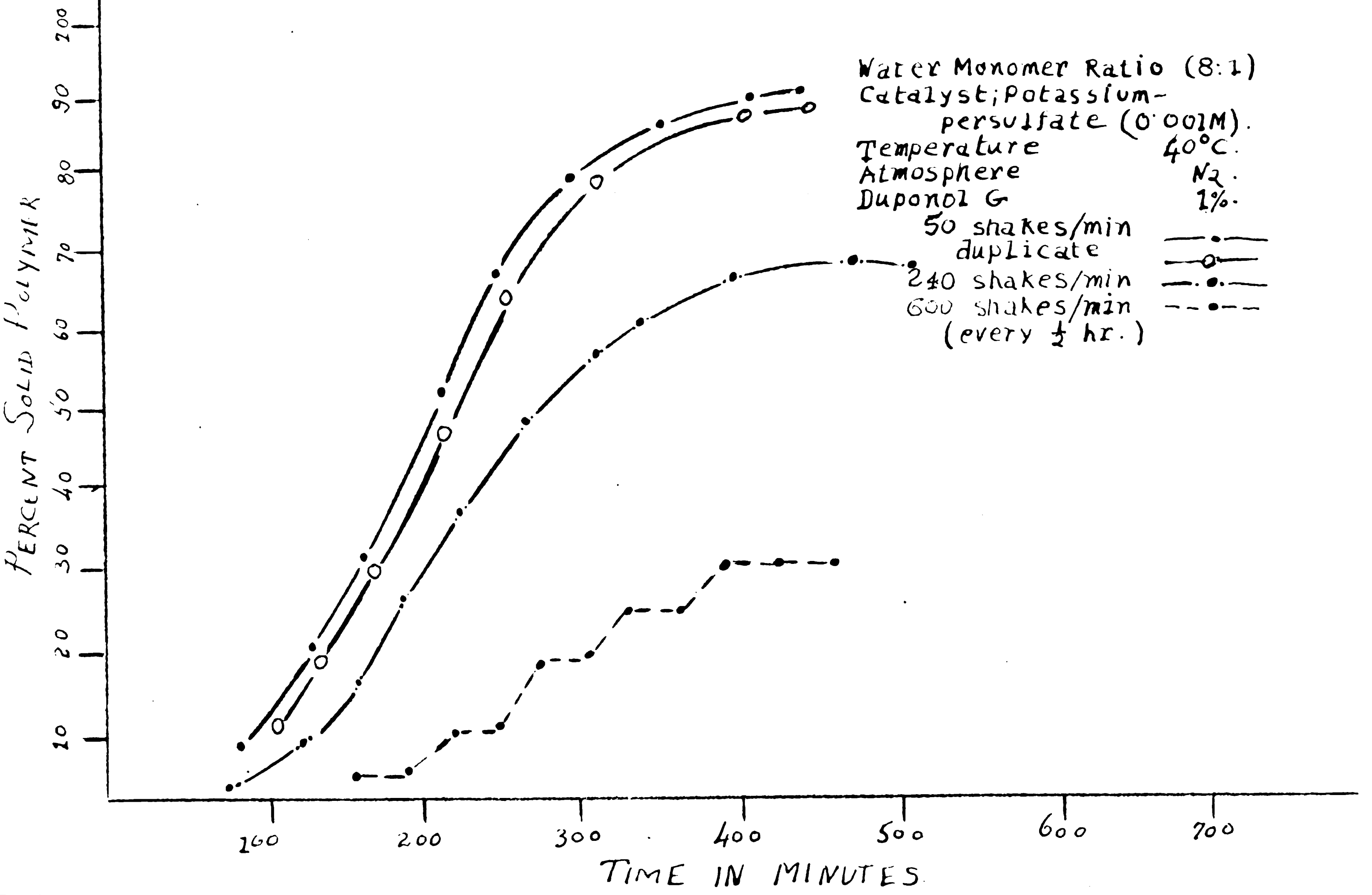
The specific viscosities η_{sp} were determined on polymer solutions at three different concentrations for some samples. A plot of specific viscosities against concentrations gives a straight line the intercept of which is the intrinsic viscosity of the polymer. (Graph V)

Intrinsic viscosities of several polymer samples were determined in this fashion.

