EFFECT OF PREMIX ON
INVERSE EMULSION
POLYMERIZATION

By

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CHAPTER I

INTRODUCTION AND LITERATURE SURVEY

Emulsion polymerization was first developed and used on a commercial scale during World War II for the production of synthetic rubber. Emulsion polymerization consists of emulsifying a water-insoluble organic monomer containing an ethylenic bond with water to form an oil-in-water emulsion (dispersed oil phase in a continuous water phase). A water soluble initiator of the type which forms free radicals, is used to initiate the polymerization reaction. Emulsion polymerization has many advantages over solution, bulk and solid-state polymerization schemes. Due to the continuous water phase, temperature control can be maintained and the relatively large heat of reaction can be removed more easily than with other types of polymerization systems. The viscosity of the emulsion is low and does not drastically change during the course of the reaction, thus giving excellent mixing and transport properties. By far, the greatest advantage is the ability to achieve a high degree of polymerization and at the same time have a high rate of polymerization. The only disadvantage of emulsion polymerization is the added cost of the ingredients and equipment necessary to form the emulsion. Following World War II, emulsion polymerization was developed for use throughout the petrochemical industry.

In 1961, John Vanderhoff (13) reported the first inverse emulsion polymerization process. Inverse emulsion polymerization consists of dissolving an organic monomer in water and emulsifying the water solution in an inert organic liquid (such as toluene or xylene) to form a water-in-oil emulsion. This is in contrast to the previously described oil-in-water emulsion. A free radical forming initiator is used to start the polymerization reaction. The advantages and disadvantages of inverse emulsion polymerization are the same as those discussed previously for emulsion polymerization.

In 1945, Harkins (6) published a paper describing a feasible mechanism for emulsion polymerization. Smith and Ewart (11) carried out elegant calculations based on the mechanism proposed by Harkins, which have since become accepted as the standard for emulsion polymerization. In 1962, Vanderhoff (14) showed that the Smith-Ewart equations applied equally well for inverse emulsion polymerizations.

Inverse emulsion polymerization as with any polymerization reaction, consists of three basic reactions: initiation, propagation, and termination. Initiation occurs in inverse emulsion polymerization when a free radical attacks a monomer molecule solubilized in a micelle. Above a certain concentration of emulsifier (designated the critical micelle concentration which varies with the type of emulsifier and solubility of the emulsifier in the components forming the emulsion) the molecules of the emulsifier form aggregates called micelles which contain a hundred or more molecules of emulsifier in a spherical form with a diameter of approximately 50 to 100 angstroms. Propagation, or polymer growth, occurs in the micelles with monomer diffusing from the water droplets to the micelles. The polymer particles grow larger than the micelles can contain and become distinct particles stabilized by emulsifier. Termination of the growing polymer chains occur either by a free radical from the initiator (or an impurity in the system), combining with a polymer chain or by two polymer chains joining to form a stable chemical bond.

Typically the graph of percent monomer conversion to polymer versus time of reaction is an S-shaped curve as shown in Figure 1. The initiation period consists of the initiatior forming free radicals which attack the double bond of the monomer to start the polymer chain. Any impurities in the reaction system which consume free radicals (such as oxygen) will decrease the number of polymer particles and retard the rate of reaction. The end of the initiation stage is marked by the disappearance of the micelles as the emulsifier is needed to stabilize the polymer particles. The propagation or growth period consists of polymer chains growing and the monomer diffuses from the monomer droplets to the polymer particles. The number of particles is constant during the propagation period, and

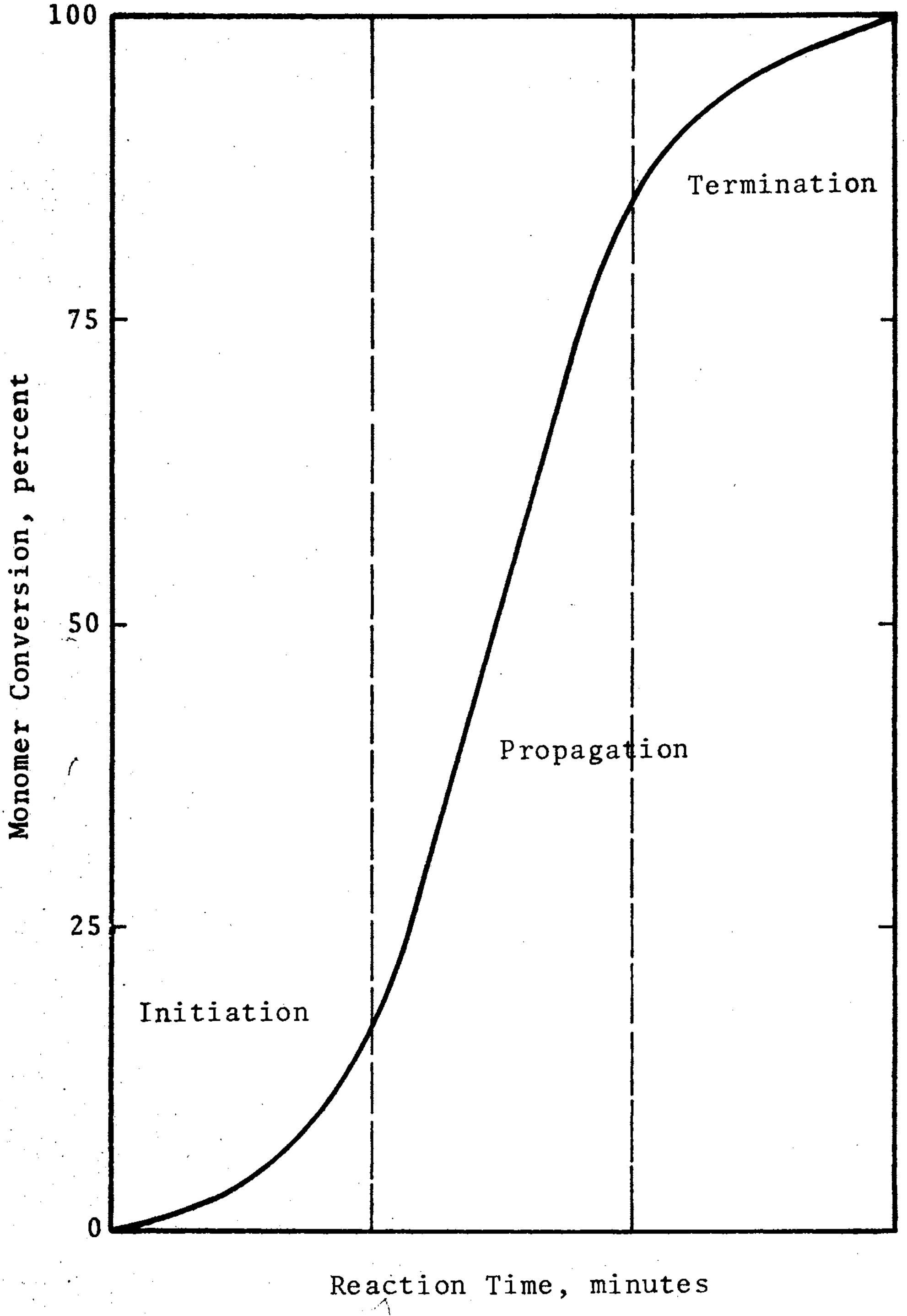

Figure 1. Typical Emulsion or Inverse Emulsion Polymerization Reaction

therefore the rate of reaction is constant (The straight line portion of Figure 1). During the termination period the number of growing polymer chains decreases and the rate decreases appropriately.

Batch reactors are used for industrial scale inverse emulsion polymerization. The effect of the degree and the rate of agitation on the course of the reaction is not well understood. However, several people have reported that the effect of stirring is to influence both the reaction rate and the product quality of emulsion polymerization. In 1951, Shunmuklam, et al. (10) reported: "Increasing the agitation increases the inhibition, decreases the polymerization rate, and lowers the average molecular weight of the polymer formed." The results of Shunmuklam, et al. were discredited on the grounds that the nitrogen used to flush the reactor was contaminated with oxygen which inhibits emulsion polymerization. In 1961, Evans, et al. (4) reported on the three stages (initiation, propagation, and termination) of emulsion polymerization of vinylidene chloride. Their results were "that the first-stage rate decreases with increasing stirring speed, that the second-stage rate increases with increasing stirring speed, and that the rate of the third stage is independent of stirring speed." Evans, et al. explained their results in terms of emulsifier adsorbed to the monomer droplets and coalescence of the monomer droplets.

In 1972, Nomura, et al. (17) published the results of an investigation of the effect of stirring on the emulsion polymerization of styrene. Nomura, et al. arrived at four basic conclusions. One conclusion is that impurities (such as oxygen and other free radical inhibitors) will greatly influence the rate of emulsion polymerization in a very complex effect which varies widely with the degree of stirring. Their second conclusion is that emulsion polymerization is affected by the degree of agitation even under a pure nitrogen atmosphere. The third conclusion is that at high speeds of stirring, coagulation and coalescence cause a decrease of the reaction rate. The polymerization reaction is diffusion-controlled at low speeds of agitation. The fourth conclusion is that emulsifier is adsorbed on the monomer droplets and at low emulsifier concentrations the loss of effective emulsifier is enhanced by higher rates of agitation.

No information has been published on the effect of stirring on inverse emulsion polymerization. However, from the information available on emulsion polymerization, the effect of stirring on inverse emulsion polymerization would be anticipated to be determined by the size of the dispersed water phase (smaller droplets would increase the total area available for diffusion of the monomer to the polymer and the larger area would require more emulsifier for stability thus reducing the number of micelles and hence reducing the number of possible reaction sites), and by the amount of emulsifier adsorbed to the water droplets (thus depleting the amount of emulsifier available to form micelles and to stabilize polymer particles). As with emulsion polymerization, the effect of impurities can be expected to be complicated and vary widely with the degree of stirring.

The degree of premixing relates to the speed and duration of mixing of the emulsion prior to adding the initiator. This experiment is a preliminary study of the effect of the degree of premixing on the rate of reaction of inverse emulsion polymerization of acrylamide with an aim to develop the apparatus and techniques, and to define the variables and problems for a more detailed study.

The initial part of the study consisted of assembling the equipment and developing the procedures used in determining the extent of conversion of monomer to polymer during the course of the reaction. In order to control the effect of impurities in the nitrogen (particularly oxygen which consumes free-radicals) the rate of stirring was held constant during the reaction itself.

The second part of the study consisted of forming the emulsion under various degrees of premixing (mixing prior to initiation of the reaction). All other variables were held constant.

In the final part of this study, the amount of initiator was reduced and the effect of the degree of premixing was studied using the same procedures as in part two.

The choice of acrylamide for the monomer was because of the present growing interest in polyacrylamide for use as a sedimentation agent for control of water pollution. Polyacrylamide is also utilized for a paper sizing agent, an adhesive, a cement, a dispersant, synthetic leather, paper, synthetic fibres, rubber, textiles, a soil stabilizing agent, and a synthetic resin.

CHAPTER II

EXPERIMENTAL

A. Description of Equipment

The experimental system is shown in Figures 2, 3, and 4. Table I contains a complete listing of the equipment used in this study, and Table II contains a listing of the chemicals used.

The batch reaction system was constructed to perform four necessary functions: (1) purging with nitrogen to prevent oxygen from stopping the reaction, (2) stirring to obtain homogeneity, enhance heat transfer, and prevent degradation of the emulsion, (3) heat addition and removal to control the emulsion temperature for essentially isothermal operation, and (4) removal of samples to determine the extent of reaction.

Referring to Figure 2, nitrogen leaves the storage bottle and goes through a 1/2-inch teflon tube to a 1/4-inch stainless steel tube which enters the reactor. The nitrogen exits the stainless steel tube approximately two inches above the top of the emulsion when the reactor is full. The nitrogen leaves the reactor through two condensers which return condensed toluene to the reactor. Tap water was used in the condensers.

