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I hereby recommend that the thesis prepared under my supervision by Clarence Elmo Albertson

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be accepted as fulfilling this part of the requirements for the degree of Doctor of Philosophy

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THE POLYMERIZATION RATES
OF ALLYL AND ACRYLIC MONOMERS

A dissertation submitted to the

Graduate School
of the University of Cincinnati

in partial fulfillment of the
requirements for the degree of

DOCTOR OF PHILOSOPHY

1949

by

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ACKNOWLEDGMENTS

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INTRODUCTION

This work was fostered by the United States Naval Bureau of Aeronautics through a fellowship granted to the University of Cincinnati for research. The problem was to develop a volatile free organic finishing system for aircraft metals. The volatile solvents used in paints create fire and toxicity hazards (20) especially in the confined space available on ships. The effective weight of the finish could be cut in half if the solvent could be omitted and perhaps the cost could be decreased even though the new media would cost a little more than the solvent. Research was justified on these points.

We proposed that allyl and acrylic compounds might be adapted for use in a volatile free paint. These substances form hard, tough, weather resistant polymers. They make desirable protective coatings when used in paints containing volatile solvents ($\frac{23}{64}$). If a suitable method of applying and hardening them could be developed, we would be able to make some very useful paints which contained no volatile solvents per se.

It is impossible to polymerize or harden these compounds at room temperature with the known polymerization techniques. The mono- and di-functional compounds will slowly harden within a day or so at 60°C. ($^{30}_{2}$) Polyfunctional monomers such as allyl starch ($^{39}_{11}$) do harden at room temperature but much too slowly for our purposes. They are solids or very viscous liquids which could not be readily painted on a surface, but which might be used in conjunction with a more fluid monomer (28).

We chose to investigate the polymerization rates of various allyl and acrylic monomers with known and new catalysts and promoters in order to evaluate the possibility of using these monomers in paints. A study of this type would reveal trends in monomer and catalyst activity, establishing a firm footing upon which the paint problem could be attacked objectively. For instance, it might be found that the more vinyl groups a monomer contains, the more rapidly it polymerizes. We would then endeavor to prepare monomers containing more vinyl groups in order to get materials more desirable for quick hardening paints. Likewise, if it were found that hydrazo-compounds were most active in reducing organic peroxides in monomer solutions, then we would investigate new hydrazo-compounds in a search for even greater activity. Combining these results we would have new compounds which polymerized more readily at lower temperatures and which might be suitable for use in fast drying, nonvolatile paints.

The progress of polymerization reactions has been determined for the most part by observing the following properties of the sample:

1. Chemical unsaturation (66 24)
2. Electrical resistance (3 27)
3. Diamagnetic susceptibility (16)
4. Viscosity (62 18)
5. Freezing point lowering (63)
6. Absorption spectra (19 42)
7. Refractive index (61 60)
8. Optical activity (34)
9. Density (56)
10. Amount of polymer
    a. Distillation of unreacted monomers (33 65)
    b. Precipitation by solvents (58)

Of these properties only unsaturation gives a direct quantitative interpretation of the reaction. All the other properties must be evaluated against known standards before their interpretation can become accurate.

The amount of polymer recovered from a sample gives a semi-quantitative picture because dimer, trimer, and other low molecular weight products are usually lost. It is not as accurate as unsaturation for characterizing the state of a system. Absorption spectra will yield quantitative data when the absorption curves of the monomer and polymer are available. Since a spectrophotometer was not available at the time this work was initiated and unsaturation analysis appeared to be satisfactory, the spectrophotometer was not investigated further. We decided to utilize unsaturation for evaluating the progress of our polymerization reactions.

An analysis for determining allylic unsaturation in monomer-polymer mixtures was found (3). Since this procedure appeared to be satisfactory we decided to use it. No specific methods were found in the literature for determining acrylate unsaturation in monomer-polymer mixtures. In a private communication C. O. Willits, Chief Analyst of the Eastern Regional Research Laboratory of the U. S. Department of Agriculture said that although they had been working with acrylic resins, they had no occasion to determine the unsaturation of the polyacrylates. He suggested that we try quantitative catalytic hydrogenation. After reviewing this method of analysis we decided it was too involved to be useful for our purpose. Therefore, we assumed that the allyl analysis would probably be applicable to acrylates and if not, that a suitable procedure could be easily evolved.

Several monomers were selected to represent the mono-, di- and poly-functional allyl and acrylic compounds. They were:

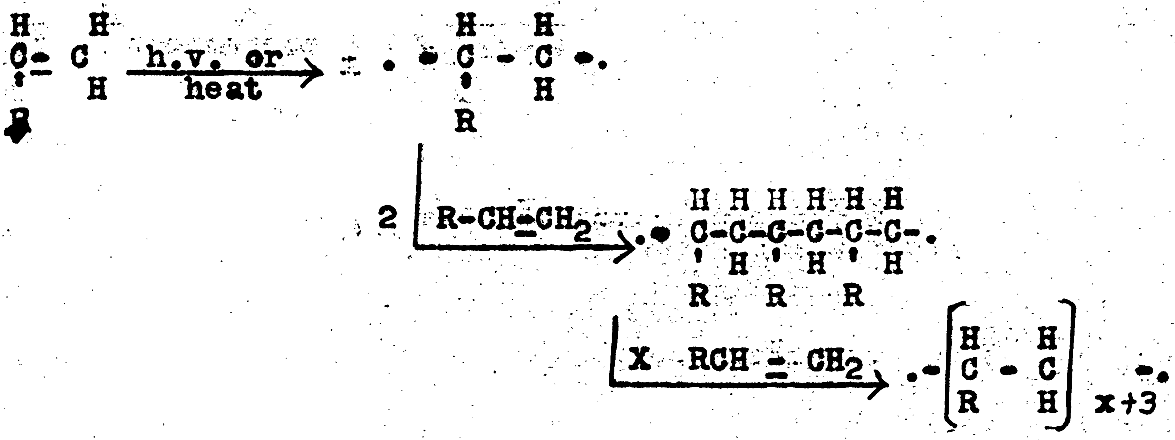
Function	Monomer Allyl	 Acrylic
Mono-	allylbutyrate	isobutylmethacrylate
Di-	diethyleneglycol-bis(allylcarbonate)	glycoldimethacrylate
Tri-	triallylcitrate	

It was felt that this range would be sufficient for the initial investigation and that it could be extended if experimental data indicated the higher poly-functional monomers to be valuable.

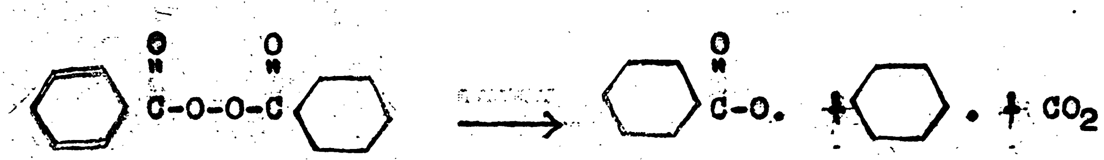
There are two general types of polymerization catalysts (46), namely ionic and free radical. The ionic catalysts are divided into cations and anions. Stannic chloride and aluminum chloride are representative of the cation group. The anionic group which consists of organo-sodium compounds has only begun to be developed recently. Free radicals are complexes of abnormal valency which possess additive properties, but do not carry an electrical charge and are not free ions. They are produced by actinic light, heat and by decomposition of certain chemical substances such as peroxides and diazonium compounds.

The ionic catalysts are generally used to polymerize styrene, coumarin and aliphatic monomers such as isoprene and butadiene. They are usually inactive toward allyl and acrylic monomers. For instance (38), borontrifluoride, a strong ionic catalyst, has been used as a dehydration catalyst for the preparation of allylacrylate with no effect on the double bonds. For this reason we felt that an investigation of this type of catalyst would not be as fruitful as an investigation of the free radical type catalysts.

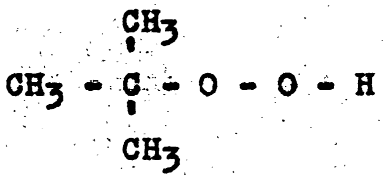
When enough light or heat energy is absorbed by the carbon-carbon double bond it becomes activated and behaves like a free radical, adding to another double bond and initiating the chain reaction.