GRAPH: I. THE EFFECT OF STIRRING ON THE EMULSION POLYMERIZATION OF STYRENE

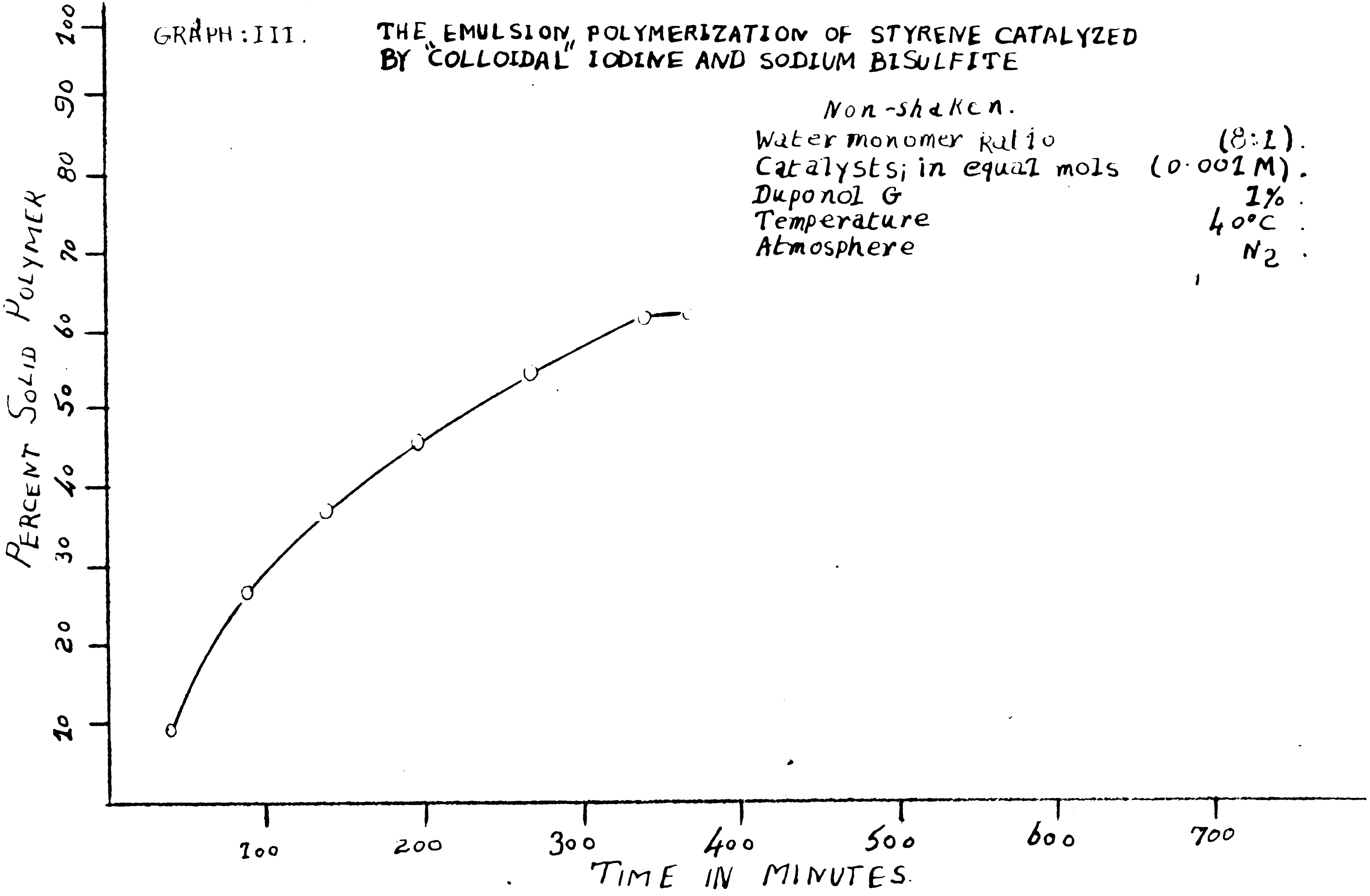


GRAPH: II. THE EFFECT OF SHAKING ON THE EMULSION POLYMERIZATION OF STYRENE.