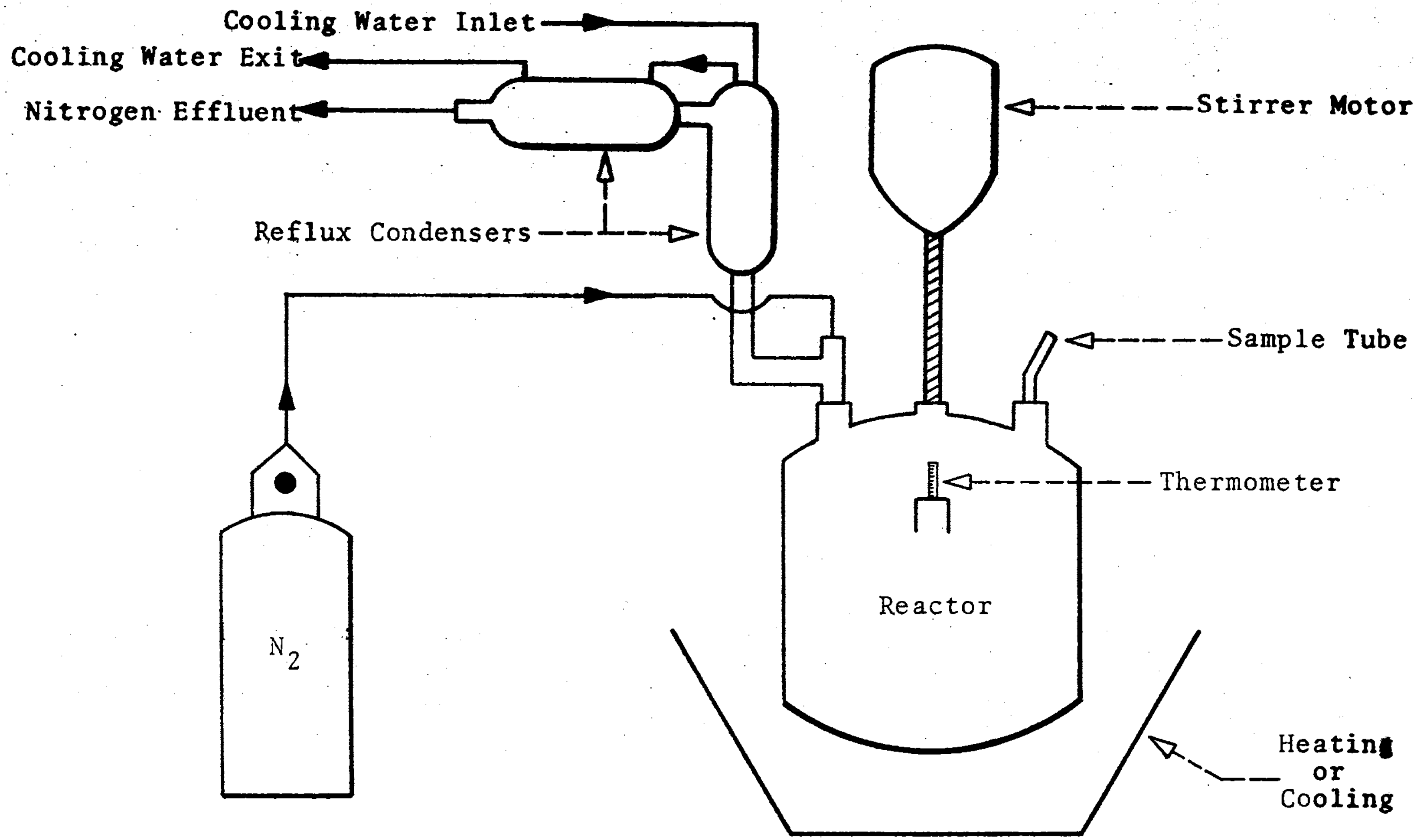

Figure 2. Flow Diagram of Reactor System

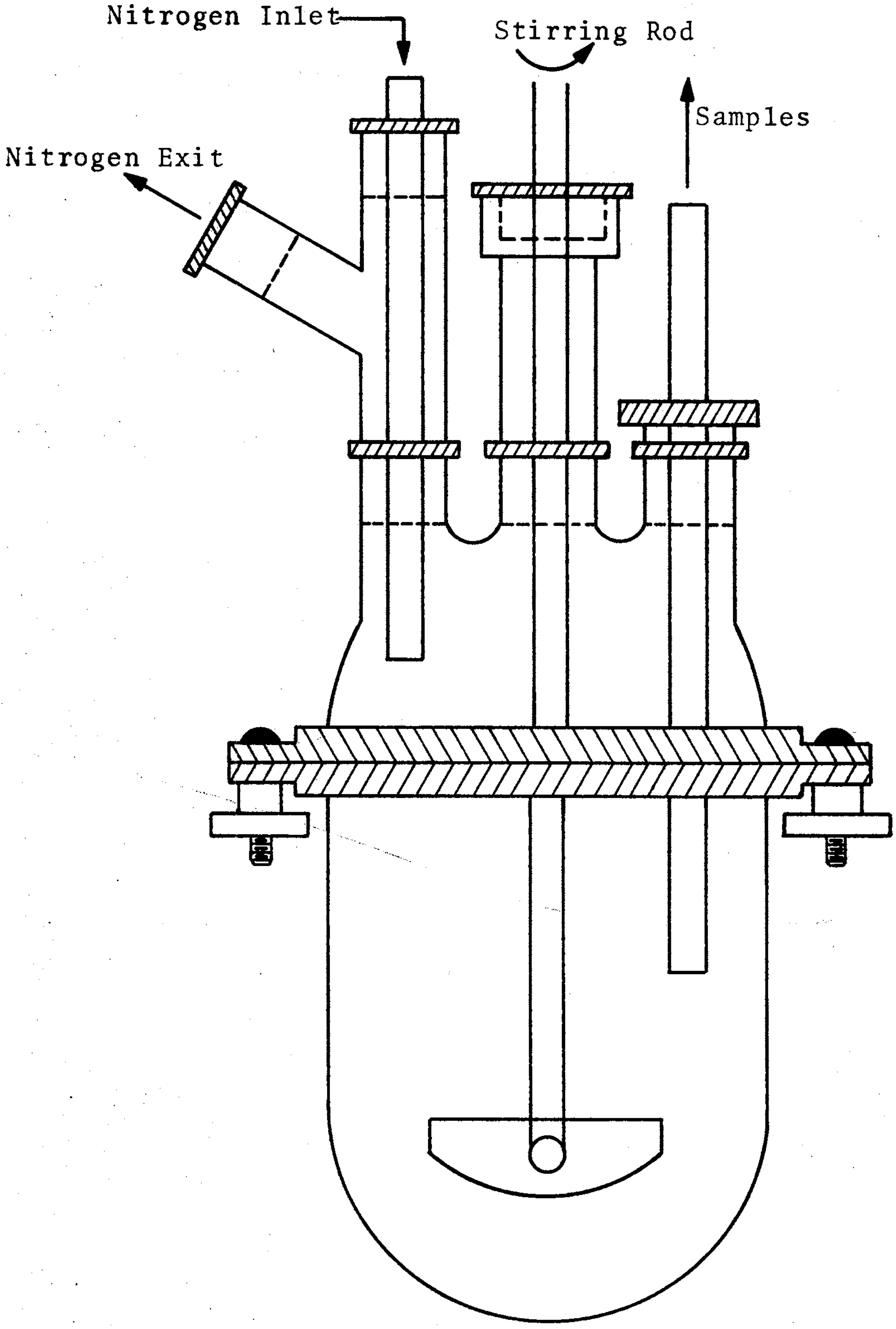

Figure 3. Reaction Vessel and Fittings

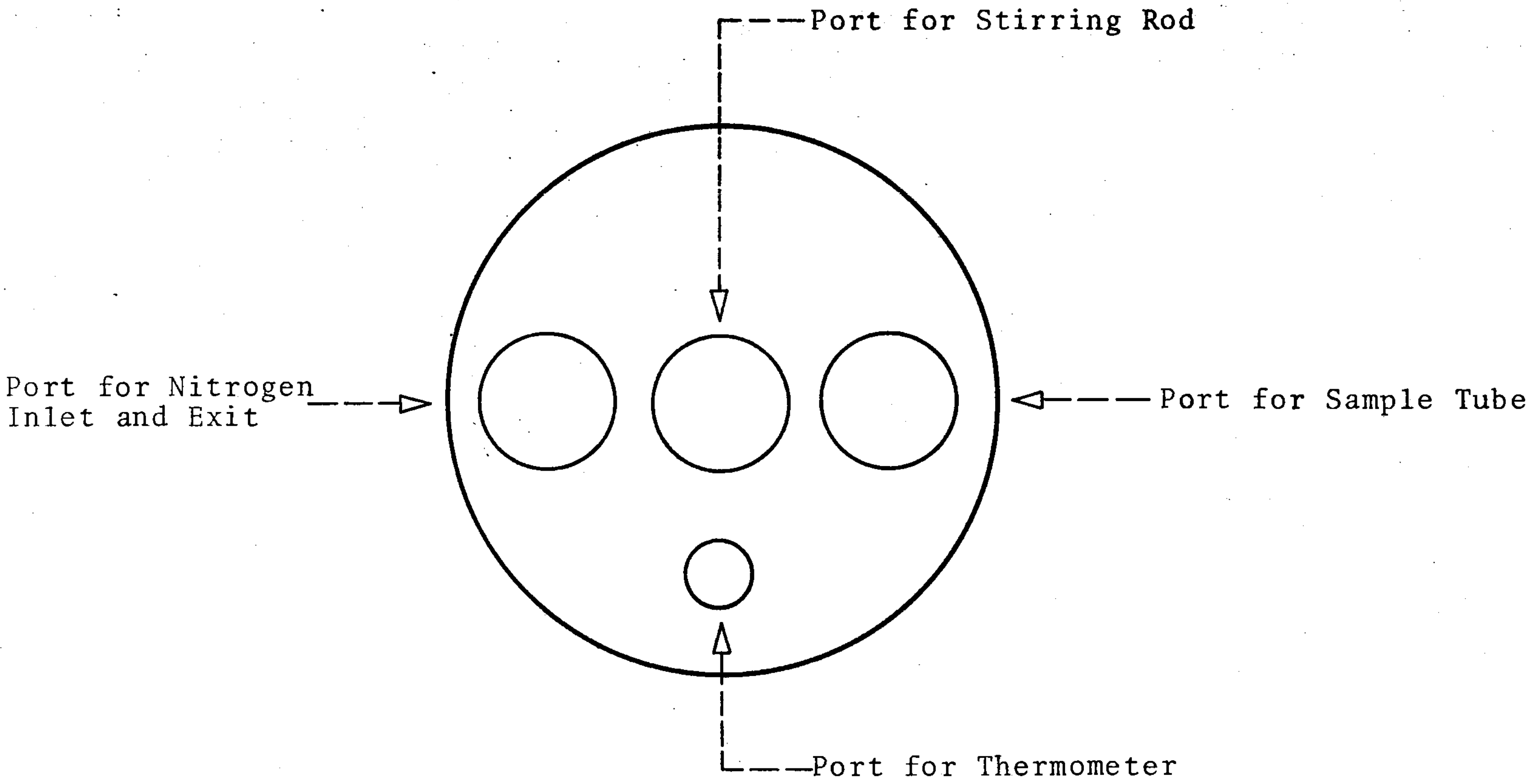

Figure 4. Top View of Reactor Vessel

TABLE I

LIST OF EXPERIMENTAL EQUIPMENT

Reactor Assembly -- Ace Glass Incorporated
    Flask head, model 6488
    Reaction flask, model 6477, 1 liter
    Stirring shaft, model 8068
    Trabor bearing, model 8039

Reaction Flask Clamp	-- number K-613750-0000, Kontes Glass Co.
Stirring Blade	-- teflon, size B, number K-789030-022, Kontes Glass Co.
Glass Connecting Tube Tee	-- 3-way, 105°, outer 24/40 on upper end and side arm, inner 24/40 at lower end Kimax
Glass Connecting Tube Elbow	-- 2-way, 105°, inner and outer 24/40 ₮ joints, Kimax
Glass Condenser	-- Friedricks, serial 2640, inner and outer vapor 24/40 ₮ joints, Pyrex
Stirrer Motor	-- model D73-10, 1/50 hp., Curtin & Co.
Heating Mantle	-- Glass-Cal Apparatus Co.
Variac	-- type 116, Superior Electric Co.
PH Meter	-- model 76, Beckman
Blender	-- model MX-280, Panasonic (3900 rpm-6300 rpm)
Oxygen Removal Cartridge	-- model 08903, Barnstead
Magnetic Stirrer	-- model S-40990, Sargent
Thermometer	-- total immersion, Fisher, $(-20^{\circ}C--110^{\circ}C)$
Syringes	-- 50cc., model D9633, B-D Yale
Filter Paper	-- 9 cm., Whatman #42
Needles	-- 13 guage, 2" length, B-D Yale
Tubing	-- teflon, 1/2", various lengths
Tubing	-- SS 1/4"
Stroboscope	-- type 63--B, Strobotac, General Radio Co.

TABLE II

LIST OF CHEMICALS

A. Chemical Used for Reaction Recipe

1. Toluene, C_7H_8, reagent grade, Fisher Scientific Co.
2. Span 60, sorbitan monostearate, Atlas Chemical Co.
3. Vazo 52, Dupont Chemical Co.
4. Nitrogen, dry commercial grade, 99.7% purity, Linde.
5. Boric Acid, H_3BO_3, reagent grade, J. T. Baker Chemical Co.
6. Sodium Hydroxide, NaOH, reagent grade, Matheson, Coleman & Bell.
7. Acrylamide, $CH_2{=}CHCONH_2$, American Cyanamid Co.
8. Distilled water.

B. Other Chemicals Used in Experiment

1. Methanol, CH_3OH, technical grade.
2. Acetone, CH_3COCH_3, technical grade.
3. Methyl Orange, $(CH_3)_2NC_6H_4NNC_6H_4SO_3Na$, reagent grade, Allied Chemical Co.
4. Sodium Sulfite, Na_2SO_3, reagent grade, J. T. Baker Chemical Co.
5. Standard Buffer, Beckman Instruments Inc.

A teflon stirring blade connected to a glass shaft provides agitation during the reaction. The glass shaft is connected to a variable speed electric motor. The glass shaft can be raised or lowered as desired. The position of the stirring blade was two inches from the top of the emulsion to the top of the blade when the reactor is full. The speed of the stirring blade was 710 rpm and as with the position of the blade, was held constant throughout all experiments. The one-liter reaction vessel has fluted sides which act as baffles and contribute to the mixing which was evidenced to be sufficient for heat transfer and homogeneity.

A mercury thermometer inserted in the top of the reactor was used to measure the temperature of the emulsion during the reaction. The same thermometer was used for all other temperature measurements reported in this study. An electric heating mantle which could be quickly attached or removed from the reaction vessel provided any required heating of the emulsion. A vessel of ice water which could be raised around the reactor provided heat removal as needed to maintain isothermal operation. The objective of the heat transfer was to maintain operation at 40°C.

Periodically, samples were withdrawn from the reactor by lowering a 1/4-inch stainless steel tube into the reactor and pulling samples out of the reactor with a syringe fitted to the top of the stainless steel tube. The sample was then transferred to a beaker for subsequent analysis.

The reactor and port details are shown in Figures 3 and 4, respectively.

B. Recipe

The standard recipe for forming the emulsion is given in Table III. The standard recipe was tailored after the recipes used by Vanderhoff (12). Vanderhoff used the water phase as 30-70% by weight of the emulsion, emulsifier in the range of .1-10% by weight of the continuous phase, and acrylamide as 5-40% by weight of the water phase. The recipe in Table III shows that the water phase is 37.40% by weight of the emulsion. The emulsifier is 3.57% by weight of the toluene phase and the acrylamide is 30.00% by weight of the acrylamide-water solution.

The pH of the water phase is adjusted to 8.45. The pH affects the surfactant properties of the emulsifier in a complex way which is not well understood. A high pH is characteristic of emulsion polymerization systems.

Vanderhoff used initiators, benzoyl peroxide and lauroyl peroxide, as .025-.2% by weight of oil phase. For this study Vazo 52 was used as .0084 and .0953% by weight of the toluene phase.

C. Experimental Procedure

The experimental procedure for Runs 1 through 9 varied greatly in an attempt to obtain reproducibility and to control as many variables as possible while removing

TABLE III

STANDARD RECIPE

Acrylamide	75 grams
Boric Acid	3 grams
De-ionized Water	175 milliliters
Toluene	450 milliliters‡
Span 60	15 grams
Initiator Solution (See Table IV)	25 milliliters*

‡ 463 milliliters for Runs 18, 19, and 20.

* 10 milliliters of a Different Solution for Runs 18, 19, and 20.

TABLE IV

COMPOSITIONS OF SOLUTIONS USED IN EXPERIMENT

1. Caustic Solution -- Dissolved 50 grams of sodium hydroxide in 500 milliliters of de-ionized water.

2. Wash Solution -- Mixed equal volumes of acetone and methanol.

3. Initiator Solution -- (Runs 1 through 17) Dissolved 4 grams of Vazo 52 in 250 milliliters of toluene, (Runs 18, 19, and 20) Dissolved 0.354 grams of Vazo 52 in 100 milliliters of toluene.

potential sources of error. A standard procedure was devised from the results of these nine runs, which was then used for Runs 10 through 20. A description of the standard procedure is as follows. (See Table III for the recipe.)

The toluene and Span 60 were placed in the blender (see Table I). The de-ionized water (distilled water put through de-oxygenizing cartridge, see Table I) was mixed with the acrylamide, and the temperature and pH were measured. The boric acid was added to the water-acrylamide solution and the temperature and pH were again measured. A caustic solution (see Table IV) was then added to adjust the water phase pH to 8.45. The water phase was then poured into the blender with the toluene phase and the temperature was measured. The blender was then purged with nitrogen. Next, the blender was turned on at the designated speed for the designated length of time. The emulsion was transferred from the blender to the reactor. The temperature of the emulsion was again measured to determine the temperature rise from mixing. The reactor was purged with nitrogen and the agitator was turned on. In the seven minutes between the blending and the addition of the initiator solution (see Table IV), the emulsion temperature was brought to 40^{o}C. One minute before the initiator solution was added, sample number zero was taken to determine if the reaction had pre-initiated (initiation of reaction by impurities) and to obtain a sample blank.

Samples were taken approximately every 5 minutes for the first 35 minutes for the high initiator runs (1-17) and every 10 minutes for the first 100 minutes of the low initiator runs (18-20). The high initiator runs normally lasted 45 minutes and the low initiator runs normally lasted 130 minutes.

Each sample was taken by lowering the sample tube into the emulsion and withdrawing the sample into the syringe. The sample was then placed in a 100-ml. beaker and weighed. After weighing, the sample was precipitated and washed in an acetone-alcohol solution (see Table IV), and the polymer precipitate was filtered and oven dried. The acetone was used to coagulate the dispersed polymer particles for filtration and also to remove emulsifier from the polymer particles. The methanol was used to precipitate the polymer particles and to remove unreacted monomer from the polymer particles. The filter paper was oven-dried and weighed prior to each experiment. The sample beakers were also cleaned and weighed prior to each experiment.

The speeds of the blender and reactor were measured with a stroboscope when the vessels were empty and represent only a qualitative measure of the degree of stirring of the blender and the reactor agitator.

As stated previously, the procedure for Runs 1 through 9 varied as improvements were made to eliminate sources of errors. During Runs 1 through 9, five major revisions were made to the procedure. Between which runs the revisions to the procedure occurred are stated quite clearly in Appendix A along with the experimental data for Runs 1 through 9. The following revisions were incorporated into the procedure:

1. Solid sodium hydroxide was added to the water phase to obtain the desired pH. Then solid sodium hydroxide and sodium hydroxide solution (see Table IV) were added to the water phase. Finally, for ease of operation and for accuracy, only the sodium hydroxide solution was used to obtain the desired pH.

2. The samples were transferred directly from the syringe into a cup containing 50 ml. of wash solution and then the cup with the sample and wash solution was weighed to determine the weight of the sample. This method was revised after Run 5 to transferring the sample from the syringe into the cup, weighing, and then adding the wash solution (so that evaporation of the wash solution did not effect the calculated conversion).

3. In the early stages of this study, the sample tube was left submerged in the emulsion throughout the run and would become plugged with polymer. This procedure was changed to lowering the sample tube, taking the sample, and raising the sample tube into the nitrogen atmosphere above the emulsion until the next sample.

4. The filter paper used to filter the precipitated polymer, was oven dried for one day prior to the next run.

5. Initially, samples were air-dried, and then the procedure was changed to oven-drying the samples for one day. Finally, the procedure was to leave the samples in the oven and weigh the samples each day until no appreciable change in weight had occurred between two subsequent weighings.

CHAPTER III

EXPERIMENTAL RESULTS

As stated in the introduction, this study consisted of three separate parts. The first part was an attempt to determine the best procedure for performing the experiment. The second part was a study of the effect of the degree of premixing on the rate of reaction. The last part was a study of the effect of the degree of premixing at a lower initiator concentration.

The basic data from the study consists of percent monomer conversion versus time of reaction. These were plotted on rectangular coordinates and the slope of the straight-line portion of these monomer conversion versus residence time curves, which corresponds to the rate of reaction for a zero-order reaction was chosen as the means of comparing the results between runs. The equations used to calculate monomer conversion from the experimental data are given in Appendix C. A standard least squares approximation computer program was used to correlate the data.

The first nine experimental runs were an attempt to establish reproducibility. Therefore, the procedure was revised from one run to the next. The variations from the standard procedure, the experimental data, and the calculated results for Runs 1 through 9 are in Appendix A. The results of Runs 2, 4 and 5 are given in Table V and shown in Figure 5. The rates of reaction calculated from the straight line portion of the curves range from 4.84 to 5.24 (percent monomer reacted per minute) and indicate an overall reproducibility of ±.2 percent conversion per minute at an average value of 5.04. Temperature control during Runs 1 and 3 was not sufficient for the desired range of 40°C ±1. The samples of Run 6 were lost during filtering.

The sample tubes were sporadically being plugged by polymer particles which had coagulated in the reactor. In an attempt to observe the extent of coagulation of the polymer particles methyl orange, a water-soluble dye, was added to the water phase of Run 7 prior to emulsification. The dye would make possible observation of the clumps of wet coagulated polymer particles. The results of Run 7 are in Table V also and are plotted in Figure 6. The rate of Run 7 was 3.77 as compared to an average of 5.04 for a standard run. Apparently, the effect of the methyl orange was to slow the rate of reaction and to act as a surfactant as the emulsion was observed to be more stable and the polymer particles appeared to be smaller and better dispersed than in any other run. Also, no clumps of polymer particles were observed either on the sides of the reactor or on the stirring blade and thermometer as were found after all the other runs.

TABLE V

SUMMARY OF RESULTS OF INITIAL PART OF STUDY

Residence Time	Monomer Conversion, Percent						
Minutes	Run 2	Run 4	Run 5	Run 7	Run 8 ‡	Run 8 *	Run 9
5	0.90	2.42	2.42	0.28	2.95	0.50	6.35
10	16.49	18.25	22.07	2.18	13.57	12.49	21.79
15	46.67	50.87	56.67	16.40	39.28	36.70	41.58
20	71.88	69.56	80.63	31.10	61.71	58.95	61.39
25	91.88	90.04	92.39	55.80	82.32	78.91	78.52
30	XXX	105.58	101.90	70.50	98.95	94.44	86.85
35	99.66	107.39	102.20	91.00	102.43	98.50	92.22
40	XXX	XXX	XXX	XXX	111.40	107.86	XXX
45	XXX	110.51	XXX	XXX	XXX	XXX	107.69
Slope of zero order (rate)	5.03	4.84	5.24	3.77	4.57	4.43	3.68
Standard error	2.55	1.60	0.98	2.01	1.28	1.07	1.08

‡ (Incomplete Drying) 20 hours of oven drying at 160°F
* (Completely Dry) 99 hours of oven drying at 200°F