Similarly, some chemical compounds contain bonds which are more unstable to heat and light than the carbon-carbon bond and may be used as the source of the free radicals which start the polymerization reaction. One class of compounds which form these free radicals is the peroxides. For instance, benzoyl peroxide, which is made from an organic acid, forms free radicals as follows (22):

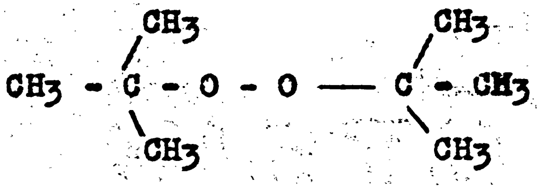


Other types of peroxides are evolved from alcohols, such as t-butyl-hydroperoxide (44)



$$CH_3-\overset{\overset{CH_3}{|}}{\underset{\underset{CH_3}{|}}{C}}-O-O-H$$

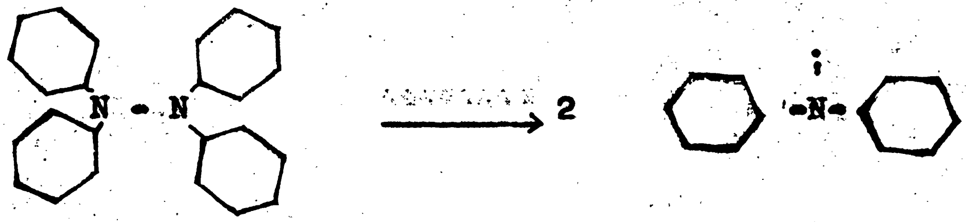
and from ethers, such as di-t- butylperoxide.



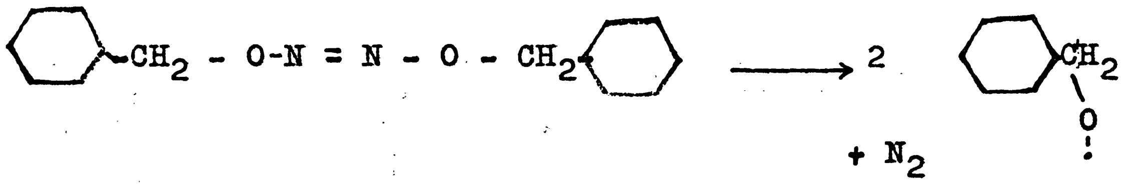
Recently it was found that reducing agents incorporated in emulsion polymerization systems caused the peroxide catalyzed reaction to occur more rapidly (1). It was assumed that the reducing agent attacked the peroxide causing it to decompose faster, thereby creating a greater free radical concentration. Substances such as sodium bisulfite and hydroxylamine hydrochloride were found to be very effective reducing agents in the aqueous solution.

No reports were found of reducing agents suitable for use in bulk polymerization. The inorganic agents would not be soluble in pure monomer, hence would not be applicable. We, therefore, decided to investigate the use of organic reducing agents as bulk polymerization promoters. Hydroquinones, hydrazo-compounds, thio-alcohols and perhaps the bisulfite addition products of long chain aldehydes might be suitable for this purpose. If the rate of bulk polymerization may be increased as much as the rate of emulsion polymerization by the use of reducing agent promoters, then we will have a catalyst suitable for use in non-volatile surface coatings.

Compounds which have nitrogen linkages frequently decompose under moderate conditions to form free radicals. For instance tetraphenylhydrazine reacts as follows:



Benzylhyponitrite (21) has been reported to catalyze the bulk polymerization of methyl methacrylate. It may form free radicals by release of nitrogen:



The rate of polymerization with the hyponitrite was said to be thirty times as fast as with an equal amount of benzoyl peroxide. This is a rough qualitative statement since it was not stated how the amounts were determined or how the polymerization rate was evaluated. Benzylhyponitrite is a solid melting at 49°C. The lower homologues are liquids and are usually very unstable. Perhaps some of the higher homologues may be used safely as polymerization catalysts. Diazomethane and ethylazide have been reported (25) to cause polymerization of butadiene. They might be applicable to allyl and acrylic compounds too. The stable diazonium fluoroborate salts might have pronounced catalytic activity since they would supply both free radicals and an ionic catalyst at the same time. Catalysts of this type will be evaluated in our study.

The role played by air in polymerization is not understood. It is usually reported that polymerization of mono- and di-functional styrene, allyl, vinyl and acrylic monomers is inhibited by air, yet we have found references (14) which indicate air to be necessary in the polymerization of these compounds. It has been found that the polyfunctional allyl monomers are more readily polymerized by air (40) or air and metal driers than by peroxides. It appears that these compounds behave more like the drying oils used in paints than the monofunctional monomers from which they were derived.

Since the effect of air upon polymerization is uncertain we felt it best to exclude air as much as possible. Toward this end we decided to use nitrogen atmospheres when possible and to use vacuum or nitrogen atmospheres when distilling monomer.

The polymerization reaction is very temperamental. It is initiated and sustained by a very low concentration of exceedingly reactive free radicals. If impurities are present in the monomer they may react preferentially with the free radicals and prevent polymerization of the monomer. Traces of these impurities give rise to an "induction period," the time before the polymerization reaction starts. Some very active impurities such as hydroquinone, picric acid, trinitrobenzene and thio-alcohols (48) are added to monomers to prevent polymerization and are known as inhibitors.

They must be incorporated in the active acrylic monomers but may be omitted from allyl monomers which are normally stable for many months at room temperature.

To make our reaction rate data useful we must fix all the variables except the one we are measuring. Toward this end great care must be exercised to insure the purity of monomer and catalyst in order to avoid lengthy induction periods and to allow the reaction to proceed at its greatest rate. The temperature must be constant. We chose 60°C. because the polymerization reactions usually occur at a convenient rate at this temperature. The heat of polymerization of the acrylic esters is about eighteen kilocalories per mole. This means that small reaction vessels must be employed in order to secure good heat transfer, otherwise the temperature of the reactants will be much higher than the surrounding constant temperature bath. Since light is a catalyst it must be kept away from the polymerization reaction. It was felt that these points constituted the variables of the polymerization system.

A few rate studies have been conducted on the allyl and acrylic monomers. The polymerization of allyl acetate catalyzed by benzoyl peroxide and p-chlorobenzoyl peroxide was found to be a first order reaction (4).

This could be calculated from either residual peroxide content or polymer content. These investigators used iodometric analysis for peroxides and the bromide-bromate reagent for determining allylic unsaturation. They found that atmospheric oxygen had relatively little effect on the rate of polymerization. It was also stated that their data was reproducible. The polymerizations were carried out at 80°C. An optically active monomer, d-Sec-butylchloroacrylate, was found to polymerize according to first order kinetics when catalyzed by benzoyl peroxide (35). The reaction was followed by use of the polarimeter.

Based on these few scattered references we felt that the reactions would probably be first order and their rate dependent upon catalyst concentration.

DETERMINATION OF UNSATURATION IN POLYACRYLIC AND POLYALLYL ESTERS

Polyester samples are precipitated in a very finely divided state from a pyridine solution by dropwise addition to aqueous bromide-bromate reagent. The bromine released upon acidification adds quantitatively to the finely dispersed sample and the excess bromine is determined by conventional iodometric analysis.

This analytical procedure was developed primarily to follow the course of bulk polymerization reactions. The total unsaturation of the sample is reported as monomer, for convenience, although it is realized that a small amount of the unsaturation is due to active polymer chains and free radicals.

The determination of unsaturation by halogen addition to solid polymerized acrylic esters has not been recorded in the literature. The difficulty in this type of analysis is partly due to the reticence of halogens to add to a double bond conjugated with an acid group (8) (9), as in the case of acrylic acid, $CH_2=CH-COOH$, and partly to the problem of exposing the unreacted bonds in the polymer to the action of the addition reagent.

No satisfactory method of adding halogen to a solution of the polymer in organic solvents was found. Bromine, whether in anhydrous organic solvents or in aqueous solution, adds very slowly to the polymer. It has been reported by Robertson and his co-workers (51) that hydrogen bromide catalyzes the addition of bromine to acrylic acid in non-aqueous solvents, but the rate was still too slow to make this reagent practical. Wijs solution, prepared according to Kemp and Mueller (26), was found to be ineffective on solutions of the polymer in acetic acid and carbon tetrachloride. An attempt was made to prepare a stable, active bromine reagent by forming bromine salts with pyridine, ethanolamine, and other organic amines in organic solvents, but these reagents proved to be unstable. Sluggish reactions were obtained using bromine-bromate reagent in methanol, with just enough water to keep the bromine in solution.