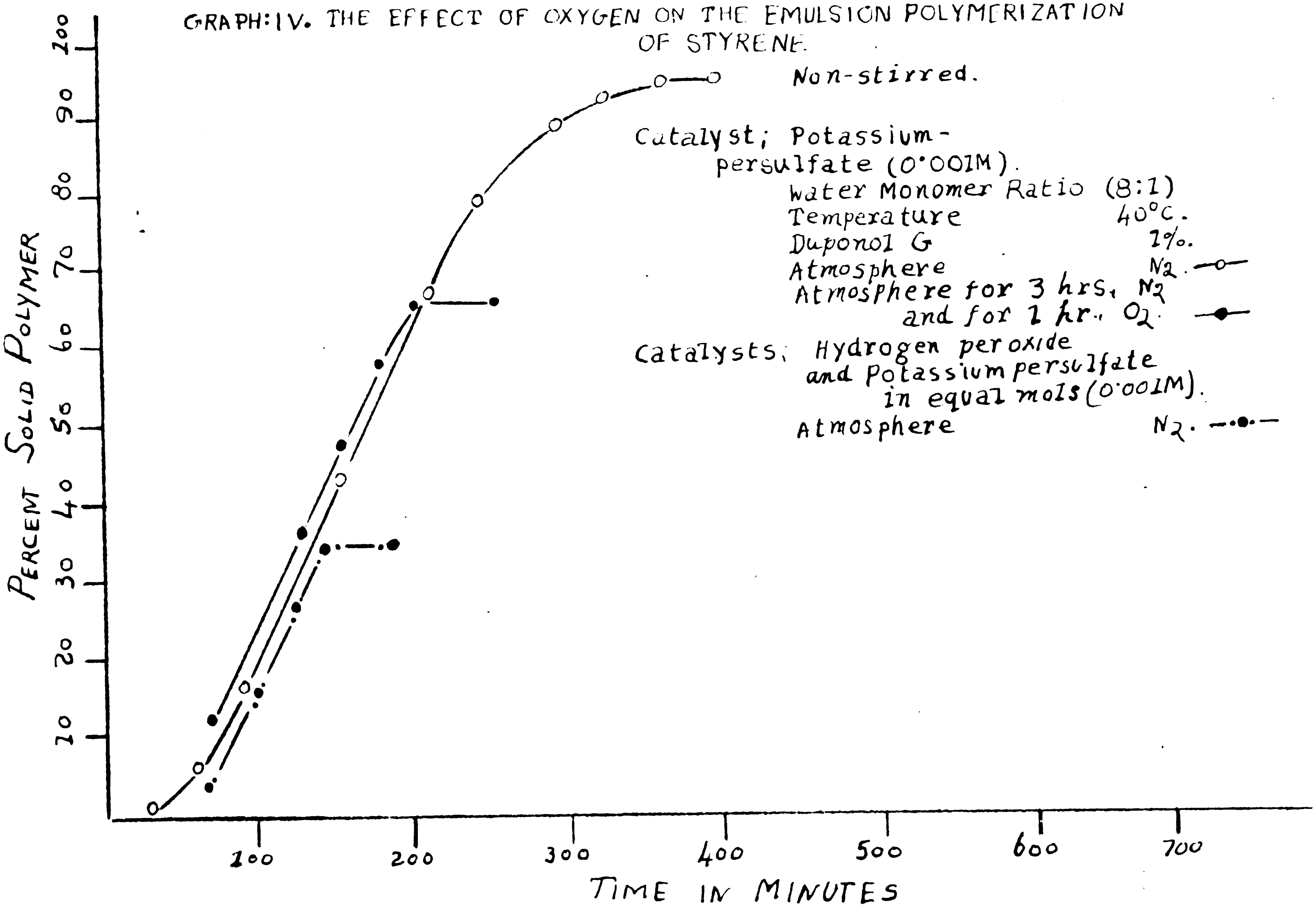