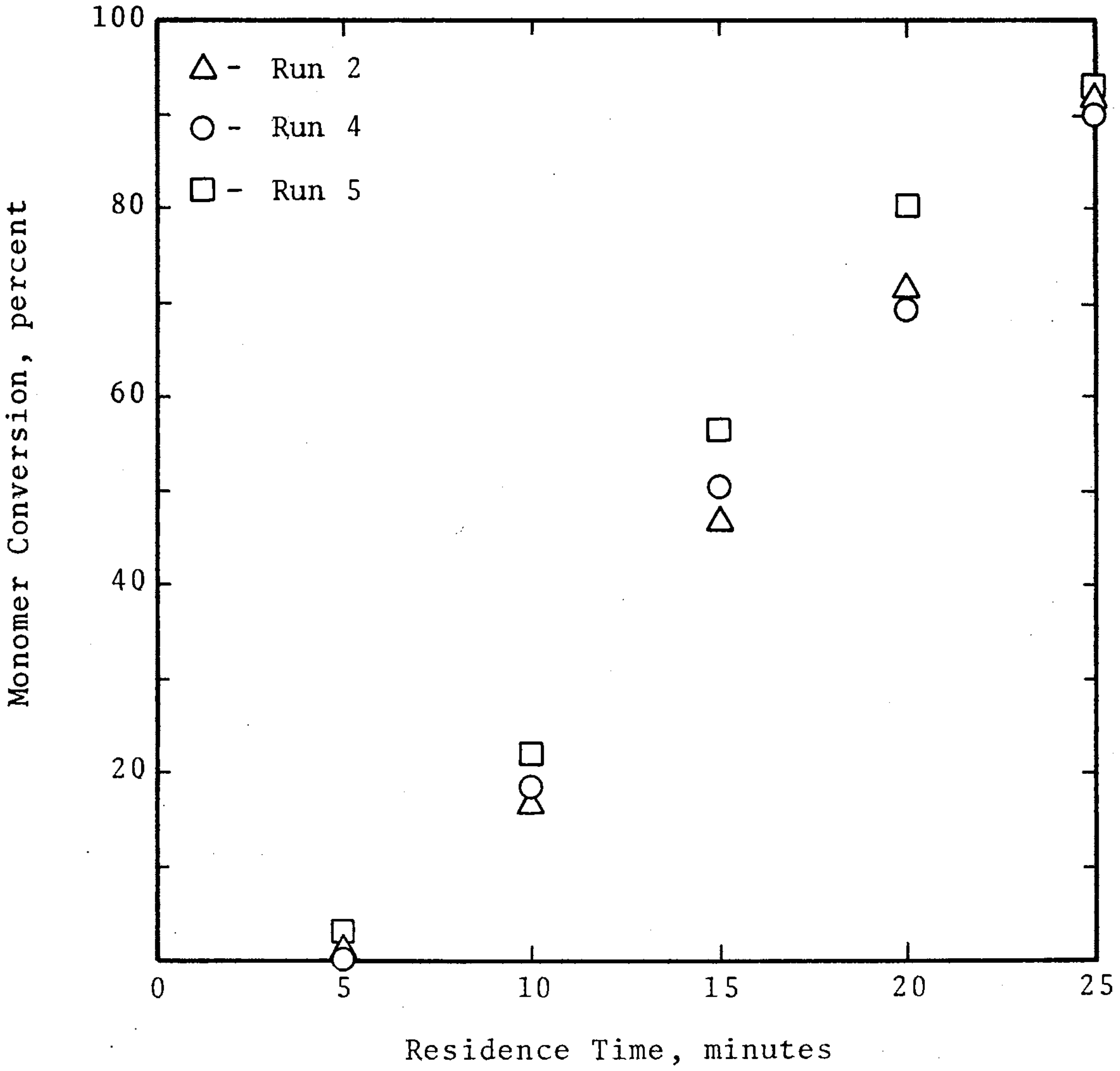

Figure 5. Range of Reproducibility

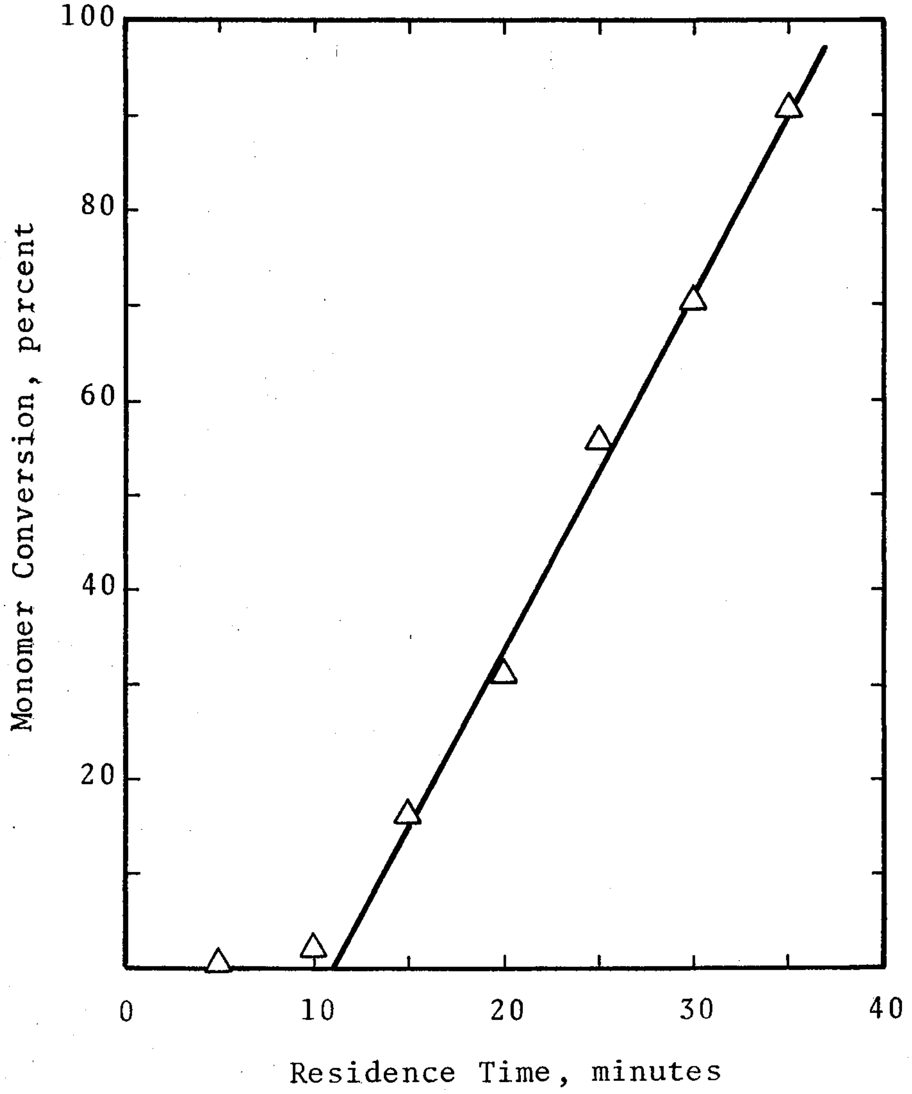

Figure 6. Results of Run 7

The results of Run 8 are in Table V, and illustrated in Figure 7. The results of Run 8 show that the maximum error of the rate of reaction which can be associated with incomplete drying of the polymer sample is +.14% conversion per minute. The results shown in Figure 7 can partly explain why conversions of over 100% were obtained. Whereas, the effect of incomplete drying on the rate of reaction is relatively small, the effect on one sample can be as much as 10% of the calculated conversion.

In an attempt to reduce the dissolved oxygen level of the de-ionized water below that obtained from the ion exchange cartridge (see Table I), an oxygen scavenger, sodium sulfite, was added to the water phase of Run 9. Pre-initiation of the reaction in the water phase before emulsification was observed. The results of Run 9 are in Table V and shown in Figure 8. The rate of reaction was 3.68 percent conversion per minute which is 1.36 below the average value for a standard run. The effect of the sodium sulfite was to cause pre-initiation of the reaction and a decreased rate of reaction.

The second part of this study which was to determine the effect of premixing on the rate of reaction consists of the results of Runs 10 through 17. The experimental data and calculated results are in Appendix B. The results of Runs 10 through 17 are also summarized in Table VI and plotted in Figures 9 through 15. A new batch of initiator solution (same chemicals and concentration as before) was

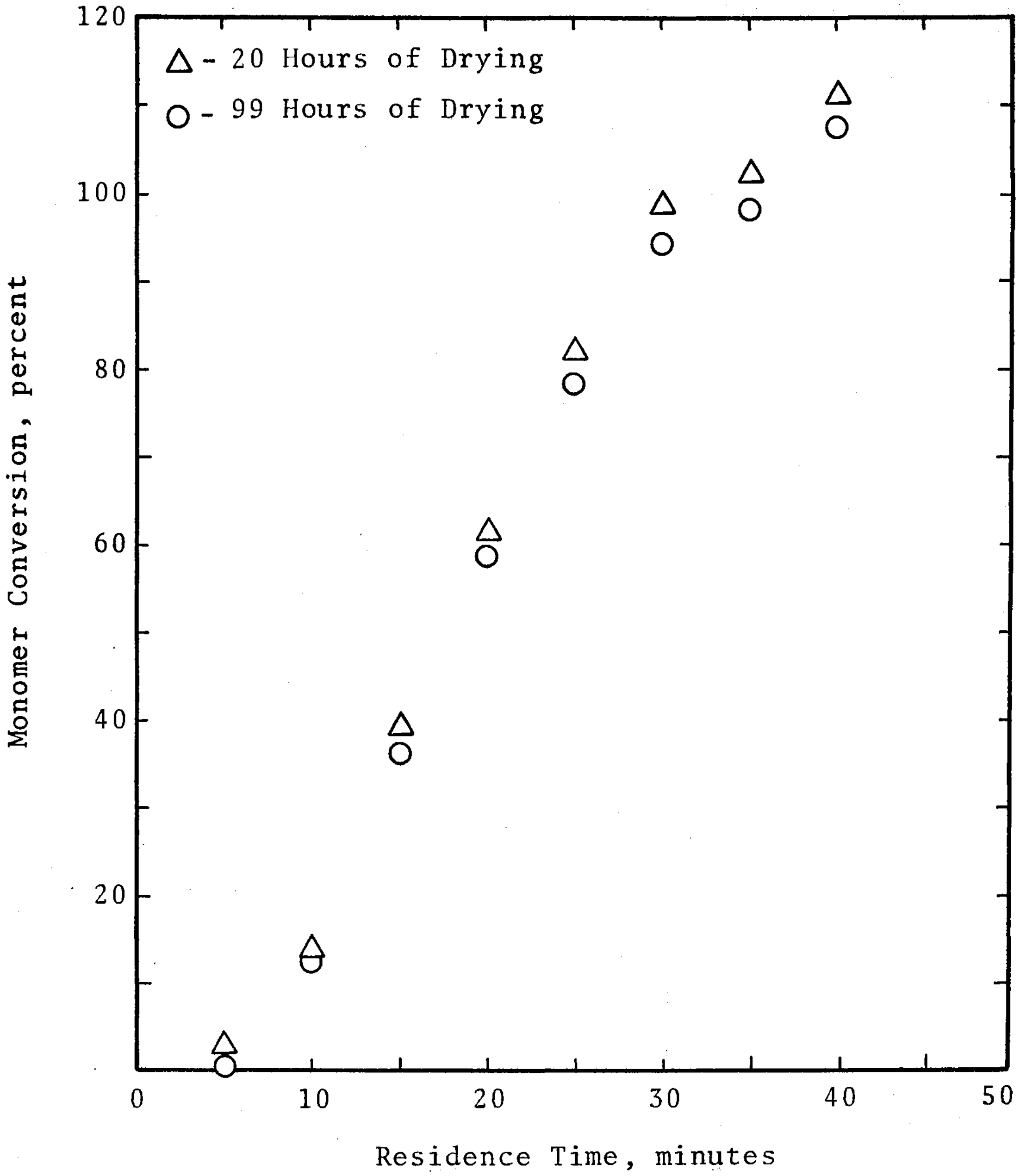

Figure 7. Results of Run 8

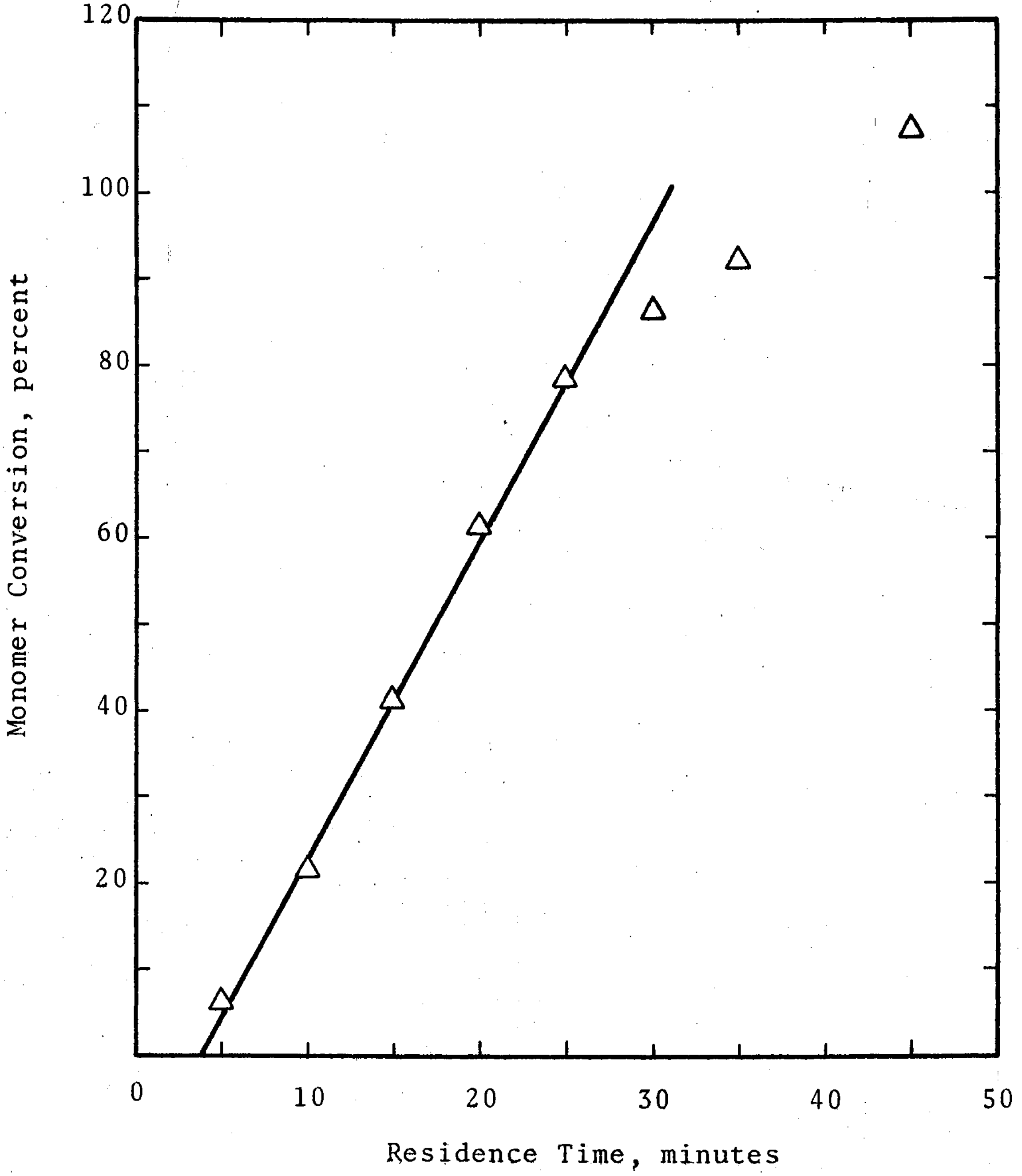

Figure 8. Results of Run 9

TABLE VI

SUMMARY OF RESULTS OF EFFECT OF PREMIXING AT HIGH INITIATOR CONCENTRATION

Residence Time	Monomer Conversion, Percent							
Minutes	Run 10	Run 11	Run 12	Run 13	Run 14	Run 15	Run 16	Run 17
-1	XXX	1.14	1.76	1.57	1.28	1.23	1.09	0.80
5	0.34	1.47	1.13	1.73	1.09	1.28	0.47	1.81
10	3.66	15.92	5.65	5.36	1.27	5.96	8.78	9.38
15	24.97	48.10	26.00	25.49	17.82	25.59	31.59	31.14
20	44.61	83.87	47.76	51.70	41.76	47.94	53.47	53.72
25	71.31	XXX	76.13*	74.13	65.99	66.71	71.62	70.25
30	94.60	XXX	96.96‡	90.40	82.74	82.70	88.58	84.45
35	110.43	XXX	107.48#	100.18	96.70	98.56	95.57	90.83
45	123.66	XXX	111.56	112.63	108.71	106.50	101.08	101.22
Slope of zero-order (rate)	4.40	6.79	4.16	4.37	3.98	3.89	3.99	4.10
Standard error	2.26	0.85	0.36	2.25	3.08	1.56	1.87	1.52
Speed of Premix, rpm	3900	6300	5850	4200	5050	5550	6300	6300
Time in blender, minutes	15	15	15	15	15	15	15	5
Temp. Rise Premix, °C	XXX	XXX	25	15.5	18	20	27.5	12