Aqueous bromide-bromate solution has been shown to be a strong halogenating reagent(37). Mercury, aluminum and nickel salts (12) were reported to promote bromine addition (29) in some of the more difficult cases; however, we have found these salts to be without appreciable effect on acrylic esters. When an attempt was made to form the soluble sodium salts of acrylic esters according to the hydrolytic procedure of Bartlett and Altschull (3) the monomers partially polymerized and gave low analyses. From the work of Evans and Tyrrall (15) it was inferred that bromide-bromate reagent adds quantitatively to emulsions of polyacrylates. On testing various solvents, pyridine was found to have the properties requisite for the production of the polymer in a state of division suitable for this type of analysis: good solubilization of the polyester; water solubility; a density less than one; and stability toward bromine in acid solution. A quantitative saturation of polymer precipitated from pyridine was obtained with aqueous bromide-bromate reagent.

ANALYTICAL PROCEDURE

An accurately weighed sample (0.04 to 0.50 g.) of polyacrylate is dissolved in, and made up with pyridine to a volume of exactly 25 ml. A five milliliter aliquot of the pyridine, solution is added dropwise from a pipet to 20 ml. of a 0.025 N to 0.05 N bromide-bromate solution in a 250 ml. g.s. Erlenmeyer flask. An effort must be made to distribute the drops evenly over the surface of the brominating reagent in order to secure the best possible dispersion of the polymer; see precipitate Figure I. The solution is acidified with 70 ml. of 10% sulfuric acid, stoppered, swirled, and allowed to stand in the dark for 20 minutes at 20° to 25°C.

Ten milliliters of carbon tetrachloride is then added and the flask is shaken in order to dissolve the solid polymer. One milliliter of 30% potassium iodide solution is added and the free iodine liberated by the excess bromine is immediately titrated with 0.05 N sodium thiosulfate solution, a few drops of fresh starch solution being used as an indicator.

The procedure may be used for determining unsaturation of polyallyl esters if the addition of bromine is carried out at 0°C. and the sample allowed to stand for only 10 to 15 minutes. This temperature-time change is necessary to avoid bromine substitution, since the allyl esters are much more active in this respect than are the acrylates.

CALCULATION

The percentage of unsaturation in the polymer sample is calculated as monomer according to the equation:

$$S = \frac{(A - B) \times M \times 50}{W \times 0.2\,E}$$

where S is the percent monomer, A is the equivalents of bromine, B is the equivalents of thiosulfate, M is the molecular weight, W is the sample weight, and E is the number of double bonds in the monomer.

DISCUSSION

This procedure is applicable only to polymers which are soluble in pyridine. This includes all the polymers formed from monofunctional monomers and some of the polymers