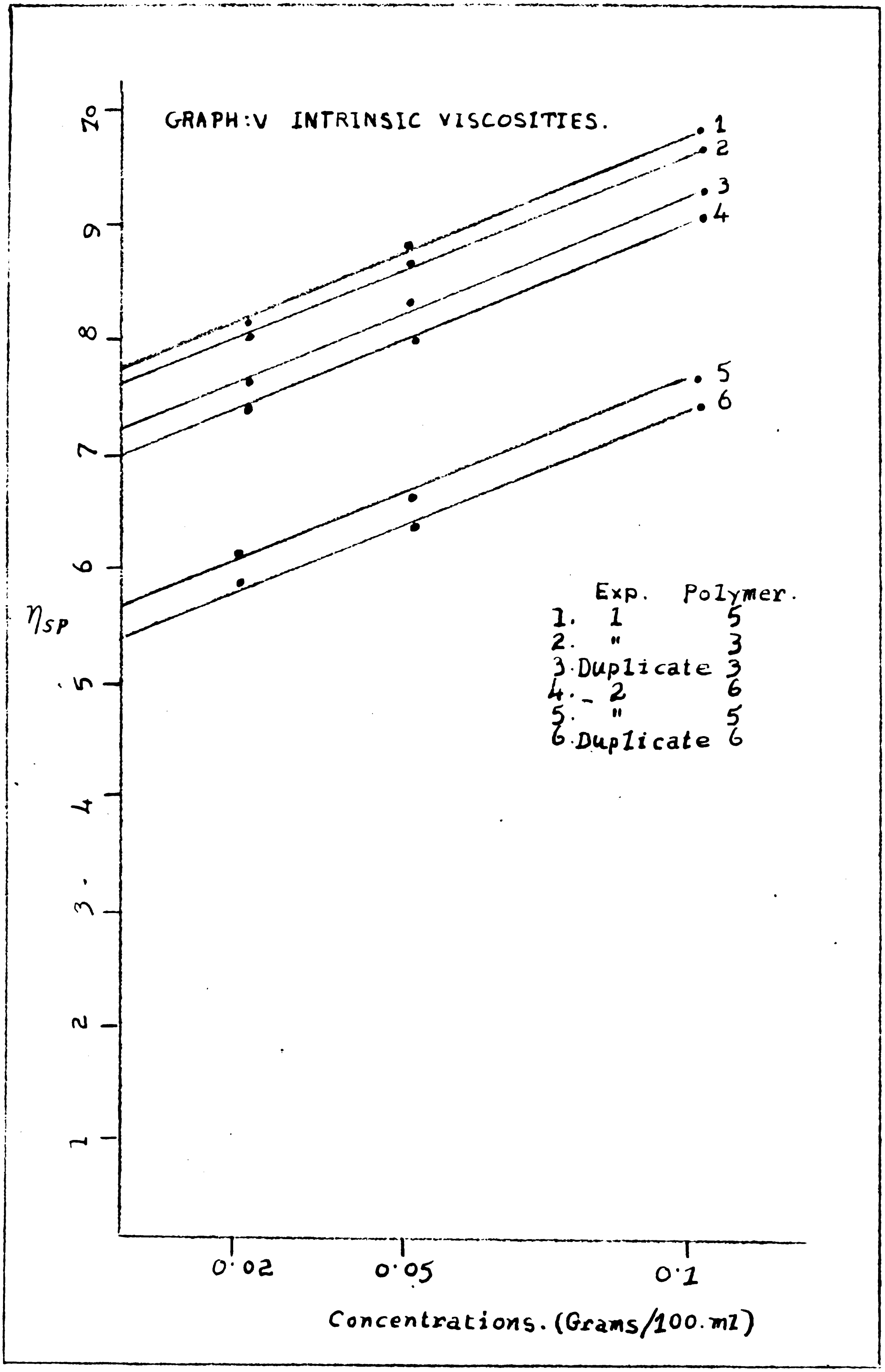
GRAPH: III.