* Residence Time = 27 ‡ Residence Time = 35 # Residence Time = 40

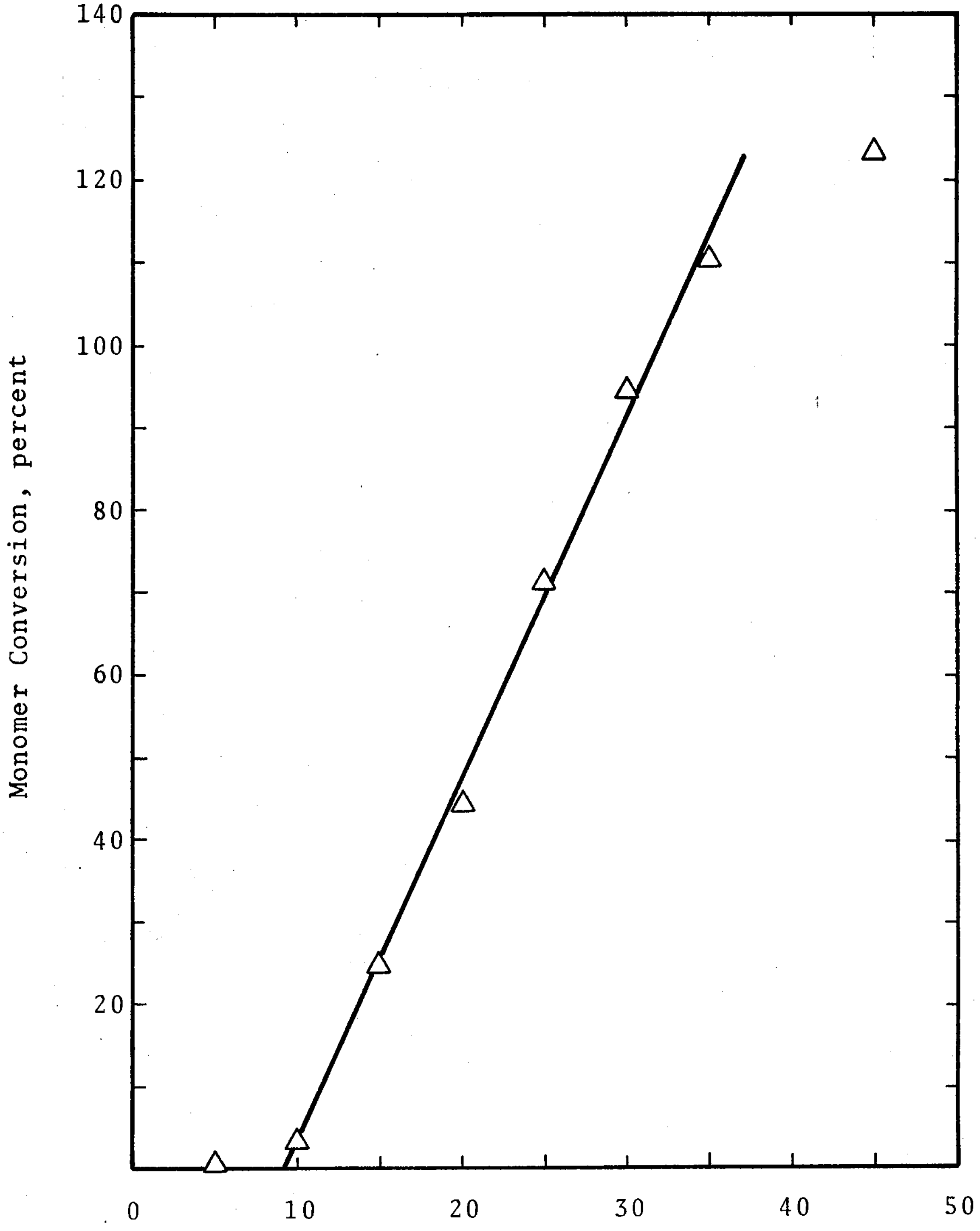

Figure 9. Results of Run 10

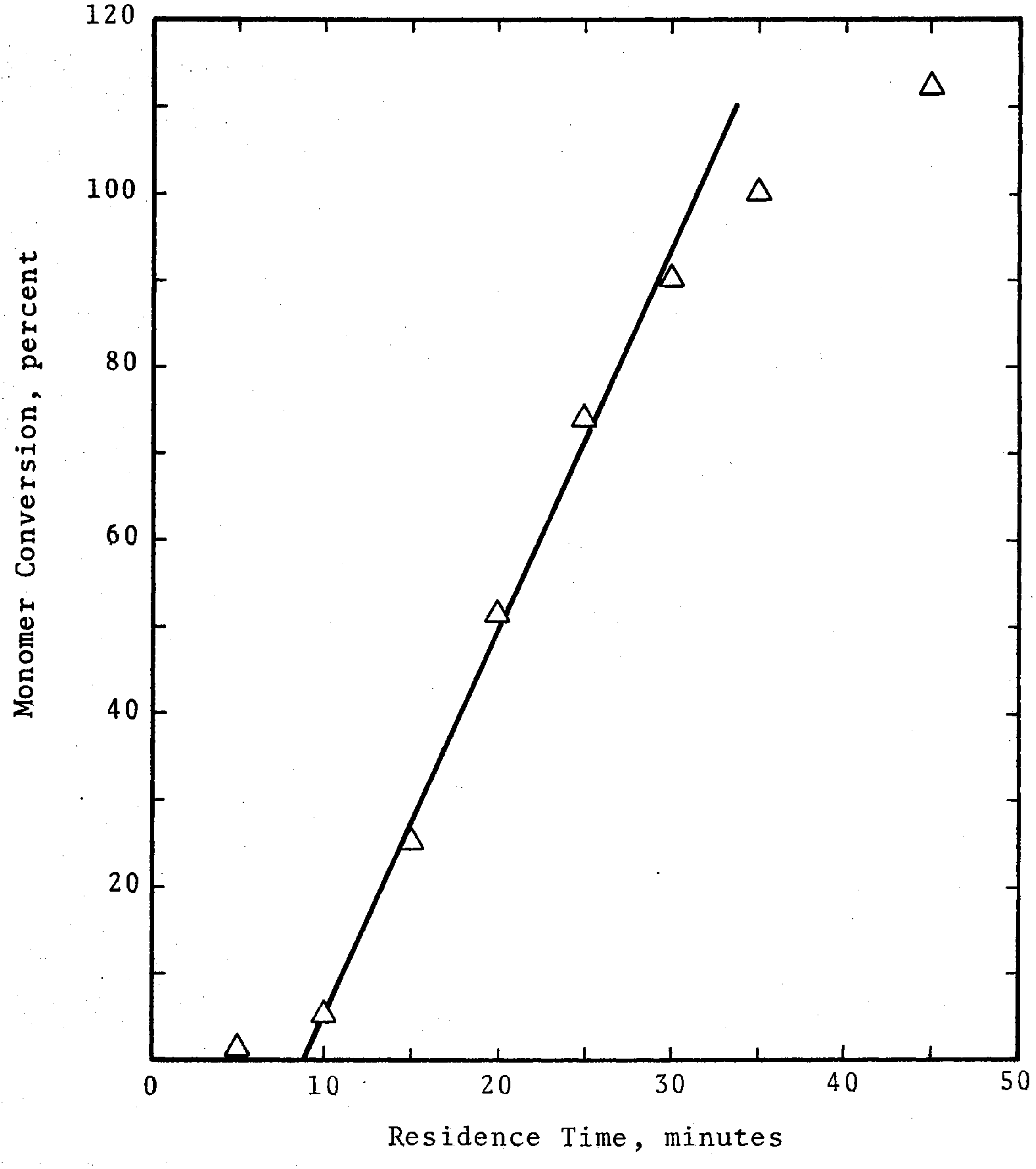

Figure 10. Results of Run 13

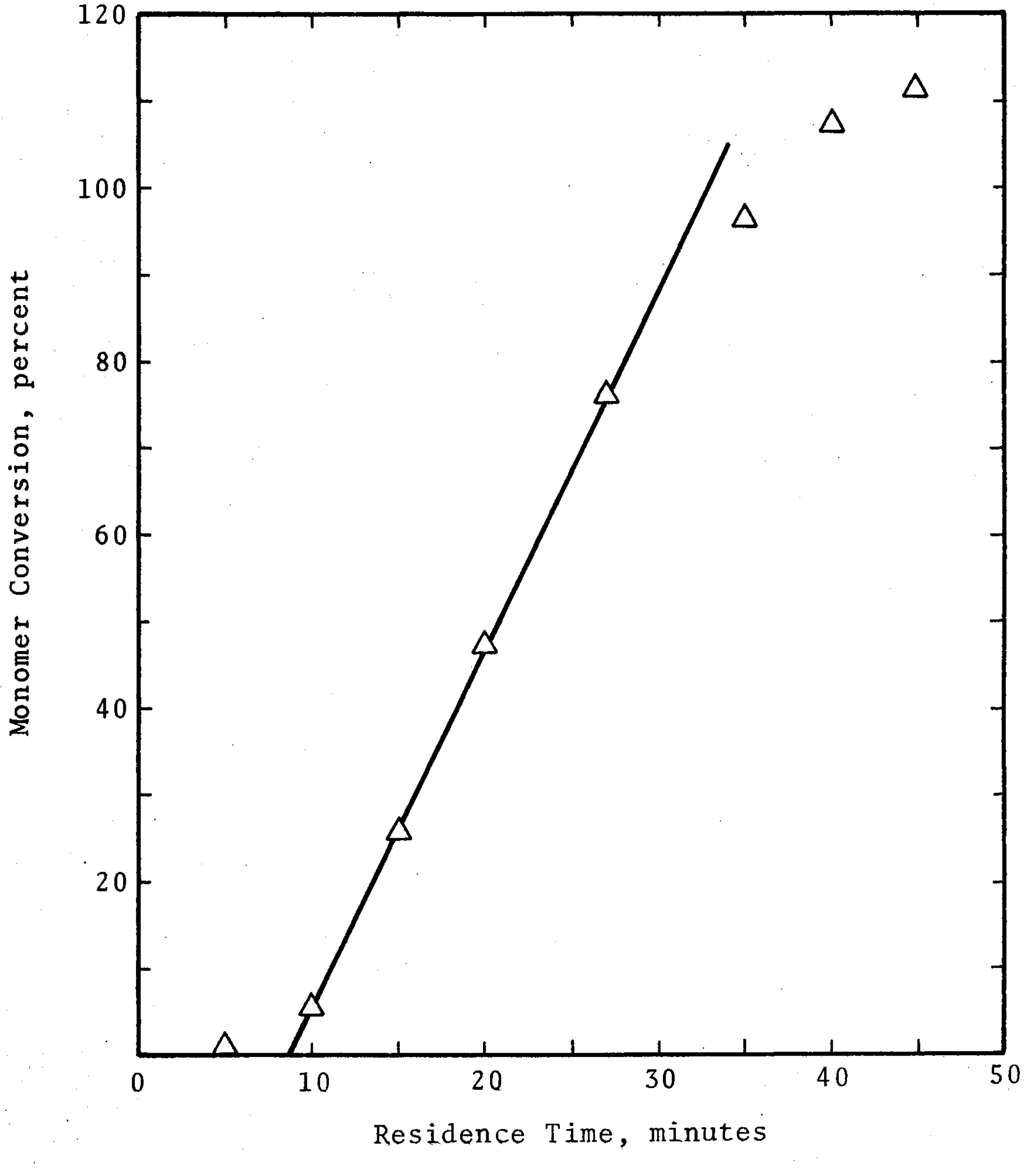

Figure 11. Results of Run 12

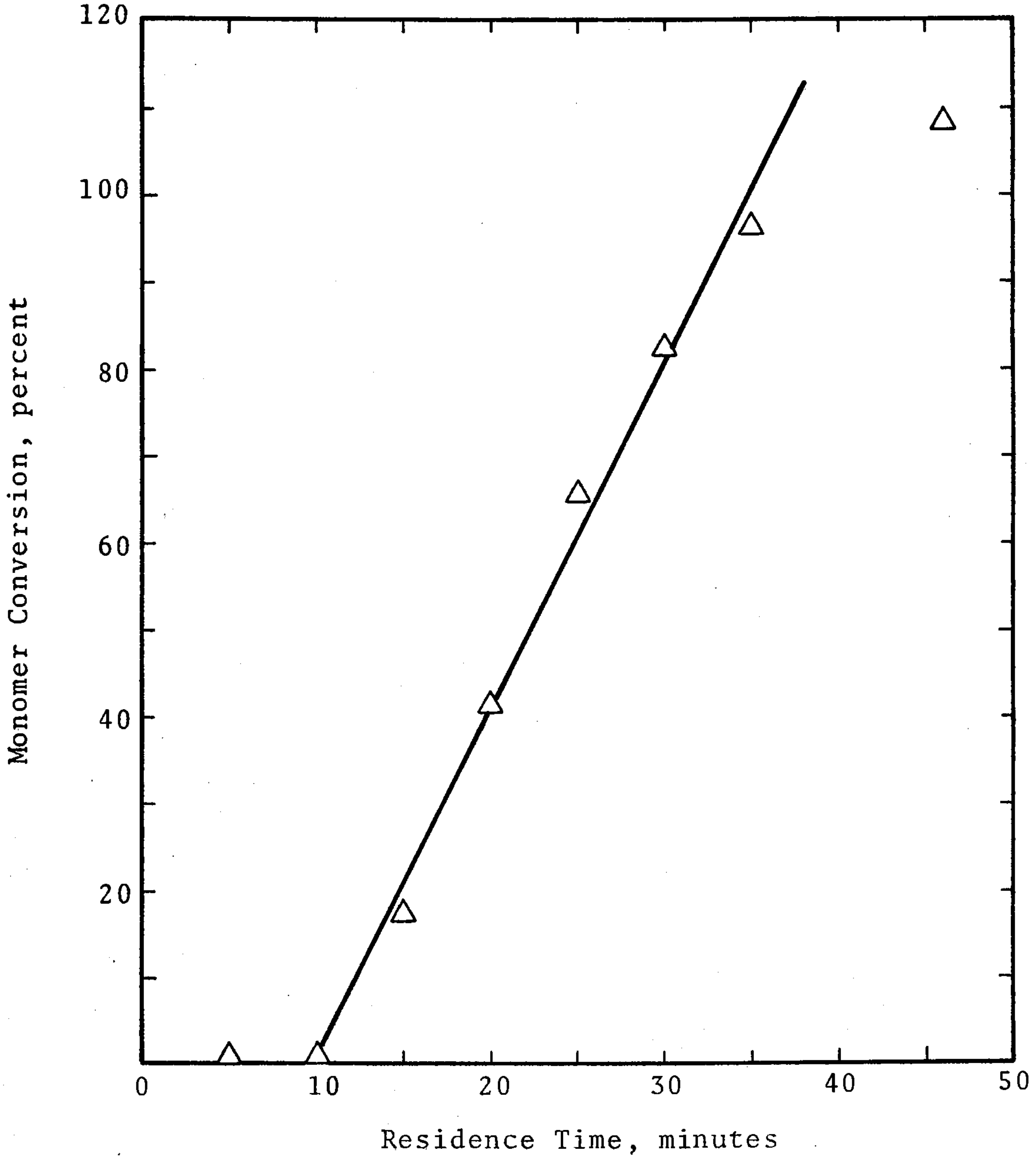

Figure 12. Results of Run 14

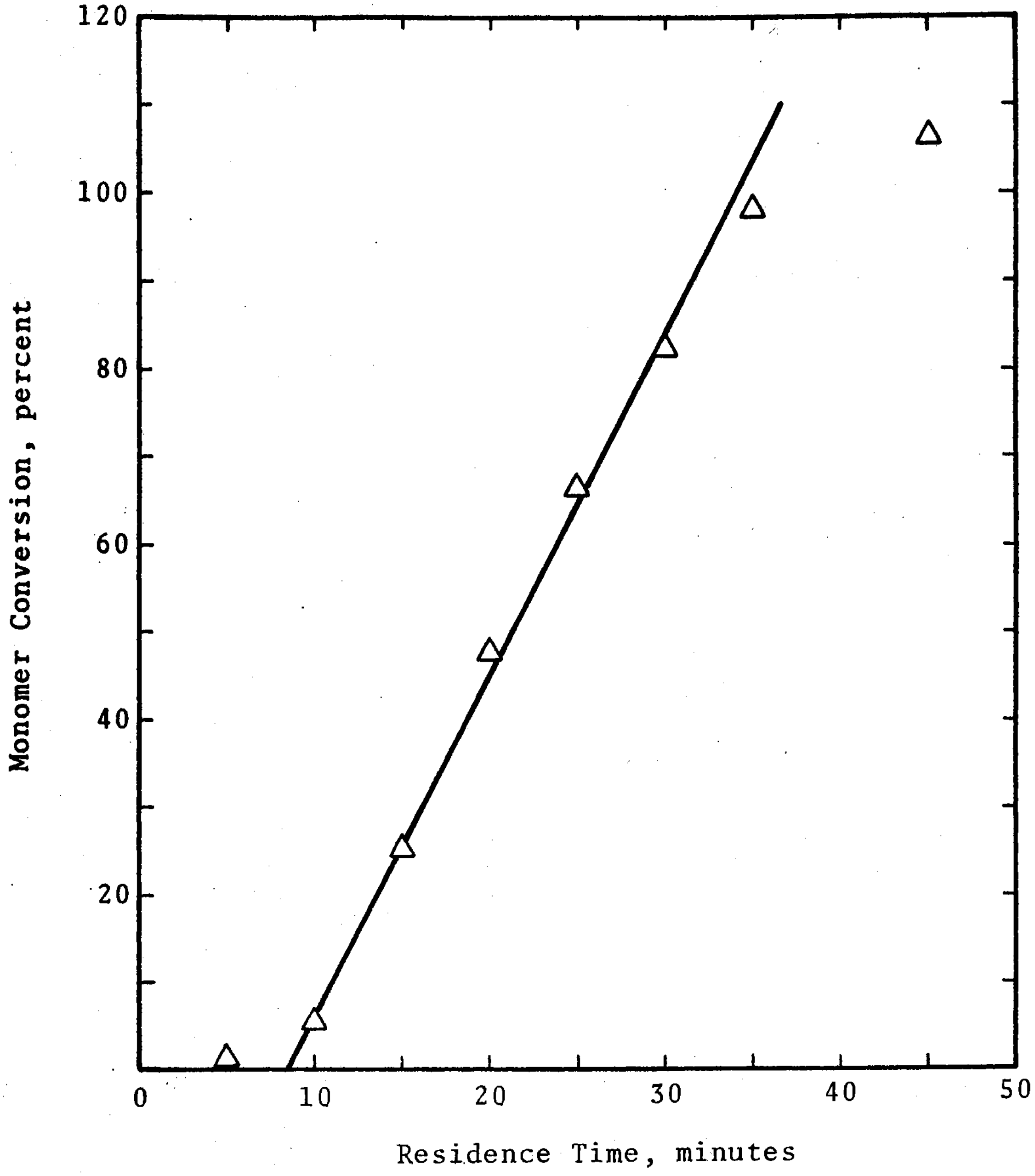

Figure 13. Results of Run 15

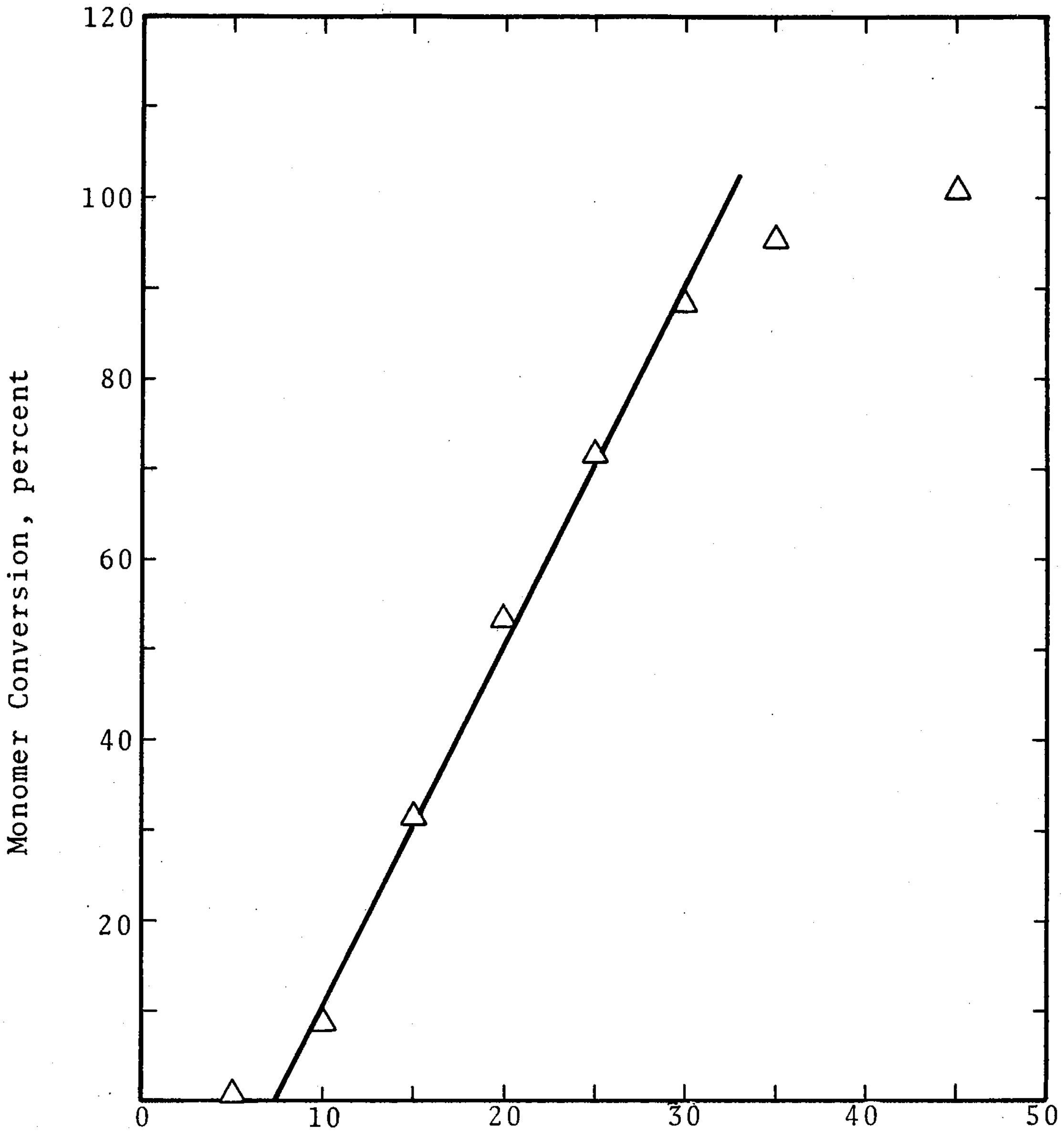

Figure 14. Results of Run 16

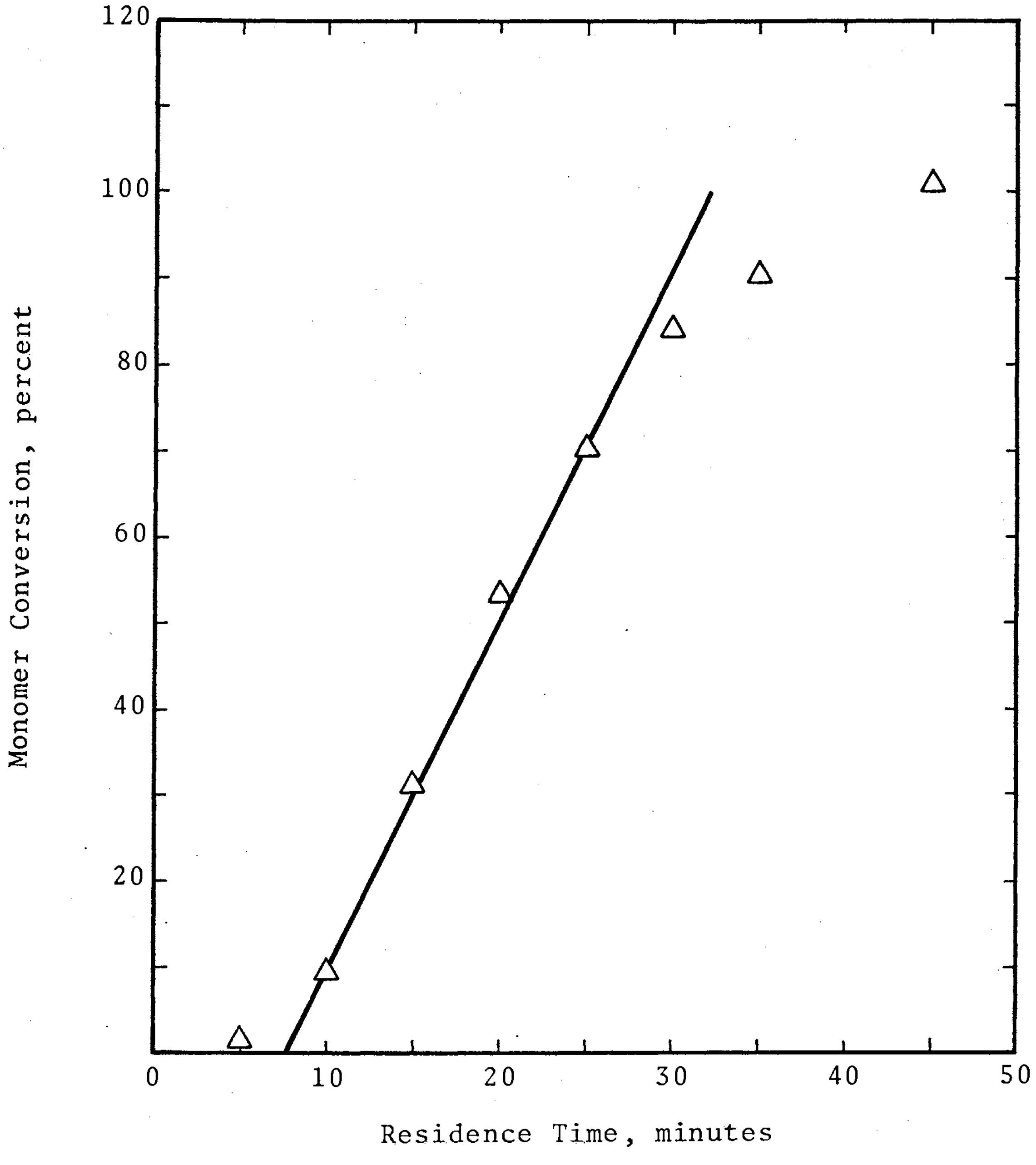

Figure 15. Results of Run 17

used for Runs 14, 15, 16, and 17. In order of increasing degrees of premixing (3900, 4200, and 5850 rpm) Runs 10, 13, and 12 have rates of reaction of 4.40, 4.37, and 4.16 percent conversion per minute respectively. During Run 12, the nitrogen effluent from the reactor system was put through an ice trap to determine how much toluene was escaping. Less than ten milliliters of toluene were recovered out of a total toluene charge of 450 ml. Again in order of increasing degrees of premixing, (5050, 5550, and 6300 rpm) Runs 14, 15, and 16 have rates of 3.98, 3.89, and 3.99 respectively. Run 11 was a "popcorn" reaction with an abnormally high rate of reaction. "Popcorn" reactions are characterized by low molecular weight polymer formed by an abnormally high rate of reaction. What causes "popcorn" reactions is at present not well understood.

Run 17 was premixed at the same speed of mixing as Run 16; however, the time in the blender was only five minutes instead of fifteen minutes. The rate for Run 17 was 4.10 as compared to 3.99 for Run 16.

Even though the rate of the zero-order portion of the conversion versus residence time curves for Runs 10 through 17 do not vary significantly or in any trend, the early part of the reactions exhibit significant variation. Figure 16 compares the initiation period of the polymerization reaction for Runs 10 through 13. Runs 11, 12, and 13 show the same retardation period, and Runs 12 and 13 also

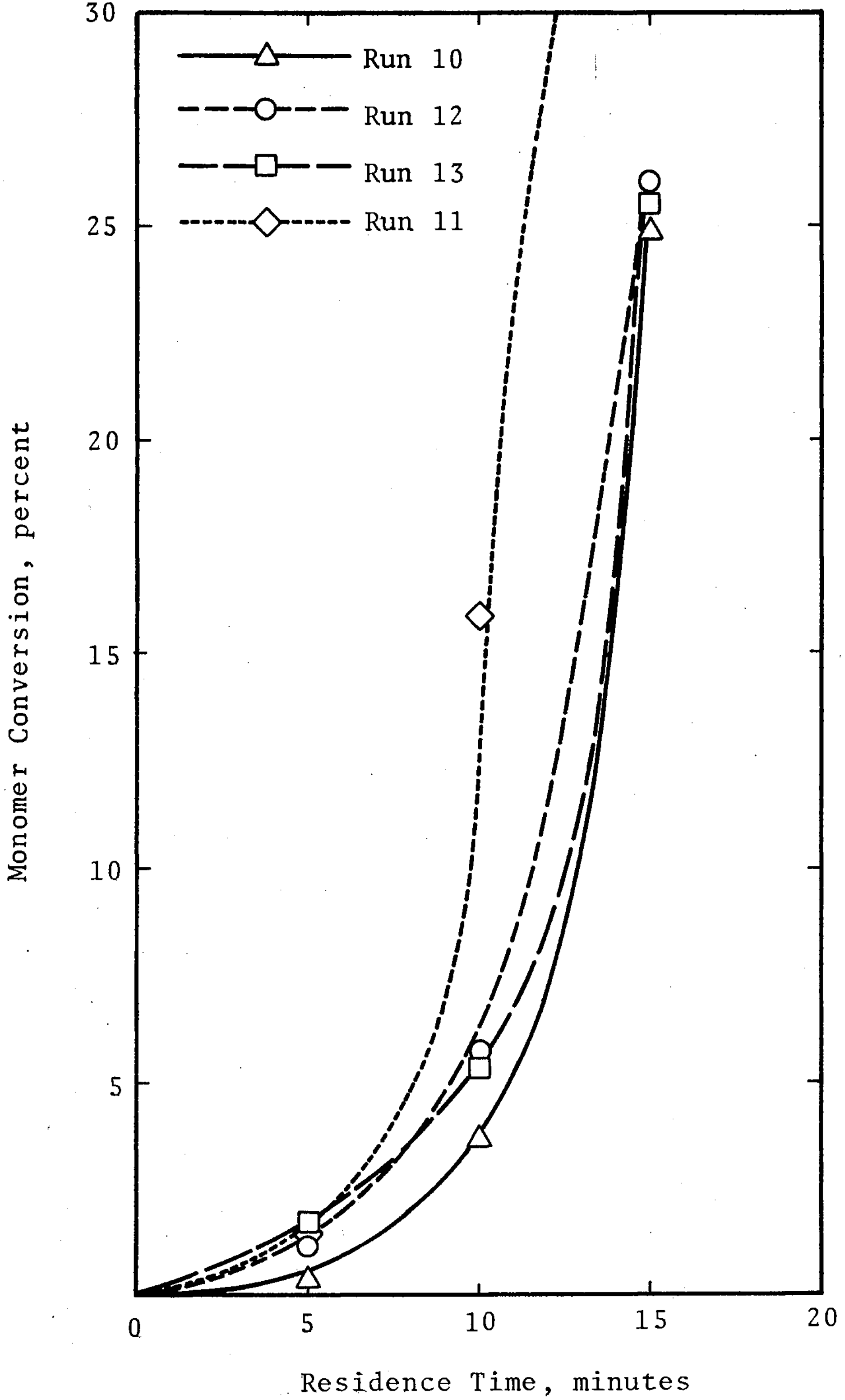

Figure 16. Comparison of Initial Period of Reaction (Runs 10, 11, 12, 13)