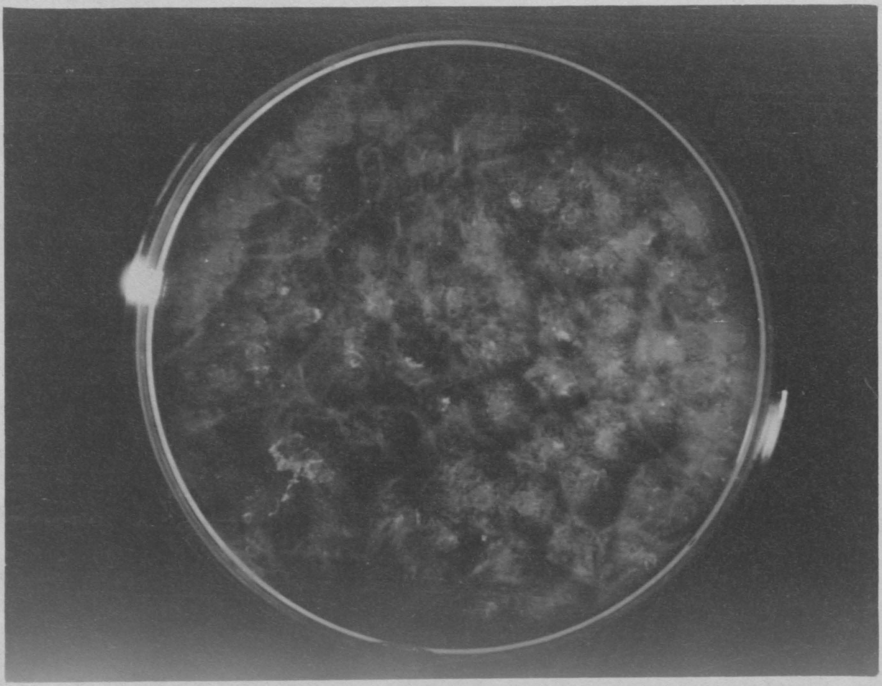


Figure 1

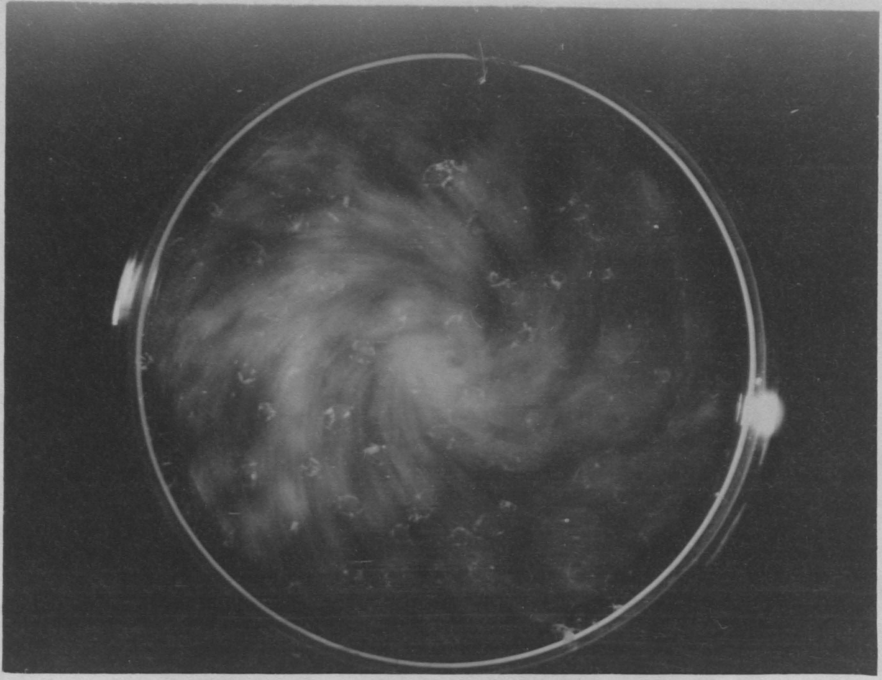


Figure 2

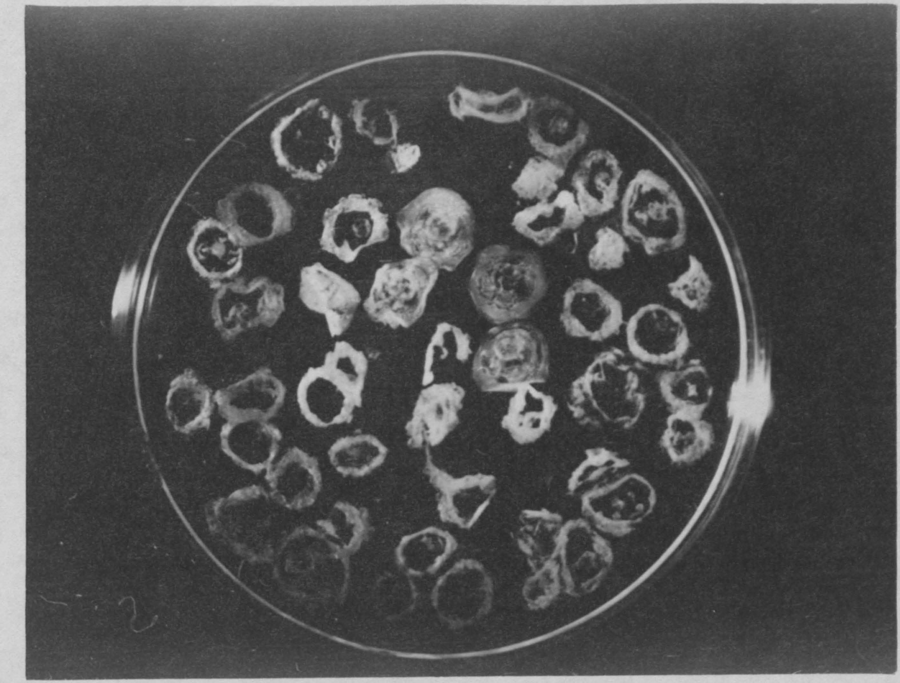


Figure 3

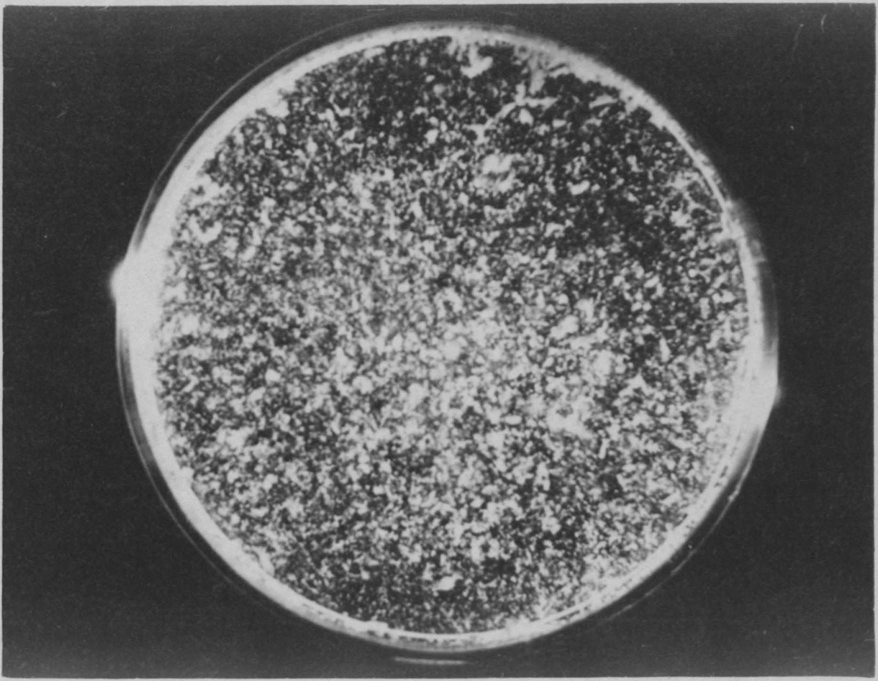


Figure 4

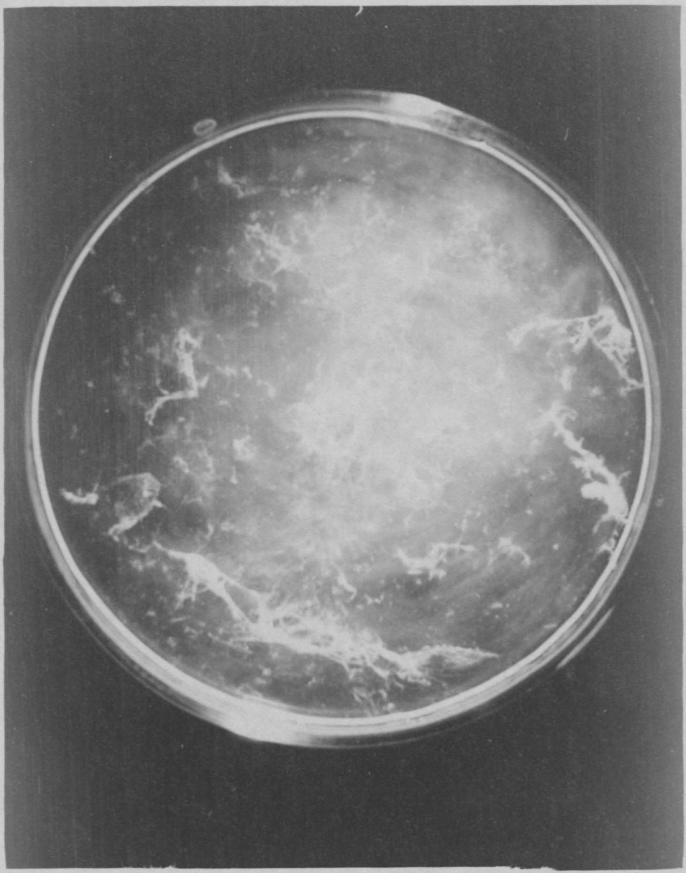


Figure 5

formed from polyfunctional monomers.

The sample weight is critical. The weight of liquid polyester must not exceed about 0.5 g., otherwise insufficient dispersion of the sample will prevent quantitative bromination. The critical weight for solid polyester samples is about 0.04 g. Sample size between these two extremes should be altered proportionally.

Figure I is a photograph of polymer precipitated by adding 5 ml. of pyridine-polymer solution dropwise to 20 ml. of water in a petri dish. Most of the precipitate is so finely divided that it appears as a white mist. Figure 2 shows the contents of the dish shown in Figure I after stirring. It is seen that the white mist-like precipitate does not tend to coalesce, but remains in a finely divided state. These particles were seen to be in violent Brownian movement when observed under the microscope. The small white polymer aggregates seen in Figure I and Figure 2 were found to be very fragile and porous and not to interfere with the analysis. Figure 5 represents the polymer precipitate from a pyridine solution which was too concentrated. The large gummy polymer aggregates which are formed tend to stick together and do not add bromine quantitatively. This condition must be avoided. Figure 3 shows the hard, dense, fragile polymer precipitated from acetic acid solution, and Figure 4 shows the effect of stirring this precipitate. It is obvious that acetic acid is not a suitable solvent for dispersing the polymer.

It is necessary to use about 100% excess bromide-bromate reagent with acrylic esters in order to force the reaction to completion in the allotted time. Samples allowed to stand for one and one half hours did not react with more bromine than those which stood only 20 minutes; hence, it was felt that the addition reaction was complete and that no appreciable substitution occurred. As much as 100% excess bromine may be used with allyl esters. The time and temperature specified must be adhered to closely, however, in order to avoid appreciable substitution of bromine. Monomers containing allyl and acrylate groups in the same molecule, such as allylacrylate, cannot be analyzed by this method because the low temperature and short period of time necessary to control substitution of the allyl group will prevent complete substitution of the acrylate group.

An excess of sulfuric acid must be added to the bromide-bromate sample solution to neutralize the pyridine and liberate the bromine. The amount of acid used should be about 75% to 100% greater than the theoretical amount in order to prevent the pyridine from reacting with an appreciable amount of free bromine.

The polyesters absorb bromine strongly, which makes it necessary to dissolve the polymer in carbon tetrachloride before analyzing the solution for excess bromine. This absorption serves to enhance the addition reaction by concentrating bromine in the polyester.

The accuracy of the analysis varies up to about 2% depending upon the size of the sample, the aliquot portion taken, and the normality of the solutions employed.

ANALYSIS FOR ALLYLIC UNSATURATION

The test procedure evolved for determining unsaturation in allyl compounds was a modification of the version outlined by Bartlett and Altschul (3). This method was not used in the rate studies.

Procedure:

1. About ½g. sample is accurately weighed into a constricted test tube and 5 ml. of 4.3 N NaOH in methanol added and the tube sealed.

   The tube must be kept in an ice bath while sealing to prevent volatilization. A glass bead should be dropped into the throat of the tube to prevent flashing of the vapors while sealing.

2. The tube is shaken to mix thoroughly the contents and then gradually heated to 100°C. in a boiling water bath and held at this temperature for one to two hours. (Long enough to degrade the polymer and make it soluble in water.)
3. Cool tube to ice temperature and transfer the contents quantitatively to a 250 ml. volumetric flask, and fill to the mark with distilled water.
4. A 10 ml. aliquot is pipetted into a 150 ml. G.S. titration flask, 15 ml. of 0.05 N bromide-bromate solution added and 25 ml. of 10% sulfuric acid added. Shake thoroughly and set in an ice bath in the dark for from 5 to 10 minutes.
5. Add ½ ml. of aqueous 30% KI solution and titrate immediately with 0.05 N sodium thiosulfate solution (hypo). Starch

indicator was used.

$$\% \text{ monomer} = \frac{(\text{N Br x ml Br} - \text{N St x ml St})\ \text{mol.wt. x } 100}{0.04 \text{ x wt. sample x } 2\ (\#\text{ double bonds})}$$

CAUTION

Samples must be quickly weighed and sealed if the monomer is volatile.

Sample must be kept in dark and cold to avoid substitution of bromine.