THE "EMULSION" POLYMERIZATION OF STYRENE CATALYZED BY "COLLOIDAL" IODINE AND SODIUM BISULFITE



GRAPH: IV. THE EFFECT OF OXYGEN ON THE EMULSION POLYMERIZATION OF STYRENE.




GRAPH:V INTRINSIC VISCOSITIES.
η_{sp}
1
2
3
4
5
6
7
8
9
10
0·02
0·05
0·1
Concentrations. (Grams/100.ml)
1
2
3
4
5
6
Exp. Polymer.
1. 1 5
2. " 3
3 Duplicate 3
4. 2 6
5. " 5
6 Duplicate 6

DATA

Part I The Effect of Stirring on the Emulsion Polymerization of Styrene under a Nitrogen Atmosphere Catalyzed by Potassium Persulfate

Experiment I

Specific Conditions: Non-stirred.

Temperature	40°C ± 1°C.
Atmosphere	Nitrogen
Water Monomer Ratio	8 : 1
Catalyst ($K_2S_2O_8$)	0.001 M
Duponol-G	1%

Time (Minutes)	Polymerization %	Av. M. Wt. Staudinger	Av. M. Wt. Kemp and Peter	[η]
8	2			
60	5	16,700		
90	16	46,300		
120	38	480,000		
150	48	640,000	210,000	7.5
220	65	632,000	319,000	7.6
240	83	670,000	198,000	
310	92	432,000		
350	98	400,000		
380	98	400,000		

Duplicate

Time (Minutes)	Polymerization %	Av. M. Wt. Staudinger	Av. M. Wt. Kemp and Peter	[η]
10	3			
70	5			
110	20			
160	43	598,000		7.2

Duplicate (Cont.)

Time (Minutes)	Polymerization %	Av. M. Wt.	
		Staudinger	Kemp and Peter
235	63	661,000	
250	83		
300	92		
320	98		
350	98		

Experiment 2

Specific Conditions: Rate of stirring 360 rev/min.

Remaining conditions were the same as in experiment 1.

Time (Minutes)	Polymerization %	Av. M. Wt. Staudinger	Av. M. Wt. Kemp and Peter	$[\eta]$
120	3			
200	13	42,200		
240	20	233,000		
280	30	240,000		
325	43	509,000	205,000	5.6
405	63	594,000	232,000	7.0
460	80	501,000		
510	90	398,000		
550	93	388,000		
580	93	386,000		

Duplicate

Time (Minutes)	Polymerization %	Av. M. Wt. Staudinger	Av. M. Wt. Kemp and Peter	$[\eta]$
140	3			
210	11			
250	18			
300	23			
320	33			
350	45	548,000	189,000	5.4
420	60	590,000	225,000	
460	80			
520	90			
550	92			
580	92			

Experiment 3

Specific Conditions: Rate of stirring 720 rev/min.

Remaining conditions were the same as in experiment 1

Time (Minutes)	Polymerization %	Av. M. Wt. Staudinger	Av. M. Wt. Kemp and Peter
430	3		
600	6		
680	10	20,000	
750	15	22,000	11,000
800	15	20,000	10,000

Part II The Effect of Shaking on the Emulsion Polymerization of Styrene under a Nitrogen atmosphere Catalyzed by Potassium Persulfate

Experiment 4

Specific Conditions: Rate of shaking 50 shakes/min.

All the other conditions were the same as in the experiment 1.

Time (Minutes)	Polymerization %	Av. M. Wt. Staudinger
90	5	
120	20	
150	30	617,000
200	50	623,000
240	64	674,000
300	80	469,000
340	88	
400	90	
450	90	

Duplicate

Time (Minutes)	Polymerization %	Av. M. Wt. Staudinger
100	8	
130	19	
190	30	
220	44	617,000
250	63	684,000
300	78	410,000
400	88	
450	88	

Experiment 5

Specific Conditions: Rate of shaking 340 shakes/min.