continue with the same initiation rate; however, Run 11 has a very high initiation rate. Run 10 has a longer retardation period followed by a higher initiation rate than Runs 12 and 13.

Figure 17 shows the early part of the reactions for Runs 14 through 17. Run 14 has a long retardation period followed by an initiation rate about equal to the initiation rate of Run 15 which has a relatively short retardation period. Runs 16 and 17 have a short retardation period followed by an initiation rate slightly higher than Runs 14 and 15. Apparently the difference between 15 minutes premixing for Run 16 and 5 minutes premixing for Run 17, does not effect the reaction.

The experimental data for Runs 18, 19, and 20 are in Appendix B. The results are summarized in Table VII and plotted in Figures 18, 19, and 20. For Runs 18, 19, and 20, the initiator concentration was approximately one-tenth of that used for Runs 1 through 17 (see Table IV). Run 18 had no premixing before initiation. Runs 19 and 20 were premixed for 15 minutes at the lowest and highest speeds respectively of the blender. Runs 18, 19 and 20 had rates of 0.82, 0.85. and 1.08 percent conversion per minute respectively.

Figure 21 compares the retardation period and initiation period for Runs 18, 19, and 20. The trend which is shown is the reaction with the shortest retardation period has the highest rate of initiation. The order of decreasing

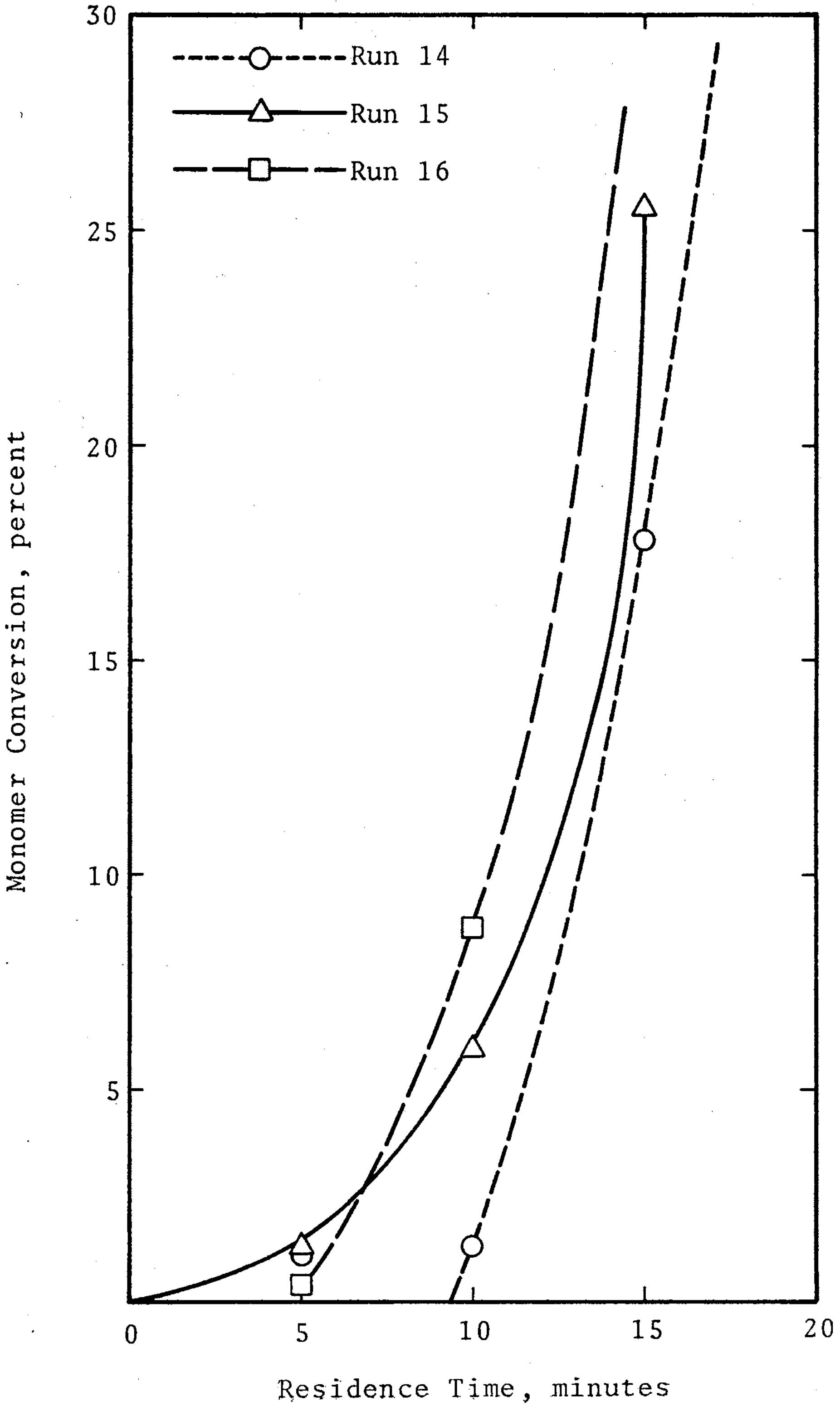

Figure 17. Comparison of Initial Period of Reaction (Runs 14, 15, 16)

TABLE VII

SUMMARY OF RESULTS OF EFFECT OF PREMIXING AT LOW INITIATOR CONCENTRATION

Residence Time	Monomer Conversion, Percent		
Minutes	Run 18	Run 19	Run 20
-1	0.72	0.06	0.43
10	0.46	0.27	1.44
20	4.35	1.69	6.51
30	9.48	6.38	14.84
40	17.75	12.05	24.46
50	25.87	18.55	36.44
60	33.97	27.06	46.62
70	42.40	37.73	56.47
80	49.98	46.78	69.41
90	58.06	53.73	73.22
100	67.89	59.26	81.05
120	75.41	80.21	91.08
140	XXX	94.66	97.77
160	XXX	104.13	XXX
Slope of zero-order (rate)	0.82	0.85	1.08
Standard Error	0.43	1.17	0.74
Speed of Premix, (rpm)	0	3900	6300
Time of Premix, minutes	0	15	15
Temp. rise Premix, °C	XXX	13.5	29