It was shown experimentally that about 100% excess of bromide-bromate reagent was necessary to force the reaction to equilibrium in 5 to 10 minutes. This was contrary to the results reported by Mulliken and Wakeman (37) and was not indicated by Bartlett and Altschul. The following data indicates this clearly:

bis(allyl-carbonate) diethylene-glycol	Ml Br	MlSt	Time of reaction	Remarks
	8 ml.	6.5 ml.	5 min.	The thiosulfate readings vary widely
Sample	8	3.9	10	
	8	2.9	20	
	15	17.75	5	Equilibrium was reached in 5 min.
	15	17.70	10	
	15	17.70	20	Calc. 92.8% monomer

This data also indicates that excessive standing in the dark on ice does not cause appreciable substitution of bromine to occur. Data for isobutylmethacrylate indicated the same conclusion. It was also found that substitution at room temperature is appreciable and causes yields of 104% or higher to be calculated. It is therefore obvious that samples must be kept cold and in the dark to get accurate results.

Considerable flashing was experienced in sealing the sample tubes. It was found that a small glass bead dropped into the neck of the tube prevented the flashing and did not hinder sealing the tube.

A 0.1 ml. of 0.05 N solution represents 1.2% unsaturation, hence it is seen that the data cannot be accurate to more than ± 0.5%. Analyses of several samples of the same material gave results within this degree of error.

ANALYSIS OF MONOMERS

Molecular Refraction

Monomer	Mol. weight Theor.	Mol. weight Rast	Ref. index @ 25°C.	Density at 25°C.	Mol. refraction Theor.	Mol. refraction Exptl.
allylbutyrate	128.17		1.4118	0.8994	35.84	35.35
diethyleneglycol-bis(allylcarbonate)	274.14	318	1.4508	1.1546	65.60	63.79
triallylcitrate	312.30	320	1.4741	1.1318	77.52	77.48
isobutylmethacrylate	142.19		1.4173	0.8849	40.46	40.48
glycoldimethacrylate	198.00		1.4518	1.1010	48.03	48.40

Unsaturation

Monomer	Sample Wt. grams	Ml. Br.	Ml. TS	Titre	% monomer
allylbutyrate	0.5888	15.00	7.77	7.23	98.18
diethyleneglycol-bis(allylcarbonate)	0.7103	15.00	7.33	7.67	91.34
triallylcitrate	0.4269	15.00	8.62	6.38	97.20
isobutylmethacrylate	0.2638	15.00	12.07	2.93	98.50
glycoldimethacrylate	0.3711	15.00	9.20	5.80	96.80

Appearance

Monomer	Source	Appearance
allylbutyrate	lab. synthesis	volatile, colorless, clear, mobile, stringent butyric odor freshly distilled at atm. pressure
diethyleneglycol-bis(allylcarbonate)	Columbia Chem. Div. Pittsburgh Plate Glass Co.	viscosity of machine oil, colorless, clear, almost odorless
triallylcitrate	lab. synthesis	viscosity of machine oil, colorless, clear, almost odorless freshly distilled at 1.5 mm. Hg pressure
isobutylmethacrylate	E.I.Dupont de Nemours Ammonia Dept. W. Va.	volatile, mobile, colorless, clear stringent acrylic odor freshly distilled at 1.5 mm. Hg pressure
glycoldimethacrylate	lab. synthesis	viscosity of glacial acetic acid, clear, colorless, slight acrylic odor freshly distilled at 1.5 mm. Hg pressure

Remarks:

a. The Rast method (5) was used for determining the molecular weight of several of the monomers. It gives a qualitative estimation of molecular weight. Triallylcitrate has a molecular weight of the proper magnitude. Diethyleneglycol bis(allylcarbonate) has a higher molecular weight than it should have.

b. The refractive index was determined with an Abbe refractometer.

c. The density was determined with a 10 ml. pycnometer which was calibrated at 25 °C. with distilled water.

d. Molecular refraction was calculated from the experimental values according to the formula of Lorenz and Lorentz:

$$M = \frac{\text{Mol. wt.}}{\text{density}} \times \frac{(RI)^2 - 1}{(RI)^2 + 2} \qquad \begin{array}{l} M = \text{mol. ref.} \\ RI = \text{ref. index} \end{array}$$

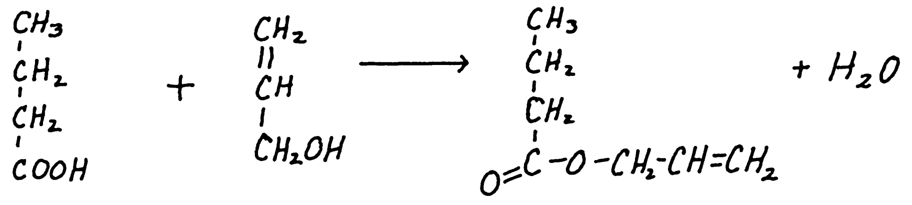
The theoretical molecular refraction was calculated from bond refraction values (13) given by K. G. Denbigh.

e. Unsaturation analyses were carried out according to the standard procedure, using 1 ml. aliquot portions.

Conclusions:

These data indicate that all the monomers, except diethyleneglycol bis(allylcarbonate) are in a fairly pure state. The diethyleneglycol bis(allylcarbonate) was an industrial sample which was specified to be only 94% monomer according to unsaturation analysis. It had polymerized slightly after standing in the laboratory for several months. It was vacuum distilled in the laboratory in an attempt to obtain a purer fraction, However, we were unsuccessful. Our vacuum fractionating column did not have enough plates to effect the desired separation. Since the material polymerized satisfactorily in subsequent experiments no further attempts were made to purify it.

SYNTHESIS OF ALLYLBUTYRATE



$$CH_3-CH_2-CH_2-COOH + CH_2=CH-CH_2OH \longrightarrow CH_3-CH_2-CH_2-C(=O)-O-CH_2-CH=CH_2 + H_2O$$

Mol. wt.	88.10	58.08	128.17	18
Exptl. quantity	220g.	218g.	320g.	45g.
Excess	0	50%	theory	theory
Mols	2.5	3.75	2.5	2.5

Esterification catalyst, 5g. p-toluenesulfonic acid

Polymerization inhibitor, 5g. quinone

Azeotrope former, 100 ml. benzene

Procedure:

1. The reactants were placed in a flask fitted with a Stark and Dean tube.
2. Heat was applied by gradually raising the oil bath temperature from 115° to 130°C. to keep the benzene-water-allyl alcohol azeotrope distilling at a reasonable rate. The water was separated from the azeotrope in the Stark and Dean tube and the allyl alcohol-benzene solution returned to the reactor.
    a. The azeotrope had a boiling point of 68.2°C.
    b. About 10 hours was necessary to complete the esterification.
3. Excess benzene and allyl alcohol were distilled from the product at atmospheric pressure by gradually raising the oil

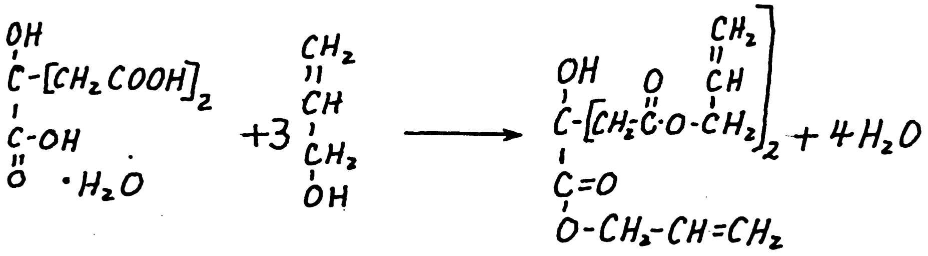
bath temperature to 150°C.

4. A 2 foot Vigreaux column was fitted on the reactor and the fraction boiling from 140° to 145°C. at 1 atmosphere pressure was taken as allylbutyrate. The yield was 246 g. or about 76.8% of theory.

Remarks:

This was a simple, straightforward esterification. No difficulties were experienced. The only precaution necessary was to avoid contact or breathing of the toxic allyl alcohol or its vapor.

SYNTHESIS OF
TRIALLYLCITRATE



Mol. wt.	210.13	58.08	312.3	18.01
Exptl. wt.	210.g.	232.3g.	312.3g.	72.04g.
Exptl. mol.	1	4	1	4

azeotrope former	200 ml. benzene
esterification catalyst	5g. p-toluenesulfonic acid
polymerization inhibitor	10g. copper turnings

This reaction was carried out according to directions given us by John Bellamy (5).