All the other conditions were the same as in experiment 4.

Time (Minutes)	Polymerization %	Av. M. Wt. Staudinger
80	2	
120	8	44,000
150	15	86,000
180	25	166,000
220	36	277,000
270	49	555,000
310	57	644,000
350	61	277,000
400	67	208,000
470	70	189,000
520	70	84,000

Experiment 6

Specific Conditions: Rate of shaking 600 shakes/min. at 30 minute intervals. (Shaken for 30 minutes and let stand without shaking for 30 minutes)

Time (Minutes)	Polymerization %	Av. M. Wt. Staudinger
30		
60		
90		
120		
150	5	
180	5	

Experiment 6 (Cont.)

Time (Minutes)	Polymerization %	Av. M. Wt. Staudinger
210	10	42,000
240	10	43,000
270	20	58,000
300	20	57,000
330	25	85,000
360	25	86,000
390	30	85,000
420	30	85,000

Part III The Effect of Shaking on the Emulsion Polymerization of Styrene under a Nitrogen Atmosphere Catalyzed by a Redox system - Iodine - Sodium Bisulfite

Experiment 7

Specific Conditions: Non-shaken

Temperature	40°C ± 1°C
Atmosphere	Nitrogen
Water Monomer ratio	8 : 1
"Colliddal" iodine	0.001 M
Duponol-G	1%

Result = There was no polymerization even at 46 hours.

Experiment 8

Specific Conditions: All the conditions were the same as in experiment 7 except for the addition of 0.03 gm. (0.001 M) of sodium bisulfite.

Time (Minutes)	Polymerization %	Av. M. Wt. Staudinger
60	9	288,000
120	28	522,000
150	37	285,000
210	45	270,000
300	55	240,000
345	60	222,000
400	60	220,000

Experiment 9

Specific Conditions: All the conditions were the same as in the experiment 8 except the rate of shaking which was 340 shakes/min.

Result: There was no polymerization reaction even after 10 hours.

Part IV The Effect of Shaking on the Emulsion Polymerization of Styrene under a Nitrogen Atmosphere Catalyzed by Potassium Persulfate and in the presence of a chain transfer agent - Dodecyl Mercaptan.

Experiment 10

Specific Conditions: Non-shaken

Temperature	40°C ± 1°C
Atmosphere	Nitrogen
Water Monomer ratio	8 : 1
Dodecyl Mercaptan	0.001 M
Potassium persulfate	0.001 M
Duponol-G	1%

Time (Minutes)	Polymerization %	Av. M. Wt. Staudinger
360	2	
420	3	
480	4	
520	5	
600	5	

After 48 hours the % of polymerization was 73 and the molecular weight of the polymer was 33,333.

Experiment 11

Specific Conditions: All the conditions were the same as in the experiment 10 except the reaction bottle was shaken at the rate of 340 shakes/min.

Result: There was no polymerization reaction for 11 hours

Part V The Effect of Oxygen on the Emulsion Polymerization of Styrene Catalyzed by Potassium Persulfate

Experiment 12

Specific Conditions: Non-stirred

Temperature	40°C ± 1°C
Water Monomer ratio	8 : 1
Potassium persulfate	0.001 M
Duponol-G	1%
Nitrogen atmosphere	3 hours
Oxygen atmosphere	1 hour

Time (Minute)	Polymerization %	Av. M. Wt. Staudinger
60	12	
120	34	
150	47	
180	56	
210	66	612,000
240	66	600,000

Experiment 13

Specific Conditions: Non-stirred

Temperature	40°C ± 1°C
Atmosphere	Nitrogen
Water Monomer ratio	8 : 1
Hydrogen peroxide	0.001 M
Potassium persulfate	0.001 M
Duponol-G	1%

Time (Minutes)	Polymerization %	Av. M. Wt. Staudinger
60	3	
100	15	
120	25	
150	35	500,000
180	35	

DISCUSSION

Since this problem was a study of the effect of mechanical agitation on the emulsion polymerization of styrene a standard set of conditions and a standard technique were employed throughout unless otherwise noted. Only the type and rate of mechanical agitation was varied and that as indicated. The standard conditions were a water monomer ratio (2 : 1), a temperature (50°C), emulsifying agent Duponol-C 1% concentration based on the aqueous phase, catalyst (Potassium persulfate) at a concentration of 0.001 M based on the aqueous phase, a nitrogen atmosphere, and the use of deoxygenated water and monomer. In stirred reaction the same stirrer was employed throughout all the experiments.