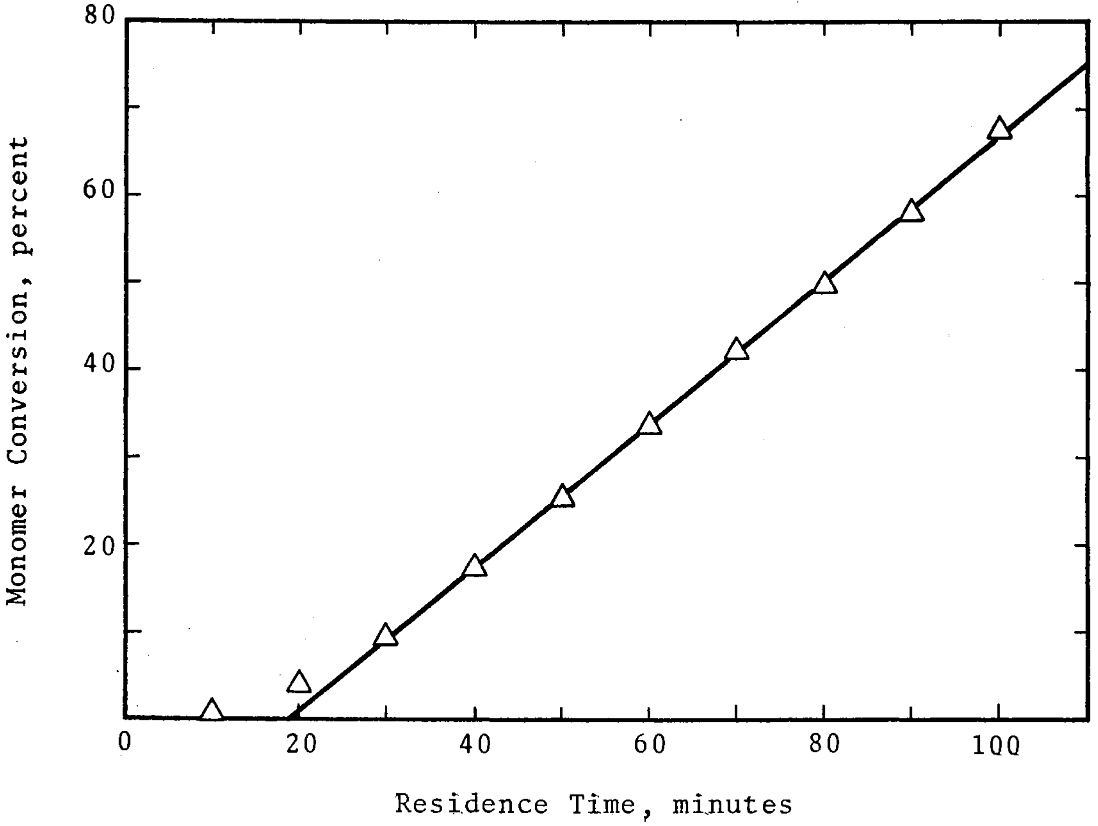

Figure 18. Results of Run 18

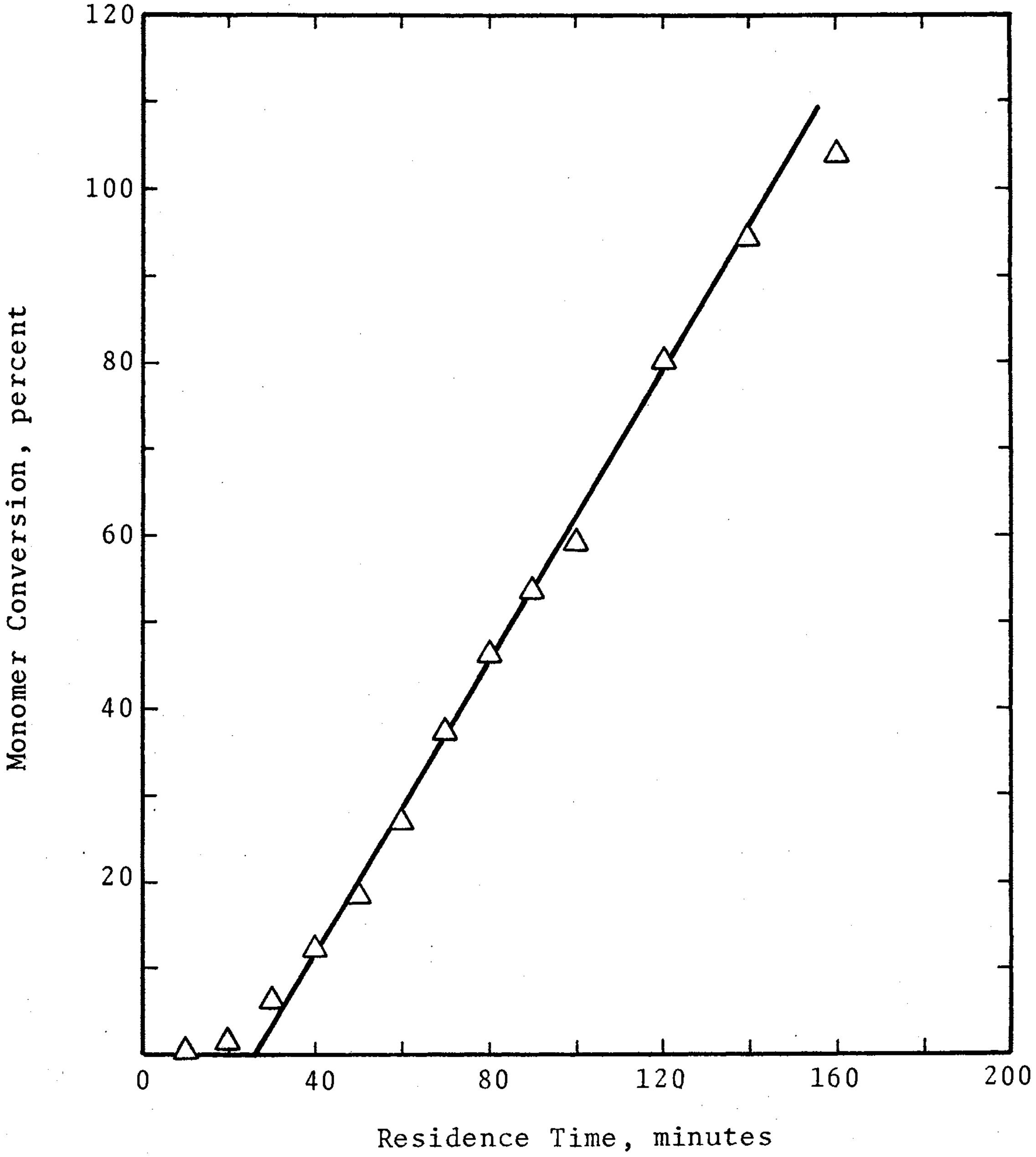

Figure 19. Results of Run 19

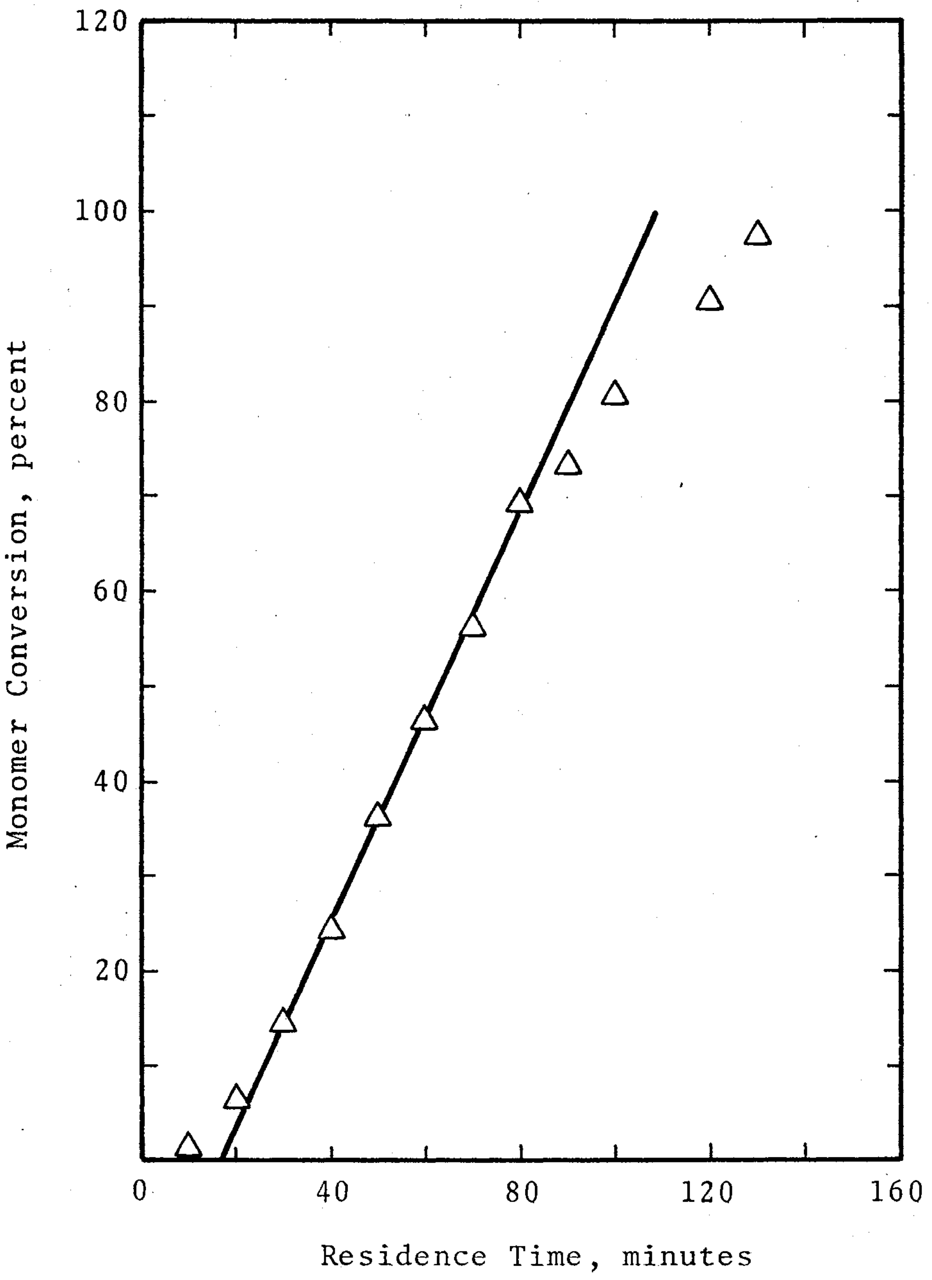

Figure 20. Results of Run 20

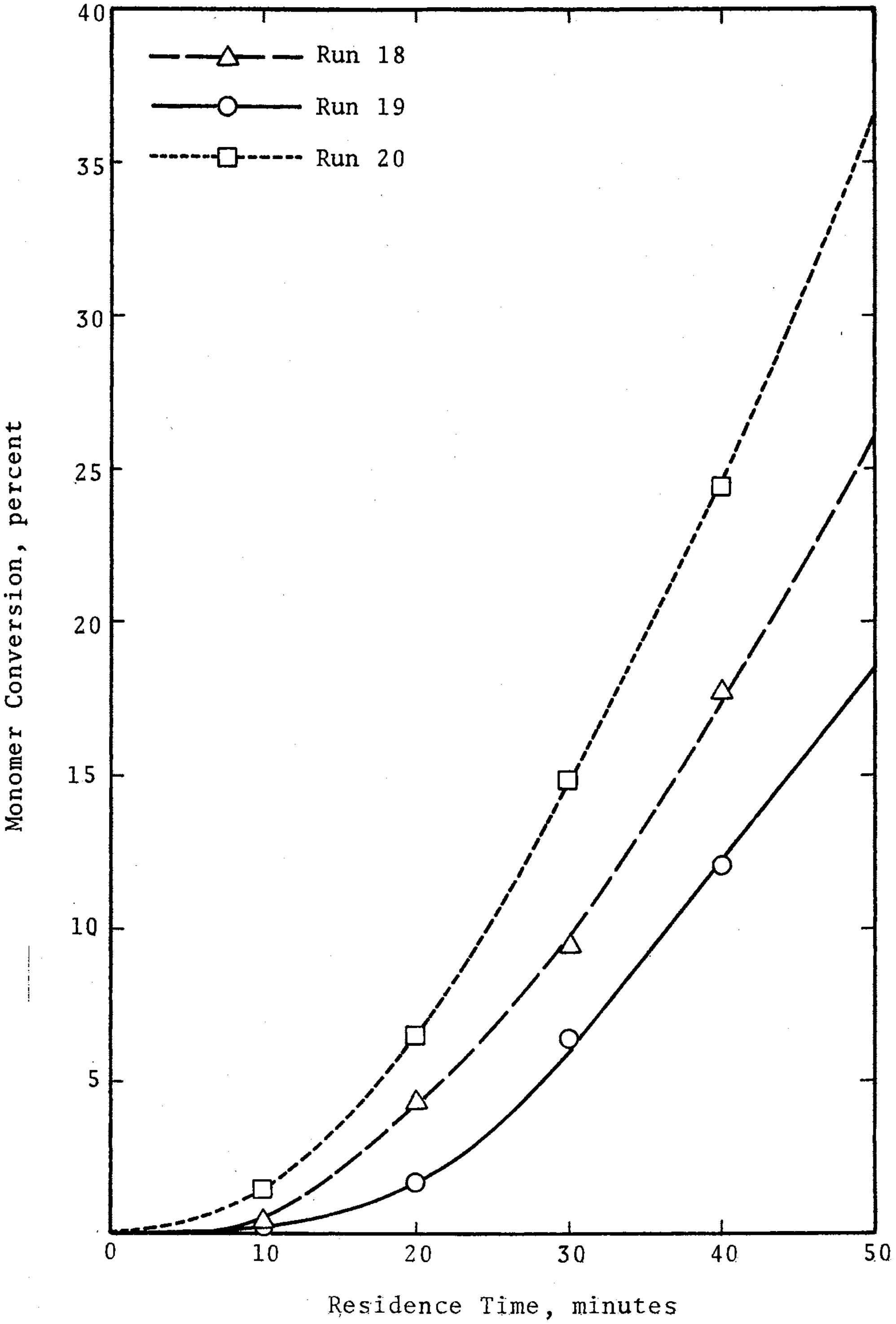

Figure 21. Comparison of Initial Period of Reaction (Runs 18, 19, 20)

rates is Run 20, Run 18 and Run 19 which corresponds to premixing of 6300 rpm, zero, and 3900 rpm.

For Runs 10 through 17 at a residence time of 45 minutes (see Table VI) the percent conversion goes from an impossible 123.66 for Run 10 to 101.22 for Run 17. The samples of Run 10 were each washed in approximately 100 milliliters of wash solution and the polymer would form one solid clump. The samples of Runs 16 and 17 were each washed in the blender at low speed for approximately twenty seconds using about 300 milliliters of wash solution.

During the course of this study, two unexpected heat effects were observed and then studied. The apparent heat of solution of the water-acrylamide mixture and the heating effect of the blender during premixing were measured.

When the de-ionized water at room temperature was mixed with the 75 grams of acrylamide, the temperature of the resulting mixture was found to be approximately 11^{o}C (51.8^{o}F) and the pH was 4.10. This effect of mixing was observed for all the runs.

The temperature rise of the emulsion as a result of the premixing in the blender, was observed during Run 11 and measured for all subsequent runs. The temperature rise was found to be proportional to the degree of premixing and is presented in Tables VI and VII and plotted in Figure 22.

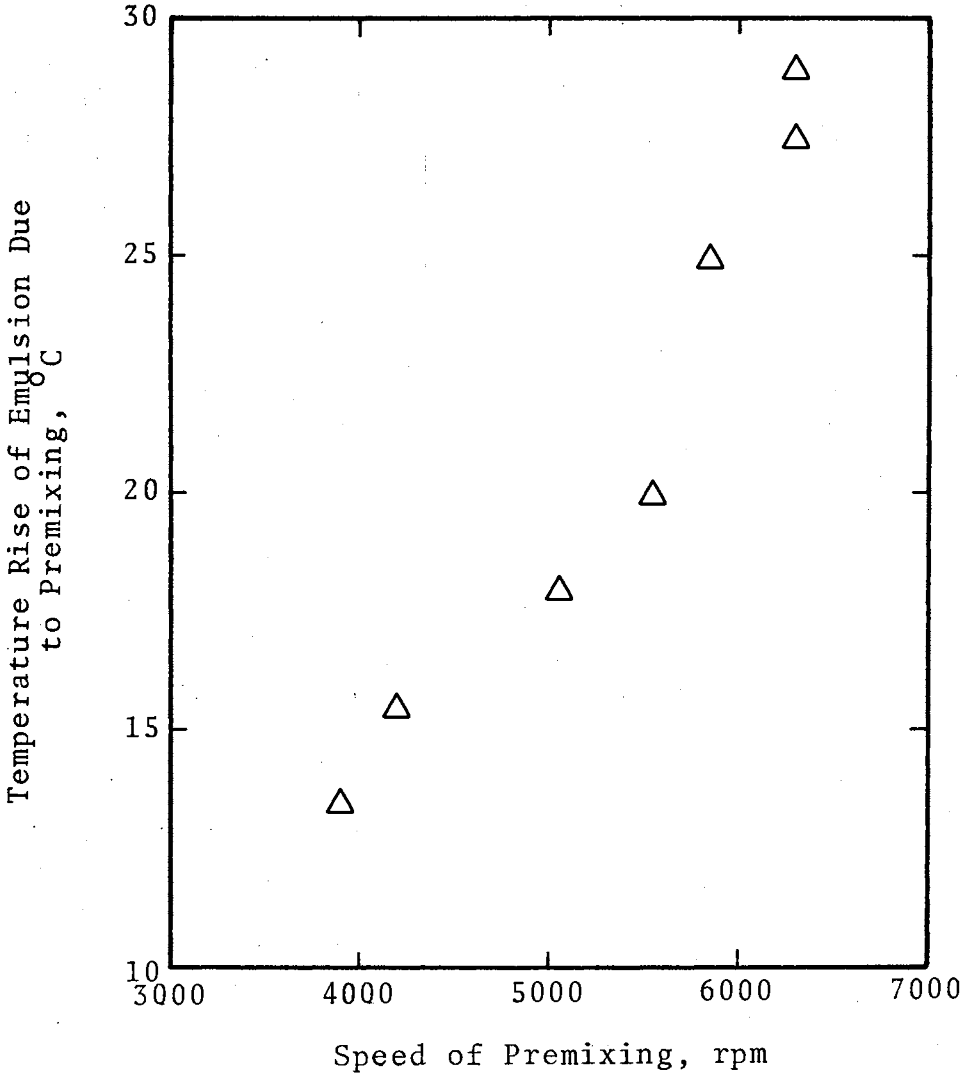

Figure 22. Temperature Rise of Emulsion Due to Premixing

CHAPTER IV

DISCUSSION

This study, as with any study of emulsion polymerization, contained many potential sources of error which could not be either removed or strictly controlled. However, a range of possible error which could be related to certain uncontrolled variables was determined and in this manner a range of precision was determined for the equipment and methods utilized for this study.

A. Initiation Period

The zero time samples for Runs 12 through 20 were to determine if pre-initiation of the reaction had occurred during the premixing step. The range of conversions of the zero sample was .06% to 1.76%. However, as shown by Run 9 in which pre-initiation had occurred, the rate during the propagation period would be significantly reduced. All the other runs had conversion rates during the zero order propagation period approximately alike compared to the drastic reduction caused by pre-initiation. The explanation of the zero time sample conversion (other than pre-initiation) relates to the effect caused by impurities in the reactants and wash solution which were removed during filtering of the samples. Also, the 1.76% conversion was calculated from total weight of polymer of only .0208 grams (see Appendix C for the calculational procedure). When the polymer samples were removed from the oven and weighed, the samples would gain as much as .0200 grams of water by absorbing moisture from the air. The range of the zero time samples describes the error of inert impurities and for weighing for all the other samples of the run, and has an average value of 1.02% monomer conversion.

Throughout this study, the initiation period of the reaction varied sporadically. Apparently, retardation caused by impurities in the reactants, by possible degradation of the initiator, by impurities in the nitrogen and solvents inhibited some of the runs more so than others. The flow rate of the nitrogen purge was not constant for all the experimental runs. If the error of 1.02 percent monomer conversion mentioned previously in reference to the time zero samples is considered to be representative of the error of the samples at residence time of five minutes, then the values of conversion at a five minutes residence time are meaningless; and therefore, not enough data points are available to accurately describe the initiation period of the reaction.

A widely accepted theory of Vanderhoff's (14) and others (3,4,7) states that the rate of propagation is determined by the number of polymer particles formed during the initiation period. Therefore, the decreased rate of propagation caused by pre-initiation was a result of the particles formed during pre-initiation growing and using the emulsifier of the micelles to remain stable. Thus, the effect is to reduce the emulsifier which will in turn reduce the number of micelles available for reaction sites when the initiator is introduced into the system.

B. Wash Effects

When the wash solution was added to the samples, the polymer would form one clump which trapped the emulsifier and any unreacted monomer inside the polymer. The effect of unsatisfactory washing was to calculate conversions over 100%. The positive deviation caused by unsatisfactory washing would increase with the size of the sample and the conversion. The range of the error is estimated to be from zero to twelve percent. The results at higher conversions of Runs 1 through 15 are unreliable due to unsatisfactory washing of the polymer. For Runs 16 through 20, washing the samples in the blender to disperse the clumps of polymer and to achieve better removal of emulsifier and unreacted monomer proved to be effictive.