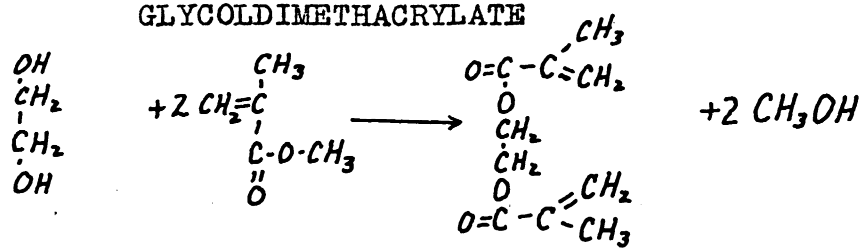
Outline of synthesis:

1. The esterification required 18 to 24 hours. A Stark and Dean tube was used to remove water.
2. The reaction product was washed thoroughly with water to remove p-toluenesulfonic acid and allyl alcohol. If this was not done excessive decomposition would occur in the final distillation.
3. The benzene and water were removed by distillation at 1.5 cm. Hg pressure (water aspirator). Careful, even heating had to be done, otherwise the reactants would undergo a violent, almost explosive, exothermic polymerization.
4. The product was vacuum distilled at 1.5 to 2.0 mm. Hg pressure. The fraction boiling at 160° to 170°C. was found to be triallylcitrate. A yield of 231 g. or 74%

was realized.

Three runs were made during the course of this research with a total production of 484 g. of triallylcitrate.

SYNTHESIS OF GLYCOLDIMETHACRYLATE



Mol. wt.	62.07	100.11	198.23	32.03
Exptl. wt.	62.07	500.55	198.23	64.06
Exptl. mol.	1	5	1	2

alcoholysis catalyst	1 ml. sulfuric acid
azeotrope former	200 ml. 65-70°C. ligroin
polymerization inhibitor	25 g. hydroquinone

This synthesis is an adaptation of a method (49 for preparing monoacrylic esters. Henry Steinmann stated that he had also prepared glycoldimethacrylate (59), by a slightly different procedure.

Procedure:

1. The alcoholysis reaction was conducted in a flask equipped with mechanical agitation. This was necessary because the glycol is not miscible with either the ligroin or the methylmethacrylate. The ternary azeotrope, methanol-ligroin-methylmethacrylate was distilled from the reaction flask as it formed. A water bath temperature of about 90 to 95°C. was necessary in this step. The total reaction time was about 36 to 40 hours.
2. The product was washed thoroughly with water to remove

the sulfuric acid and any unreacted glycol. This was necessary because glycol has almost the same boiling point as its dimethacrylic ester. Since the hydroquinone was also washed out, it was necessary to add another 5 g. of hydroquinone after washing was completed.

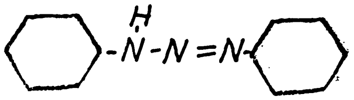
3. Unreacted methylmethacrylate and residual ligroin were removed by distillation at 1.5 cm. Hg pressure (water aspirator).
4. The product distilled at 83°C. when under a pressure of 1.5-2mm. Hg. The yield was 167 g. or about 84%.

A water bath was sufficient for all the heating operations. It was felt that poorer yields would have resulted if temperatures much over 100°C. had been employed.

Three runs were made during the course of this research with a total production of 497 g. glycoldimethacrylate.

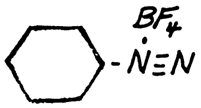
PREPARATION AND PROPERTIES OF PROMOTERS

Diazoaminobenzene (1,3-diphenyltriazene)



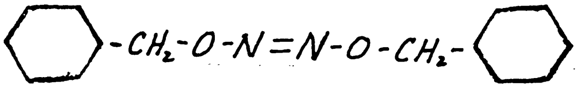
Diazoaminobenzene was prepared accoding to the procedure in Vol. II of Organic Synthesis (6). Only one fifth of the specified amounts were used. About 27 g. of product, which had a melting range of 95.7° to 96.2°C., was recovered in the second crystallization from ligroin in the form of bright golden-yellow plates.

Benzenediazoniumfluoroborate



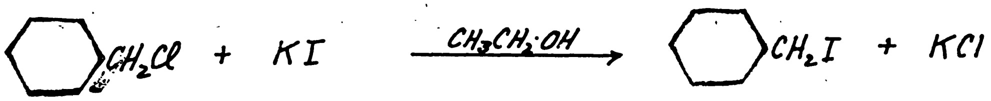
Benzenediazoniumfluoroborate was prepared according to the procedure in Vol. II of Organic Synthesis (7). Only one twentieth of the specified amounts were used, yielding 74 g. of a light yellowish-brown granular solid.

Benzylhyponitrite



This synthesis was divided into four parts, the preparation of benzyliodide, sodium hyponitrite, silver hyponitrite and benzylhyponitrite.

Benzyliodide was prepared by a metathesis reaction (45).



Mol. wt.	126.58	166.02		218.05	75.56
Exptl. wt.	12.6 g.	35 g.	150 ml.	21.8 g.	15 g.

The reactants were refluxed for 6 hours. The insoluble potassium salts were filtered from the solution and the alcohol boiled off at 1.5 cm. Hg. pressure. About 15 ml. of ligroin was added and the remaining potassium salts were filtered from the solution. The ligroin was distilled from the product at 1.5 cm. Hg. pressure. The product was crystallized at about 0°C. and the mother liquor filtered from it in a cooled sintered gooch crucible. A yield of 18 g. of light yellow benzyliodide crystals, m.p. 23.5° to 24°C., was recovered.

Sodium hyponitrite solution was prepared according to Mellor (36).

$$2NaNO_2 + 4Na[Hg] + 2H_2O \xrightarrow[H_2O]{Cold} Na_2N_2O_2 + 4NaOH$$

Mol. wt.	69.01	22.99	18.01		106.01	40.01
Exptl. wt.	13.7g.	12.0g.		200g.	10.5g.	20.8g.

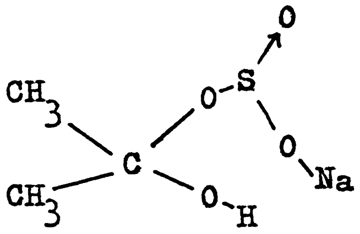
The sodium amalgam was added slowly to the sodium nitrite solution, keeping the temperature of the reactants below 5°C. and agitating vigorously with a mechanical stirrer to insure good contact. About 3 g. of yellow mercuric oxide powder was then agitated with the product for about 15 minutes to destroy any hydroxylamine which might have formed.

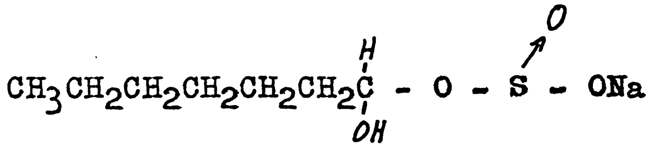
The solution was decanted from the mercury and filtered to remove mercuric oxide.

Silver hyponitrite was prepared according to Partington and Shah (43). The sodium hyponitrite solution was made neutral to phenolphthalein with acetic acid. Silver hyponitrite was precipitated by treating the solution with silver nitrate, exactly as directed, and was recovered and dried over P_2O_5.

Benzylhyponitrite was prepared by reacting dry silver hyponitrite with benzyliodide in anhydrous ether at 0°C. (43) exactly according to the procedure given by Partington and Shah. About 12.7 g. of fine yellow powdered benzylhyponitrite was recovered which had a melting range of 48.3 to 48.8°C.

Bisulfite addition products





$CH_3CH_2CH_2CH_2CH_2CH_2\overset{H}{\underset{OH}{C}} - O - \overset{O}{\overset{\nearrow}{S}} - ONa$

The bisulfite addition products of acetone and heptaldehyde were prepared by reacting the organic compounds with a saturated solution of sodium bisulfite and recovering the precipitate on a small buchner funnel (17). The acetone product was a hard white crystalline material. The heptaldehyde salt was a soap like, yellowish-white material.

Hydrazobenzene

The hydrazobenzene from the stock room appeared to be fairly pure. It was crystallized once from ligroin to yield yellowish-orange crystals which melted from 129.7° to 130.2°C.

Tetrachlorohydroquinone

Tetrachlorohydroquinone, purchased from Eastman Kodak Co., was crystallized from acetic acid to yield light yellow crystals melting from 231.6° to 232.1°C.