For the sake of convenience of discussion, the characteristics of the emulsion polymerization that have been shown to be affected are classified as follows:

1. The induction period
2. The overall rate of conversion of monomer into polymer per unit time.
3. The total amount of monomer converted into polymer at the completion of the polymerization reaction.
4. The intrinsic viscosity of the polymer solution.
5. The average molecular weight of the polymer.

1. The induction period: It can be seen from graph I that the induction period without stirring is almost zero.

When the reaction is stirred at the rate of 360 revolutions per minute, the induction period is increased to 2 hours, and when the rate of stirring is increased to 720 revolutions per minute, the induction period is increased to 8 hours.

One may wonder why the induction period keeps increasing, when the rate of stirring is increased, in-as-much as there is a greater possibility of the collisions of the activated monomer nuclei against the monomer molecule to build up long chain polymers. This effect may be due to two factors. Firstly, the stirring acts to destroy or prevent formation of active nuclei. Secondly, when the rate of stirring is increased, the amount of impurities diffusing into the aqueous phase from the monomer[22,23,24] is also increased. Therefore more activated monomers may be deactivated by impurities and thus the induction period may increase.

2. The overall rate of conversion of monomer into polymer per unit time: The slope of the reaction rate curve, when the rate of stirring is 720 revolutions per minute is the smallest of the three (non-stirred, 360 revolutions, and 720 revolutions per minute). This indicates that the rate at which the monomer is converted into polymer in this case is the slowest. This fact suggests that the stirring destroys or prevents the formation of active nuclei and hence the rate of conversion of monomer into polymer decreases in stirred systems. The slope of the curve, when the stirring rate is only 360 revolutions per minute, is greater than that when the stirring rate is 720 revolutions per minute. The stirring effect is still noticeable but to a lesser extent. The slope of the curve in the case of non-stirred system is the greatest of the three, which indicates that the conversion of monomer into polymer per unit time is the greatest in reactions carried out with minimum amount of agitation.

3. The total amount of monomer converted into polymer at the completion of the polymerisation reaction: The total amount of monomer converted into polymer at the end of the reaction decreases with the increase in agitation (graphs I and II). This is especially true when

the rate of stirring is 720 revolutions per minute and the reaction stops when only 20 percent of monomer is converted into polymer. This can be explained on the assumption that all the catalyst has been used up in forming active nuclei some of which have been destroyed by increasing the agitation. Therefore, there would not be enough catalyst to activate more monomers so that the conversion could be completed.

It has been observed in this laboratory that polymerization reactions when only partially completed will continue to polymerize on further addition of catalyst. Therefore, it is probable that if sufficient catalyst is present the final conversion will be independent of the rate of stirring. Stirring effects will be observed only when low concentrations of catalysts are employed.

4. The intrinsic viscosity: The intrinsic viscosities of the styrene polymers are obtained by determining the specific viscosities (η_{sp}) at three different concentrations and plotting against the concentrations. Straight and parallel lines are obtained. The intercepts of these lines on the ordinate of η_{sp} are the intrinsic viscosities of the polymers. (Graph V)

The intrinsic viscosities of the polymers of the non-stirred system are greater than that of the stirred system. This agrees with the fact that the average molecular weight of the former is greater than the latter. (Experiments 1 and 2)

5. The average molecular weight: The average molecular weights of samples from a typical emulsion polymerization have been shown to remain fairly constant and at a maximum value for the system between 40 and 60% polymerization. Comparisons can be made, therefore, at approximately 50% conversion between the average molecular weights of polymer produced under different conditions. Average molecular weights are lower in the

stirred and shaken systems covered by this work than are the average molecular weights in the non-stirred systems. The difference in the average molecular weights of the polymer in stirred and non-stirred systems can be attributed to the termination effect of the stirring which has a tendency to cause the formation of short chain polymers.