C. Toluene Loss

Another source of error is that of loss of toluene during purging. If toluene were allowed to escape from the reactor with the effluent nitrogen purge, the weight fraction of monomer in the emulsion would increase above the initial value prepared from the recipe, and the result would be to calculate conversions higher than the actual value. As mentioned in the preceding chapter, the nitrogen effluent of Run 12 was put through an ice trap and only 10 milliliters of toluene was recovered, which would indicate that the escaping toluene did not present a significant source of error (10 ml. out of 450 ml. toluene initially and 8.9 gram out of a total reactor charge of 677 grams).

D. Temperature Control

Maintaining temperature control of ± 1°C for the runs with high initiator concentration was difficult but not impossible. Heat must be added to the reactor to maintain 40°C prior to adding the initiator and during the initiation period of the reaction. The polymerization reaction is exothermic with a heat of reaction of -19.5 kcal/mole (14). During the constant rate of polymerization (propagation) period of the reaction heat must be removed from the reactor for isothermal operation. When termination slows the rate of reaction, heat must be added to the reactor to maintain 40°C. A small rise in temperature causes a large increase in the rate of reaction and a "runaway" reaction can occur in which the heat is evolved faster than the ice water will remove the heat and the temperature of the reactor will increase causing another increase in the rate of reaction. The runs with low initiator concentration were probably controlled to ± 0.5°C as the system would practically maintain 40°C without external heating or cooling.

E. Polymer Samples Drying

The effect of inadequately drying the polymer samples was described in the previous chapter. The samples at higher conversions contain more polymer and thus more water than samples taken early in the reaction. Therefore, the effect of inadequate drying of the polymer samples becomes larger at higher conversions. Inadequate drying always gives conversions higher than the actual value (always a positive deviation). The deviation is less than one percent at low conversions and increases to as much as ten percent at higher conversions. During the initiation period of the reaction the deviation of the samples is approximately one percent monomer conversion. The data collected during the propagation period of the reaction has an average deviation of about four percent monomer conversion. The termination period has a range of deviation of approximately 25 percent monomer conversion for Runs 1 - 9, 15 percent monomer conversion for Runs 10 - 15 (better drying) and two percent monomer conversion for Runs 16 - 20 (better drying and washing).

F. Methyl Orange

Methyl orange was added to the recipe for Run 9 only. Since the particle sizes were not measured in this study, the effect of the methyl orange cannot be determined exactly. However, the methyl orange was observed to enhance the emulsion stability and decrease the rate of reaction. A possible explanation is that the methyl orange acts as a surfactant but offers greater resistance to monomer diffusion than the sorbitan monostearate (Span 60).

G. Premix Effects

The effect of the degree of premixing within the range of speeds tested (3900 to 6300 rpm) would appear to be negligible at the high initiator concentration for the propagation part of the reaction. For inverse emulsion polymerization, Vanderhoff, et al. (14) has shown that more than one free radical exists in each polymer particle. In addition, Vanderhoff, et al. states that the initiator (benzoyl peroxide, lauroyl peroxide, and potassium persulfate), enters the particles before forming free radicals and that the free radicals in the continuous phase cannot initiate polymer chains. Therefore, even if the number of particles formed in the initiation period varied due to the degree of premixing, the rate of the propagation at high initiator concentrations would be dependent on the concentration of initiator and independent of the number of particles formed during initiation.

At the low initiator concentration, the system's operation was more stable than at the high initiator concentration and the reproducibility was improved. However, the variation of the rate of propagation was not large enough to warrant further investigation. For Runs 18, 19, and 20, the rate of reaction averaged 0.92 ± .16 percent conversion per minute. The reproducibility was ± .2 percent conversion per minute.

The process of forming emulsions at high shear rates is discussed by Sherman (9) and others (8,1,2). The temperature rise during mixing is a result of the friction of the fluid particles undergoing viscous shear, and is proportional to the viscosity of the emulsion. A toluene-emulsifier-water mixture was mixed in the blender for 15 minutes at 6300 rpm and the temperature rise was 29°C which is consistent with the observed temperature rise for the standard recipe. Therefore, the temperature rise was caused by the mixing and not any reaction of the polymer. Sherman states that the particular speed of mixing corresponds to a certain size of droplet of the dispersed phase being formed when all other variables are constant. After approximately five minutes of mixing, the size of the droplets is constant and equilibrium exists between the dispersion mechanism and coalescence. Sherman also states that in general the stability of the emulsion decreases as the temperature increases. In general water-in-oil emulsions are not stable and the toluene was observed to immediately begin separating from the emulsion whenever the emulsion was not being agitated. Determination of any degradation of the emulsion was beyond the scope of this study.

H. Data Points for Zero-Order Rate

The choice of which points to be used for the least squares approximation of the zero order region of the reaction curves was somewhat arbitrary (the points which were used for the approximation are given in Appendix B). The distinction between a datum point being in the initiation period or in the propagation period was made by using those data points which were obviously in the propagation period (range of conversion of about 30% to 75%) for the least squares approximation and comparing the standard error of that line against the standard error of the line determined when the data points which were in question were used in the least squares approximation. The points chosen for the final results were those points which would give the smallest percent deviation and standard error for the line determined by the least squares approximation. The determination of the transition between the propagation period and the termination period was made in a similar manner.

CHAPTER V

CONCLUSIONS AND RECOMMENDATIONS

A. Conclusions

The following conclusions are made from this work:

1. The overall operability of the experimental system with respect to controlling the temperature and analyzing the samples for conversion is satisfactory.

2. Experimental results reveal that the rate of reaction does not depend on the degree of premixing over the range studied and within the present reproducibility.

3. The effect of pre-initiation of the reaction during premixing is to inhibit the rate of reaction.

4. Impurities of the reactants affect the initiation period of the reaction in a complex manner. Reproducibility of the first part of the reaction is unsatisfactory.

B. Recommendations

This study is satisfactory as a preliminary step to determine the best procedures for a more detailed program. The equipment used in this study is adequate to follow the course of the inverse emulsion polymerization reaction at the desired temperature and level of agitation. However, modifications must be made to control impurities in the reactants and the nitrogen purge so that reproducibility during the initiation period of the reaction is possible. Also, before meaningful results can be obtained, techniques must be developed to determine the particle sizes and the degree of polymerization throughout the course of the premixing and reaction.

Further studies can be made using this apparatus to determine the effect of premixing on the polymer quality and to determine the effect of the degree of agitation during the reaction on the rate of reaction and on product quality. However, studies should first be made to determine the effect of pH and temperature on the stability of the emulsion and the equilibrium particle size as a function of degree of stirring.

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APPENDIX A

EXPERIMENTAL DATA FOR RUNS 1 THROUGH 9

EXPERIMENTAL DATA FOR RUNS 1 THROUGH 9

Appendix A contains the results of Runs 1 through 9. The recipe for Runs 1 through 9 is given in Table VIII. The experimental data necessary to determine the monomer conversion and the calculated conversions for Runs 1 through 9 are presented in Tables IX through XVI. Comments about the temperature control, changes in the procedure and the manner of handling and drying the samples are presented with the data for each run.

No results are reported for Run 6 because the samples were lost during filtering.

TABLE VIII

STANDARD RECIPE FOR RUNS 1 THROUGH 9

Boric Acid (runs 1-5)	3.5 grams
(runs 6-9)	3.0 grams
Sodium Hydroxide	Varied
Acrylamide	75 grams
De-ionized Water	175 ml.
Toluene	450 ml.
Sorbitan Monostearate (Span 60)	15 grams
Initiator Solution	25 ml.

TABLE IX

EXPERIMENTAL DATA AND CALCULATED RESULTS OF RUN 1

Sample Number	Residence Time Minutes	Wt. of Cup grams	Wt. of Filter Paper grams	Wt. of Cup + Sample + Wash grams	Wt. of Dried Polymer + Filter-grams	Monomer Conversion Percent
1	5	5.661	.631	60.127	.645	0.81
2	10	5.493	.644	59.830	.795	8.84
3	15	5.700	.635	62.010	1.647	52.49
4	20	5.825	.642	60.708	1.670	58.08
5	25	6.451	.638	63.860	2.263	79.27
6	30	5.670	.641	57.580	1.925	89.17
7	36	5.442	.627	53.427	1.610	97.91

Comments: Temperature control was not good ± 3°C. Temperature reached 57°C at one instance before being cooled to 40°C. Each sample was washed in 50 ml. of wash solution. The samples were allowed to dry at ambient condition. The amount of sodium hydroxide added to the water phase was .5 gram which gave a pH of 8.86.

TABLE X

EXPERIMENTAL DATA AND CALCULATED RESULTS OF RUN 2

Sample Number	Residence Time Minutes	Wt. of Cup grams	Wt. of Filter Paper grams	Wt. of Cup + Sample + Wash grams	Wt. of Dried Polymer + Filter-grams	Monomer Conversion Percent
1	5	5.530	.640	59.400	0.655	0.90
2	10	5.742	.633	57.465	0.865	16.49
3	15	5.327	.623	60.844	1.430	46.67
4	20	5.642	.633	61.523	1.985	71.88
5	25	5.323	.633	60.235	2.252	91.88
7	35	5.329	.633	55.003	1.821	99.66

Comments: Temperature was maintained at $40^{\circ}C \pm 1^{\circ}C$. The attempt to take sample number 6 failed when the sample tube plugged with polymer. Each sample was washed in 50 ml. of wash solution and air dried. The amount of sodium hydroxide added to the water phase was .3 gram which gave a pH of 8.40.

TABLE XI

EXPERIMENTAL DATA AND CALCULATED RESULTS OF RUN 3

Sample Number	Residence Time Minutes	Wt. of Cup grams	Wt. of Filter Paper grams	Wt. of Cup + Sample + Wash grams	Wt. of Dried Polymer + Filter-grams	Monomer Conversion Percent
1	5	5.361	.628	69.585	0.649	0.75
2	10	5.678	.629	61.840	0.850	11.56
3	15	5.775	.634	60.829	1.314	38.01
4	20	5.448	.630	59.818	1.634	58.61
5	25	5.687	.633	62.915	2.321	83.20
7	35	5.702	.634	56.750	2.011	97.60

Comments: Temperature was maintained at $39^{\circ}C \pm 2$. Sample tubes jammed on attempts to take samples number 6 and 8. Samples were washed with 50 ml. of wash solution and air dried. The .3 gram of sodium hydroxide added to the water phase gave the water phase a pH of 8.40.

TABLE XII

EXPERIMENTAL DATA AND CALCULATED RESULTS OF RUN 4

Sample Number	Residence Time Minutes	Wt. of Cup grams	Wt. of Filter Paper grams	Wt. of Cup + Sample + Wash grams	Wt. of Dried Polymer + Filter-grams	Monomer Conversion Percent
1	5	5.344	.626	59.110	0.630	0.24
2	10	5.655	.622	60.940	0.953	18.25
3	15	5.742	.638	59.059	1.450	50.87
4	20	5.412	.641	57.872	1.685	69.56
5	25	5.650	.625	58.972	2.063	90.04
6	30	5.658	.637	64.291	2.945	105.58
7	35	5.671	.631	61.537	2.649	107.39
8	45	5.607	.637	60.428	2.634	110.51

Comments: Temperature was maintained at 40°C ± 1. The sample tube was pulled out of the emulsion between samples. Each sample was washed in 50 ml. of wash solution and oven dried for 18.5 hours at 100°C. The pH of the water phase was adjusted to 8.40 by adding .3 gram sodium hydroxide and .1 ml. sodium hydroxide solution.

TABLE XIII

EXPERIMENTAL DATA AND CALCULATED RESULTS OF RUN 5

Sample Number	Residence Time Minutes	Wt. of Cup grams	Wt. of Filter Paper grams	Wt. of Cup + Sample + Wash grams	Wt. of Dried Polymer + Filter-grams	Monomer Conversion Percent
1	5	5.911	.633	65.700	0.689	2.42
2	10	6.034	.628	52.358	0.809	22.07
3	15	5.358	.631	64.294	1.889	56.67
4	20	5.775	.630	57.917	1.812	80.63
5	25	5.644	.641	63.290	2.560	92.39
6	30	5.270	.632	59.222	2.331	101.90
7	35	5.923	.616	54.000	1.652	102.20

Comments: Temperature was maintained at 40°C ± 1. Each sample was washed in 50 ml. of wash solution and oven dried for 18 hours at 100°C. The pH of the water phase was adjusted to 8.40 by adding .3 gram sodium hydroxide.

TABLE XIV

EXPERIMENTAL DATA AND CALCULATED RESULTS OF RUN 7

Sample Number	Residence Time Minutes	Wt. of Cup grams	Wt. of Filter Paper grams	Wt. of Cup and Sample grams	Wt. of Dried Polymer + Filter-grams	Monomer Conversion Percent
1	5	5.669	.630	15.303	0.633	0.28
2	10	5.663	.636	21.347	0.674	2.18
3	15	5.304	.632	23.442	0.963	16.40
4	20	5.676	.633	23.260	1.241	31.10
5	25	5.677	.631	22.929	1.700	55.80
6	30	5.748	.639	22.418	1.944	70.50
7	35	5.619	.635	23.078	2.400	91.00

Comments: Twenty drops of methyl orange dye was added to water phase. Sample placed in cup and weighed before washing instead of after washing as in previous runs. Samples washed in 50 ml. of wash solution and oven-dried for 25 hours at 100°C. The water phase pH was adjusted to 8.45 by adding .3 gram sodium hydroxide. Temperature maintained at 40°C ± 1.

TABLE XV

EXPERIMENTAL DATA AND CALCULATED RESULTS OF RUN 8

Sample Number	Residence Time Minutes	Wt. of Cup grams	Wt. of Filter Paper grams	Wt. of Cup and Sample grams	Wt. of Dried Polymer + Filter-grams		Monomer Conversion Percent	
					*	**	*	**
1	5	4.5543	.6254	17.3523	.6673	.6325	2.98	0.50
2	10	4.5986	.6228	30.0926	1.0069	.9762	13.57	12.49
3	15	4.4754	.6400	22.4567	1.4240	1.3725	39.28	36.70
4	20	4.5159	.6334	24.2046	1.9820	1.9218	61.71	58.95
5	25	4.4933	.6250	21.7680	2.2035	2.1380	82.32	78.91
6	30	4.5220	.6200	12.9495	1.5456	1.5034	98.95	94.44
7	35	4.4877	.6405	13.7486	1.6934	1.6530	102.43	98.50
8	40	4.4966	.6323	21.5330	2.7390	2.6720	111.40	107.86

* 20 hours oven drying at 70°C

** 99 hours oven drying at 100°C

Comments: Temperature control was poor, 40°C ± 3. Each sample was washed in 50 ml. wash solution. The filter paper was dried for one day in the oven at 100°C for this run and all runs after this run. The pH of the water phase was adjusted to 8.65 by adding 0.3 gram sodium hydroxide. Also, .630 gram of sodium sulfite was added to the water phase.

TABLE XVI

EXPERIMENTAL DATA AND CALCULATED RESULTS OF RUN 9

Sample Number	Residence Time Minutes	Wt. of Cup grams	Wt. of Filter Paper grams	Wt. of Cup and Sample grams	Wt. of Dried Polymer + Filter-grams	Monomer Conversion Percent
1	5	15.8000	.6290	42.7100	.8140	6.35
2	10	15.4600	.6294	33.7130	1.0655	21.79
3	15	15.4715	.6377	32.2470	1.3940	41.58
4	20	15.5460	.6263	35.7498	1.9840	61.39
5	25	15.4822	.6234	35.0632	2.3065	78.52
6	30	15.4675	.6185	31.0016	2.1023	86.85
7	35	15.4330	.6272	32.2837	2.3404	92.22
8	45	15.4439	.6215	38.1777	3.3200	107.69

Comments: Temperature was maintained at 40°C ± 1. Mixed the water, .5 gram sodium sulfite, and the boric acid. Then added the monomer and noticed that the temperature was 14°C so the water solution was heated to 26°C and found the pH to be 8.0. Added wash solution to a sample of the water solution and determined pre-initiation of the reaction. Samples were dried for 5 days at 100°C.

APPENDIX B

EXPERIMENTAL DATA FOR RUNS 10 THROUGH 20

EXPERIMENTAL DATA FOR RUNS 10 THROUGH 20

Appendix B contains the experimental data and calculated results for Runs 10 through 20 presented in Tables XVII through XXVII. Along with the data necessary to calculate the monomer conversion is data concerning the heat of mixing of the acrylamide and water, the temperature rise of the emulsion due to mixing, and the curve fit data with standard error and percent deviation. The procedure and recipe for Runs 10 through 20 was presented in Chapter II and were held constant.