PEROXIDE ANALYSIS

Analysis:

Peroxide	Mol.wt.	Sample wt.	Ml.TS	% Peroxide
Benzoylperoxide	242.08	0.0497	8.18	99.66
1-hydroxycyclohexyl-hydroperoxide-1	132.15	0.0683	20.45	98.91
ditertiarybutyldi-perphthalate	310.34	0.0441	8.98	79.06
purified ditertiary-butyldiperphthalate	310.34	0.0526	13.42	99.04

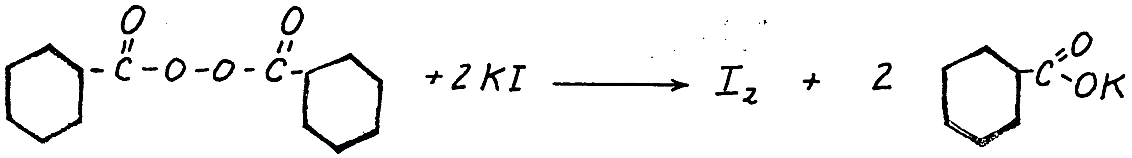
Remarks:

The benzoylperoxide and 1-hydroxycyclohexylhydroperoxide-1 were used in the polymerization experiments without further purification.

Analysis showed that the ditertiarybutyldiperphthalate was about 20% low in peroxide content. This peroxide was crystallized four times from methanol to yield the purified product which tested 99.04% peroxide.

Iodometric analysis was used to determine peroxide according to the procedure of K. Nozaki (41).

The organic peroxide in acetic acid solution was reacted with potassium iodide and the iodine, which was set free, was titrated with standard 0.05N sodium thiosulfate. This reaction is illustrated with benzoylperoxide:



Peroxide = 2 equivalents of iodine.

Oxygen from the air was excluded from the titration flasks because it causes a reoccurring end point.

$$\% \text{ Peroxide} = \frac{\text{Ml.TS} \times \text{Mol. wt.} \times 0.0025}{\text{Sample weight} \times \#O_2}$$

Ml.TS = Milli-liters of thiosulfate

Mol.wt. = Molecular weight of organic peroxide

$\# O_2$ = Number peroxide groups per molecule

GENERAL PROCEDURE OF POLYMERIZATION AND ANALYSIS

A six inch test tube was scrubbed and rinsed with distilled water and acetone. It was then allowed to dry inverted in a test tube rack. A 50 ml. distillation flask, which was to be used as the receiver for distilled monomer, was cleaned in the same manner. Both pieces were heated to redness in a bunsen flame just prior to use, to drive out the remaining moisture and impurities.

The monomer was placed in a distillation apparatus and distilled under the conditions:

Monomer	Dist. temp.	Dist. press. Hg
allylbutyrate	143°-145°C.	1 atm.
diethyleneglycol bis(allylcarbonate)	Not Distilled	
triallylcitrate	160°-170°C.	1.5 - 2.0 m.m.
isobutylmethacrylate	55°- 60°C.	1.5 cm.
glycoldimethacrylate	83°C.	1.5 - 2.0 m.m.

A 10 to 15 ml. foreshot fraction was taken to wash out the apparatus and to get the feel of the equipment so that distillation of the main fraction could be carried out correctly. The foreshot receiver was quickly replaced by the freshly cleaned main fraction receiver and distillation continued until about 25 to 30 ml. of distillate was recovered.

The test tube which had been previously cleaned was tared on the balance and the desired monomer weight added to the balance pan. A slight excess of the distilled monomer was poured into the test tube and then reduced to the correct value by withdrawing small amounts of the monomer with a glass tube, which had previously been cleaned and fired. The test tube was then stoppered with a tin foil covered cork and set aside.

A weighing dish was tared on the balance and the desired catalyst or promoter weight added to the balance pan. The correct amount of catalyst or promoter was then transferred to the dish with a small spatula.

The catalyst and promoter were added to the monomer. The test tube was then rocked to facilitate their solution and placed in the constant temperature bath at 60°C. ± 0.3°C. It was then withdrawn at about one minute intervals and rocked gently for a moment until the solution was homogeneous. This operation required about five minutes. A sample was then taken for analysis and designated, zero time.

In a few cases the reactants were dissolved at room temperature and the homogeneous solution was then divided and sealed in 10 to 15 glass tubes, each 6 mm. in diameter and about six inches long. The glass tubes had previously been washed with water, rinsed with acetone and fired to a red heat before filling.

An indicator run was made of each monomer-catalyst combination. After the first sample was taken the reaction was allowed to proceed for a week or until a jel formed. If no jel formed a sample was taken to determine the degree of polymerization. Based upon this indication another run was made and samples taken at appropriate intervals during the reaction. The kinetic interpretation and reaction rates were then derived from the data made during the second run.

Sampling was done as simply and quickly as possible. A 25 ml. volumetric flask was tared on the balance, and then carried to the thermostat bath. The bath was opened and a sample transferred to the volumetric flask from the reaction tube with a pipet. The reactor was then stoppered and the bath lid replaced.

The volumetric flask was weighed and the sample weight determined by difference. The sample was diluted to 25 ml. with pyridine.

A ml. or a 5 ml. aliquot portion of the pyridine-polymer solution was taken for analysis. See appendix for a detailed discussion of the analytical procedure.

Exactly 0.05 N titrants were used in all experiments. The solutions were made up slightly more concentrated than 0.05 N and then standardized against iodine and corrected to exactly 0.05 N by addition of distilled water.

The unsaturation of the polymer samples was expressed as monomer. The equations used were:

Allylbutyrate

$$\% M = \frac{\text{Titre} \times 0.3200}{S \times F}$$

Diethyleneglycol bis(allylcarbonate)

$$\% M = \frac{\text{Titre} \times 0.3427}{S \times F}$$

Triallylcitrate

$$\% M = \frac{\text{Titre} \times 0.2602}{S \times F}$$

Isobutylmethacrylate

$$\% M = \frac{\text{Titre} \times 0.3551}{S \times F}$$

Glycoldimethacrylate

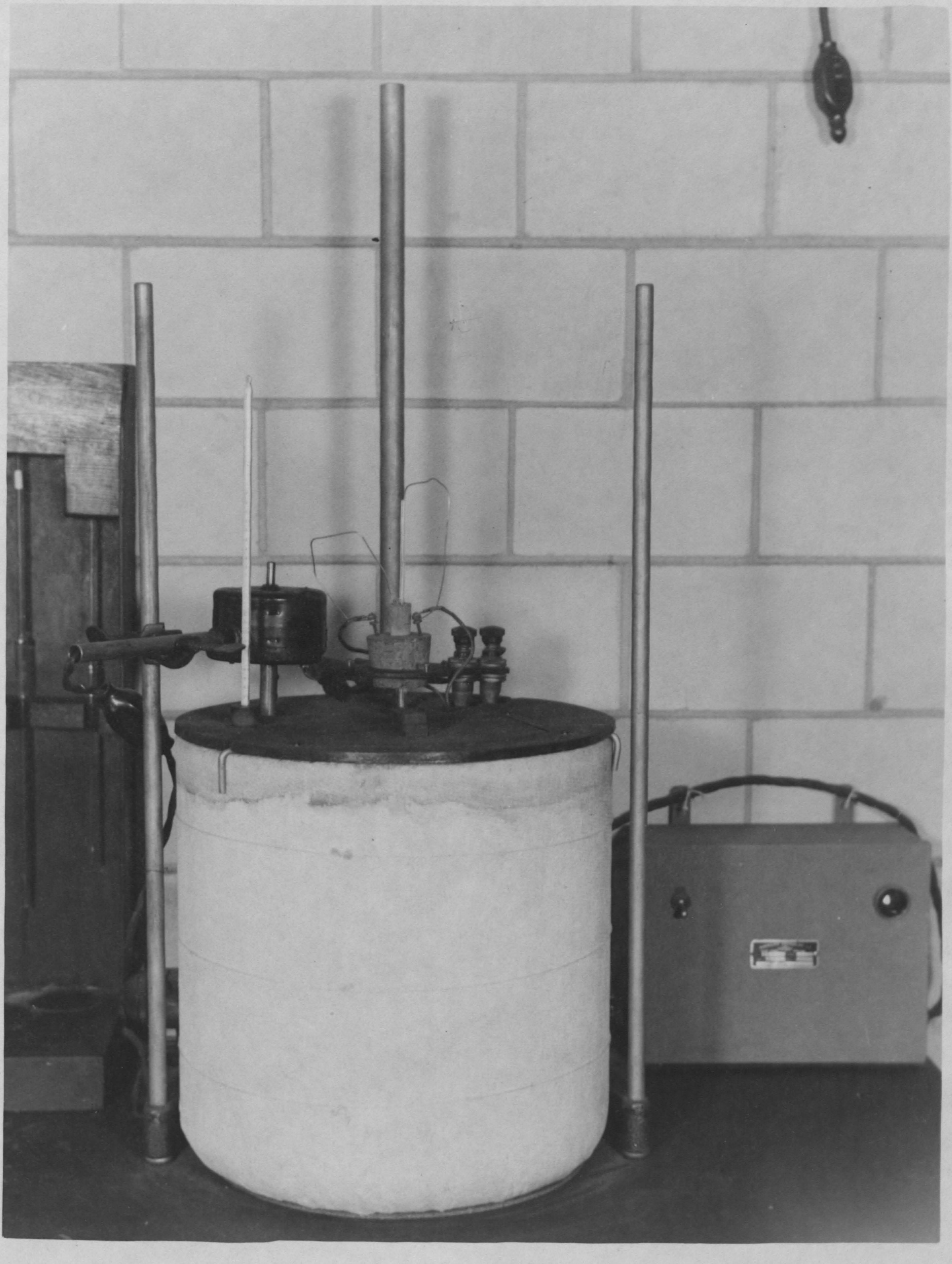
$$\% M = \frac{\text{Titre} \times 0.2477}{S \times F}$$