The determination of average molecular weight by Staudinger's equation [29] has been criticized by many people and many modifications proposed. One of these modifications was by Kemp and Peter[26,27] who developed an equation to determine the average molecular weight of polystyrene based on relative viscosities. The results obtained by either of the equations are valid for comparison purposes only.

For example, the average molecular weights of the polymers, calculated by Staudinger's equations is fifty or sixty percent higher than those obtained by Kemp and Peter's equation (Refer to Experiments 1, 2, 3)

Graph II represents the effect of shaking, at different rates, on the emulsion polymerization of styrene catalyzed by potassium persulfate. The effect of shaking has the same effect on the emulsion polymerization of styrene as that of stirring; but the effect is not as great as in the case of stirring.

The polymerization rate of the styrene, catalyzed by "Colloidal" iodine and sodium bisulfite, without stirring and under condition outlined for experiment 1, is shown in graph III.

When the "Colloidal" iodine alone was used as a catalyst (0.001 M) there was no reaction for 1.6 hours. On the addition of sodium bisulfite in equal molal quantity to the iodine (0.001 M), the reaction started and the polymerization in half an hour was about 9%.

This suggests that the iodine acts as an oxidizing agent and the sodium bisulfite as a reducing agent and they thus constitute a typical redox system. Such systems are known to polymerize styrene in emulsion.

When the same reaction mixture was agitated at the rate of 360 shakes per minute there was no reaction for 12 hours. This shows that agitation also affects this system. When the emulsion polymerization of styrene in the presence of dodecyl mercaptan and catalyzed by potassium persulfate dodecyl mercaptan was agitated at the rate of 360 shakes per minute, there was no polymerization for 10 hours.

These observations suggest that the shaking and stirring also have a terminating effect on the emulsion polymerization of styrene, in the presence of a redox system or a chain transfer agent.

The effect of oxygen on the emulsion polymerization of styrene is shown in graph IV. A nitrogen atmosphere was used for the first 3 hours and an atmosphere of oyxgen was used for 2 hours. The reaction is stopped in 40 minutes by oxygen which acts as an inhibitor by destroying or preventing formation of active nuclei. Graph IV presents the polymerization curve when hydrogen peroxide and potassium persulfate were used in equal mols (0.001 M). A nitrogen atmosphere was used throughout the reaction. The rate of polymerization is slow and the reaction is stopped when the percentage of polymerization is about 30. This is probably due to the oxygen produced by the action of hydrogen peroxide and potassium persulfate. It will also be noted that the average molecular weights of the polymers formed are low. (Experiments 12 and 13).

CONCLUSIONS

Under the conditions of this investigation, the following observations have been made on emulsion polymerization of styrene at 40°C.

1. The induction period increases with the increase in agitation.

2. The rate of conversion of monomer to polymer per unit time decreases with the increase in rate of agitation.

3. The total amount of monomer converted into polymer at a given catalyst concentration decreases with the increase in rate of agitation.

4. The average molecular weight of polymer formed decreases with increased rate of agitation.

5. Similar effects as ~~sighted~~ cited above have been demonstrated also in redox catalyzed systems and in systems employing a chain transfer agent.

6. "Colloidal" iodine at 0.001 M is not effective as a catalyst.

7. The redox system 0.001 M "Colloidal" iodine vs. 0.001 M sodium bisulfite is an effective catalyst. The amount of monomer converted into polymer before the reaction stops was 60%.

8. The redox system 0.001 M hydrogen peroxide vs. 0.001M potassium persulfate will cause polymerization. The total amount of monomer converted to polymer before the reaction stops was 35%.

9. Addition of oxygen will stop the polymerization.

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