TABLE XVII

EXPERIMENTAL DATA AND CALCULATED RESULTS OF RUN 10

Sample Number	Residence Time Minutes	Wt. of Cup grams	Wt. of Filter grams	Wt. of Cup and Sample grams	Wt. of Dried Polymer and Filter grams	Monomer Conversion Percent	Curve-Fit Calculated Conversion Percent	Deviation from Curve Percent
1	5	15.8074	.6316	29.9905	0.6370	000.34	XXX	XXX
2	10	15.4645	.6330	36.1485	0.7170	000.66	03.30	-9.74
3	15	15.4813	.6240	34.4445	1.1480	024.97	25.28	1.27
4	20	15.5480	.6300	27.1164	1.2010	044.61	47.27	5.97
5	25	15.4942	.6344	32.7004	1.9920	071.31	69.25	-2.88
6	30	15.4840	.6314	32.0064	2.3608	094.60	91.23	-3.55
7	35	15.4334	.6430	32.6135	2.7420	110.43	113.22	2.53
8	45	15.4477	.6470	39.2606	3.9050	123.66	XXX	XXX

Speed of Blender: 3900 rpm
Time in Blender: 15 minutes
Water-Acrylamide-Boric Acid Solution: Temperature: 11.0°C pH: 3.90
Amount of Sodium Hydroxide Solution Added: 3.0 ml.
Slope of Curve Fit: 4.40
Standard Error: 2.26

TABLE XVIII

EXPERIMENTAL DATA AND CALCULATED RESULTS OF RUN 11

Sample Number	Residence Time Minutes	Wt. of Cup grams	Wt. of Filter grams	Wt. of Cup and Sample grams	Wt. of Dried Polymer and Filter grams	Monomer Conversion Percent	Curve-Fit Calculated Conversion Percent	Deviation from Curve Percent
0	-1	15.4415	.6030	28.1250	0.6190	1.14	XXX	XXX
1	5	15.8021	.6240	27.5398	0.6431	1.47	XXX	XXX
2	10	15.4650	.6162	28.2703	0.8418	15.92	15.32	-3.76
3	15	15.4713	.6253	28.9870	1.3446	48.10	49.30	2.49
4	20	15.5433	.6167	31.2480	2.0740	83.87	83.27	-0.71

Speed of Blender: 6300 rpm
Time in Blender: 15 minutes
Nitrogen Flush of Blender: 30 seconds
Water-Acrylamide-Boric Acid Solution: Temperature: 11.0°C pH: 4.00
Amount of Sodium Hydroxide Solution Added: 2.5 ml.
Slope of Least Squares Curve Fit: 6.79
Standard Error: 0.85

TABLE XIX

EXPERIMENTAL DATA AND CALCULATED RESULTS OF RUN 12

Sample Number	Residence Time Minutes	Wt. of Cup grams	Wt. of Filter grams	Wt. of Cup and Sample grams	Wt. of Dried Polymer and Filter grams	Monomer Conversion Percent	Curve-Fit Calculated Conversion Percent	Deviation from Curve Percent
0	-1	15.4442	.5972	26.1475	0.6180	1.76	XXX	XXX
1	5	15.8058	.6002	30.9580	0.6192	1.13	XXX	XXX
2	10	15.4632	.6024	27.5293	0.6778	5.65	5.59	-0.98
3	15	15.4730	.5994	26.8583	0.9269	26.00	26.40	1.54
4	20	15.5440	.6002	27.0430	1.2078	47.76	47.20	-1.16
5	27	15.4717	.6180	31.1946	1.9423	76.13	76.34	0.27
6	35	15.4373	.5965	31.0325	2.2696	96.96	XXX	XXX
7	40	15.4468	.6100	31.6228	2.5336	107.48	XXX	XXX
8	45	15.4837	.6269	31.5008	2.6040	111.56	XXX	XXX

Speed of Blender: 5850 rpm
Time in Blender: 15 minutes
Nitrogen Flush of Blender: 30 seconds
Temperature of Emulsion Before Blending: 19.0°C
Temperature of Emulsion After Blending: 44.0°C
De-ionized Water Temperature: 24.0°C
Water-Acrylamide Solution: Temperature: 11.0°C pH: 4.20
Water-Acrylamide-Boric Acid Solution: Temperature: 12.0°C pH: 4.00
Amount of Sodium Hydroxide Solution Added: 2.8 ml.
Slope of Least Squares Curve Fit: 4.16
Standard Error: 0.36

TABLE XX

EXPERIMENTAL DATA AND CALCULATED RESULTS OF RUN 13

Sample Number	Residence Time Minutes	Wt. of Cup grams	Wt. of Filter grams	Wt. of Cup and Sample grams	Wt. of Dried Polymer and Filter grams	Monomer Conversion Percent	Curve-Fit Calculated Conversion Percent	Deviation from Curve Percent
0	-1	15.4410	.5956	27.8248	0.6171	1.57	XXX	XXX
1	5	15.8058	.5938	28.3721	0.6178	1.73	XXX	XXX
2	10	15.4640	.5962	29.3069	0.6783	5.36	5.67	5.82
3	15	15.4740	.5955	31.4952	1.0473	25.49	27.54	8.06
4	20	15.5440	.5920	31.7923	1.5215	51.70	49.41	-4.42
5	25	15.4890	.5942	31.6295	1.9180	76.13	71.29	-3.83
6	35	15.4715	.5993	29.4113	1.9936	90.40	93.16	3.05
7	35	15.4367	.6074	26.9365	1.8820	100.18	XXX	XXX
8	45	15.4472	.5906	28.0617	2.1626	112.63	XXX	XXX

Speed of Blender: 4200 rpm
Time in Blender: 15 minutes
Nitrogen Flush of Blender: 30 seconds
Temperature of Emulsion Before Blending: 18.5°C
Temperature of Emulsion After Blending: 34.0°C
De-ionized Water Temperature: 25.0°C
Water-Acrylamide Solution: Temperature: 12.0°C pH: 4.15
Water-Acrylamide-Boric Acid Solution: Temperature: 12.0°C pH: 4.05
Amount of Sodium Hydroxide Solution Added: 2.0 ml.
Slope of Least Squares Curve Fit: 4.37
Standard Error: 2.25

TABLE XXI

EXPERIMENTAL DATA AND CALCULATED RESULTS OF RUN 14

Sample Number	Residence Time Minutes	Wt. of Cup grams	Wt. of Filter grams	Wt. of Cup and Sample grams	Wt. of Dried Polymer and Filter grams	Monomer Conversion Percent	Curve-Fit Calculated Conversion Percent	Deviation from Curve Percent
0	-1	15.4410	.5910	27.3346	.6078	1.28	XXX	XXX
1	5	15.8053	.6044	30.2953	.6219	1.09	XXX	XXX
2	10	15.4650	.6033	28.600	.6217	1.27	1.32	4.12
3	15	15.4753	.5990	29.9434	.8843	17.82	21.21	19.04
4	20	15.5457	.6063	31.1910	1.3292	41.76	41.10	-1.58
5	25	15.4858	.5953	32.1750	1.8138	65.99	60.99	-7.58
6	30	15.4720	.5997	28.4365	1.7865	82.74	80.88	-2.25
7	35	15.4378	.5966	30.0946	2.1647	96.70	100.77	4.21
8	40	15.4476	.5865	31.0454	2.4625	108.71	XXX	XXX

Speed of Blender: 5050 rpm
Time in Blender: 15 minutes
Nitrogen Flush of Blender: 30 seconds
Temperature of Emulsion Before Blending: 19.0°C
Temperature of Emulsion After Blending: 37.0°C
De-ionized Water Temperature: 24.0°C
Water-Acrylamide Solution: Temperature: 11.0°C pH: 4.20
Water-Acrylamide-Boric Acid Solution: Temperature: 12.5°C pH: 4.20
Amount of Sodium Hydroxide Solution Added: 2.4 ml.
Slope of Least Squares Curve Fit: 3.98
Standard Error: 3.08

TABLE XXII

EXPERIMENTAL DATA AND CALCULATED RESULTS OF RUN 15

Sample Number	Residence Time Minutes	Wt. of Cup grams	Wt. of Filter grams	Wt. of Cup and Sample grams	Wt. of Dried Polymer and Filter grams	Monomer Conversion Percent	Curve-Fit Calculated Conversion Percent	Deviation from Curve Percent
0	1	15.4415	.5900	27.2260	.6060	1.23	XXX	XXX
1	5	15.8055	.5963	26.4317	.6113	1.28	XXX	XXX
2	10	15.4651	.5802	26.8030	.6550	5.96	6.86	15.10
3	15	15.4743	.5914	27.5644	.9330	25.59	26.32	2.85
4	20	15.5453	.5954	27.8728	1.2490	47.94	45.78	-4.51
5	25	15.4853	.5972	26.7054	1.4246	66.71	65.24	-2.20
6	30	15.4740	.6059	29.8510	1.9180	82.70	84.70	2.42
7	35	15.4385	.6045	32.3574	2.4109	98.56	XXX	XXX
8	45	15.4473	.6027	27.9916	2.0800	106.50	XXX	XXX

Speed of Blender: 5550 rpm
Time in Blender: 15 minutes
Nitrogen Flush of Blender: 30 seconds
Temperature of Emulsion Before Blending: 20.0°C
Temperature of Emulsion After Blending: 40.0°C
De-ionized Water Temperature: 24.0°C
Water-Acrylamide Solution: Temperature: 11.0°C pH: 4.20
Water-Acrylamide-Boric Acid Solution: Temperature: 11.0°C pH: 4.20
Amount of Sodium Hydroxide Solution Added: 2.5 ml.
Slope of Least Squares Curve Fit: 3.89
Standard Error: 1.56

TABLE XXIII

EXPERIMENTAL DATA AND CALCULATED RESULTS OF RUN 16

Sample Number	Residence Time Minutes	Wt. of Cup grams	Wt. of Filter grams	Wt. of Cup and Sample grams	Wt. of Dried Polymer and Filter grams	Monomer Conversion Percent	Curve-Fit Calculated Conversion Percent	Deviation from Curve Percent
0	-1	15.4401	.5906	26.5926	.6040	1.09	XXX	XXX
1	5	15.8035	.5776	27.4132	.5837	0.47	XXX	XXX
2	10	15.4632	.5970	27.3590	.7125	8.78	10.88	23.94
3	15	15.4739	.5944	27.4609	1.0133	31.59	30.85	-2.36
4	20	15.5448	.5934	27.3510	1.2919	53.47	50.81	-4.98
5	25	15.4848	.5884	28.1445	1.5916	71.62	70.77	-1.18
6	30	15.4714	.5881	31.1395	2.1237	88.58	90.73	-2.43
7	35	15.4350	.5951	29.2500	2.0559	95.57	XXX	XXX
8	45	15.4455	.5944	30.2040	2.2449	101.08	XXX	XXX

Speed of Blender: 6300 rpm
Time in Blender: 15 minutes
Nitrogen Flush of Blender: 30 seconds
Temperature of Emulsion Before Blending: 19.0°C
Temperature of Emulsion After Blending: 46.5 °C
De-ionized Water Temperature: 24.0°C
Water-Acrylamide Solution: Temperature: 11.0°C pH: 4.20
Water-Acrylamide-Boric Acid Solution: Temperature: 13.0°C pH: 4.25
Amount of Sodium Hydroxide Solution Added: 1.5 ml.
Slope of Least Squares Curve Fit: 3.99
Standard Error: 1.87

TABLE XXIV

EXPERIMENTAL DATA AND CALCULATED RESULTS OF RUN 17

Sample Number	Residence Time Minutes	Wt. of Cup grams	Wt. of Filter grams	Wt. of Cup and Sample grams	Wt. of Dried Polymer and Filter grams	Monomer Conversion Percent	Curve-Fit Calculated Conversion Percent	Deviation from Curve Percent
0	-1	15.4425	.5850	23.1408	.5909	0.80	XXX	XXX
1	5	15.8050	.5969	26.5854	.6162	1.81	XXX	XXX
2	10	15.4660	.5880	27.8402	.7120	9.38	10.34	10.28
3	15	15.4742	.5910	27.2588	.9930	31.14	30.86	-0.89
4	20	15.5475	.5883	29.2925	1.4000	53.72	51.38	-4.35
5	25	15.4860	.5878	26.0902	1.4095	70.25	71.90	2.35
6	30	15.4712	.5982	31.4120	2.0762	84.45	XXX	XXX
7	35	15.4459	.5985	32.2070	2.2780	90.83	XXX	XXX
8	45	15.4476	.5883	30.6217	2.2820	101.22	XXX	XXX

Speed of Blender: 6300 rpm
Time in Blender: 5 minutes
Nitrogen Flush of Blender: 30 seconds
Temperature of Emulsion Before Blending: 19.0°C
Temperature of Emulsion After Blending: 31.0° C
De-ionized Water Temperature: 24.0°C
Water-Acrylamide Solution: Temperature: 12.0°C pH: 4.20
Water-Acrylamide-Boric Acid Solution: Temperature: 12.0°C pH: 4.15
Amount of Sodium Hydroxide Added: 1.5 ml.
Slope of Least Square Curve Fit: 4.10
Standard Error: 1.52

TABLE XXV

EXPERIMENTAL DATA AND CALCULATED RESULTS OF RUN 18

Sample Number	Residence Time Minutes	Wt. of Cup grams	Wt. of Filter grams	Wt. of Cup and Sample grams	Wt. of Dried Polymer and Filter grams	Monomer Conversion Percent	Curve-Fit Calculated Conversion Percent	Deviation from Curve Percent
0	-1	15.4382	.5870	26.3132	.5957	0.72	XXX	XXX
1	10	15.8035	.5867	28.6735	.5933	0.46	XXX	XXX
2	20	15.4636	.5904	28.5263	.6532	4.35	XXX	XXX
3	30	15.4754	.5845	28.1837	.7178	9.48	9.34	-1.44
4	40	15.5446	.5931	27.6828	.8315	17.75	17.59	-0.93
5	50	15.4829	.5808	27.9727	.9383	25.87	25.83	-0.16
6	60	15.4743	.5930	27.0138	1.0266	33.97	34.07	0.29
7	70	15.4443	.5800	26.1670	1.0830	42.40	42.31	-0.21
8	80	15.4465	.5966	26.4422	1.2045	49.98	50.55	1.15
9	90	15.4379	.5915	26.4130	1.2964	58.06	58.80	1.27
10	100	15.4409	.5900	26.4850	1.4194	67.89	67.04	-1.25
11	110	15.4505	.5884	28.2899	1.6595	75.41	75.28	-0.17

De-ionized Water Temperature: 24.0°C
Water-Acrylamide Solution: Temperature: 11.0°C pH: 4.20
Water-Acrylamide-Boric Acid Solution: Temperature: 12.0°C pH: 4.20
Amount of Sodium Hydroxide Added: 1.8 ml.
Slope of Least Squares Curve Fit: 0.82
Standard Error: 0.43

TABLE XXVI

EXPERIMENTAL DATA AND CALCULATED RESULTS OF RUN 19

Sample Number	Residence Time Minutes	Wt. of Cup grams	Wt. of Filter grams	Wt. of Cup and Sample grams	Wt. of Dried Polymer and Filter grams	Monomer Conversion Percent	Curve-Fit Calculated Conversion Percent	Deviation from Curve Percent
0	-1	15.4420	.5940	24.8000	.5946	.06	XXX	XXX
1	10	15.8042	.6108	27.8881	.6144	.27	XXX	XXX
2	20	15.4647	.5921	27.3040	.6142	1.69	XXX	XXX
3	30	15.4811	.6090	26.3562	.6857	6.38	XXX	XXX
4	40	15.5447	.6078	26.4659	.7534	12.05	XXX	XXX
5	50	15.4853	.6192	26.7658	.8503	18.55	19.69	6.17
6	60	15.4702	.6035	26.4008	.9307	27.06	28.19	4.17
7	70	15.4343	.6067	27.3000	1.1020	37.73	36.68	-2.77
8	80	15.4445	.6044	27.2718	1.2165	46.78	45.18	-3.424
9	90	15.4308	.6054	26.2903	1.2509	53.73	53.67	-.11
10	100	15.4361	.5962	28.8851	1.4779	59.26	XXX	XXX
11	120	15.4519	.6088	25.1940	1.4732	80.21	79.16	-1.31
12	140	15.5070	.6045	26.9754	1.8054	94.66	96.15	1.57
13	160	15.5114	.6031	27.4279	1.9758	104.13	XXX	XXX

Speed of Blender: 3900 rpm
Time in Blender: 15 minutes
Nitrogen Flush of Blender: 30 seconds
Temperature of Emulsion Before Blending: 19.0°C
Temperature of Emulsion After Blending: 32.5°C
De-ionized Water Temperature: 24.0°C
Water-Acrylamide Solution: Temperature: 11.5°C pH: 4.15
Water-Acrylamide-Boric Acid Solution: Temperature: 12.0°C pH: 4.15
Amount of Sodium Hydroxide Added: 1.8 ml.
Slope of Least Squares Curve Fit: 0.85
Standard Error: 1.17

TABLE XXVII

EXPERIMENTAL DATA AND CALCULATED RESULTS OF RUN 20

Sample Number	Residence Time Minutes	Wt. of Cup grams	Wt. of Filter grams	Wt. of Cup and Sample grams	Wt. of Dried Polymer and Filter grams	Monomer Conversion Percent	Curve-Fit Calculated Conversion Percent	Deviation from Curve Percent
0	-1	15.4478	.5850	27.3542	.5906	0.43	XXX	XXX
1	10	15.8040	.5912	25.9910	.6074	1.44	XXX	XXX
2	20	15.4631	.5863	26.2876	.6642	6.51	XXX	XXX
3	30	15.4764	.5922	25.7684	.7612	14.84	14.30	-3.65
4	40	15.5451	.5876	25.2926	.8514	24.46	25.13	2.73
5	50	15.4846	.5819	26.8272	1.0391	36.44	35.96	-1.32
6	60	15.4725	.5896	27.1055	1.1896	46.62	46.79	0.36
7	70	15.4370	.5822	27.0546	1.3079	56.47	57.62	2.03
8	80	15.4495	.5870	27.0860	1.4805	69.41	68.45	-1.38
9	90	15.4304	.5763	26.0930	1.4400	73.22	XXX	XXX
10	100	15.4378	.5796	27.4142	1.6534	81.05	XXX	XXX
11	120	15.4511	.5725	28.3100	1.8681	91.08	XXX	XXX
12	130	15.5089	.5846	29.5755	2.1060	97.77	XXX	XXX

Speed of Blender: 6300 rpm
Time in Blender: 15 minutes
Nitrogen Flush of Blender: 30 seconds
Temperature of Emulsion Before Blending: 18.0°C
Temperature of Emulsion After Blending: 47.0°C
De-ionized Water Temperature: 24.5°C
Water-Acrylamide Solution: Temperature: 12.0°C pH: 4.10
Water-Acrylamide-Boric Acid Solution: Temperature: 12.0°C pH: 4.10
Amount of Sodium Hydroxide Added: 1.5 ml.
Slope of Least Squares Curve Fit: 1.08
Standard Error: 0.74

APPENDIX C

SAMPLE CALCULATIONS FOR ANALYTICAL RESULTS

A. Calculation of Weight Fraction of Monomer

$$\text{weight fraction of monomer} = \frac{\text{(wt. of monomer)}}{\text{(total mixture weight)}}$$

Component	Weight Grams	
Boric Acid	3.0000	
Acrylamide	75.0000	
De-ionized Water	173.6900	(Density .9925 gm/ml)
Toluene	386.4500	(Density .8580 gm/ml)
Span 60	15.0000	
Initiator Solution	21.4700	(Density .8580 gm/ml)
Caustic Solution	3.2550	(Density 1.085 gm/ml)
Total Wt. of Mixture	677.8650	grams

$$\text{weight fraction monomer} = \frac{\text{75.0000 grams of monomer}}{\text{677.8650 grams of emulsion}}$$

wt. frac. monomer = 0.1106

B. Calculation of Monomer Conversion

monomer conversion = fraction of initial monomer converted to polymer

$$\text{monomer conversion, percent} = \frac{\text{wt. of polymer x 100\%}}{\text{wt. of monomer before reaction}}$$

wt. of polymer = wt. of dried polymer and filter paper minus wt. of dry filter paper

wt. of polymer = .7612 grams - .5922 grams (Sample #3 from Run 20 used as example)

wt. of polymer = .1690 grams

wt. of monomer before reaction = (wt. of sample) x (wt. frac. monomer)

wt. of sample = wt. of cup and sample minus wt. of cup (Runs 6-20) = wt. of cup, sample, and 50 ml. wash minus wt. of cup and wash (Runs 1-5)

wt. of sample = 25.7684 grams - 15.4764 grams
= 10.2920 grams

wt. of monomer before reaction = (10.2920 grams) X (0.1106) = 1.1383 grams

$$\text{monomer conversion, \%} = \frac{(\ .1690)\ \text{x}\ 100\%}{1.1383\ \text{grams}}$$

$$= 14.84\%$$

VITA

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Master of Science

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