S = sample weight

F = aliquot factor
    1 ml. aliquot F = 0.04
    5 ml. aliquot F = 0.20

% M = percent monomer

Titre = milli-liters of 0.05 N solution necessary to titrate the sample



CONSTANT TEMPERATURE BATH

The constant temperature bath is pictured on the opposite page. It consisted of a standard set of equipment with the exception that the faulty bimetallic regulator furnished with the apparatus was replaced with a mercury contact, chloroform vapor thermostat. Chloroform boils at about 60°C. By using it to control the mercury movement the temperature of the bath could be maintained at 60°C. ± 0.2°C.

A masonite cover was provided to keep out light and dirt. A coat of black asphalt paint prevented it from absorbing water and being warped out of shape. The glass jar was covered with asbestos paper to insulate it and keep out the light.

The only precautions necessary in operating this apparatus were to oil the agitator motor and to clean the mercury contacts of the thermoregulator about every two months.

POLYMERIZATION REACTIONS

The following abbreviations were used in these experiments:

Ml.Br = milli-liters of 0.05 N bromide-bromate reagent.
Ml.TS = milli-liters of 0.05 N sodium thiosulfate reagent.
Titre = Ml.Br - Ml.TS
% M = % monomer, equivalent to the unsaturation found in the sample.
Log %M = Common logarithm of % M.
Aliquot, ml. = the number of ml. used for analysis.

The rate of each reaction was calculated, assuming the reactions to be first order. The rate was written on the graph accompanying each experiment.

$$K = \frac{2.303}{t} \log \frac{C_o}{C}$$

K = specific reaction rate per hour
C_o = concentration of monomer at zero time
C = concentration of monomer at time t
t = hours after reaction was started when C was recorded

Each percentage graphed was circumscribed by a circle representing its value ± 1%. It was felt that this represented a fair approximation of the data since the accuracy of the analysis varied from about ± 0.6% to ± 2%. The data are graphed to different scales depending upon the percentage range. The ± 1% circles are a quick visual aid for realizing this range and correlating the different graphs.

The mol fraction values for the reactants were selected to provide uniformity of experimental data. In each case 1.5 molecules of catalyst or a whole number multiple thereof was provided per 100 molecules of monomer and 0.5 molecule of promoter per 100 molecules of monomer. The values are derived:

$$\text{mol fraction} = \frac{\text{mols A}}{\text{mols A} + \text{mols B} + \ldots}$$

Catalyst

1.5 catalyst/100 monomer

$$\frac{0.015}{1 + 0.015} = 0.01477 \text{ mol fraction catalyst}$$

3/100 $$\frac{0.03}{1 + 0.03} = 0.0291$$

1.5/100 with 0.5/100 promoter

$$\frac{0.015}{0.015 + 1 + 0.005} = 0.0147$$

1.5/100 with 1/100 promoter

$$\frac{0.015}{0.015 + 1 + 0.01} = 0.0146$$

Promoter

0.5/100 promoter with 1.5/100 catalyst

$$\frac{0.005}{0.005 + 1 + 0.015} = 0.0049 \text{ mol fraction promoter}$$

1/100 promoter with 1.5/100 catalyst

$$\frac{0.01}{0.01 + 1 + 0.015} = 0.0097$$

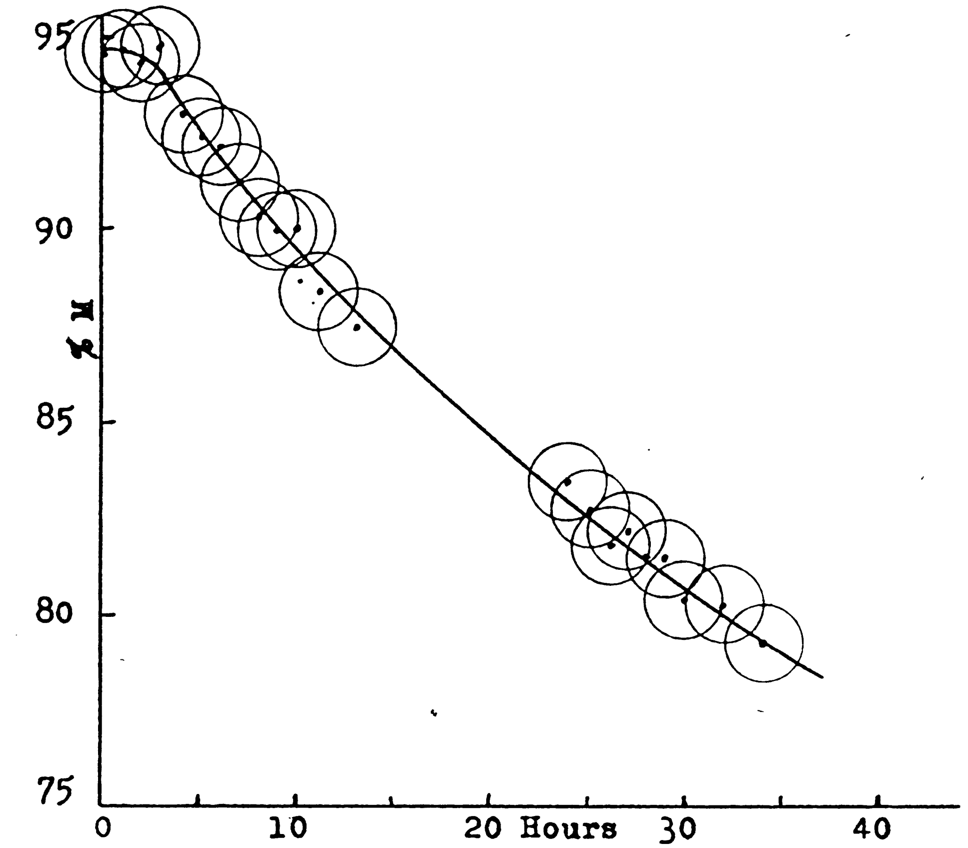
POLYMERIZATION: (a) THERMAL

The five monomers were freshly distilled, poured into six inch test tubes and stoppered with tin foil covered corks. The tubes were allowed to stand for one week at 60°C. Analyses before and after this treatment were as follows:

Time weeks	Sample weight grams	Ml.Br	Ml.TS	Titre	% M	Aliquot ml.
Allylbutyrate						
0	0.3453	15.00	10.73	4.27	98.8	1
1	0.4082	15.00	9.95	5.05	98.9	1
Diethyleneglycolbisallylcarbonate						
0	0.3723	15.00	10.98	4.02	92.5	1
1	0.3149	15.00	11.63	3.37	91.8	1
Triallylcitrate						
0	0.2531	15.00	11.20	3.80	97.6	1
1	0.1357	15.00	12.98	2.02	97.0	1
Isobutylmethacrylate						
0	0.2390	15.00	12.36	2.64	98.1	1
1	0.2651	15.00	12.13	2.87	96.2	1
Glycoldimethacrylate						
0	0.2978	15.00	10.32	4.68	97.3	1
1	0.2143	15.00	11.66	3.34	96.1	1

Remarks:

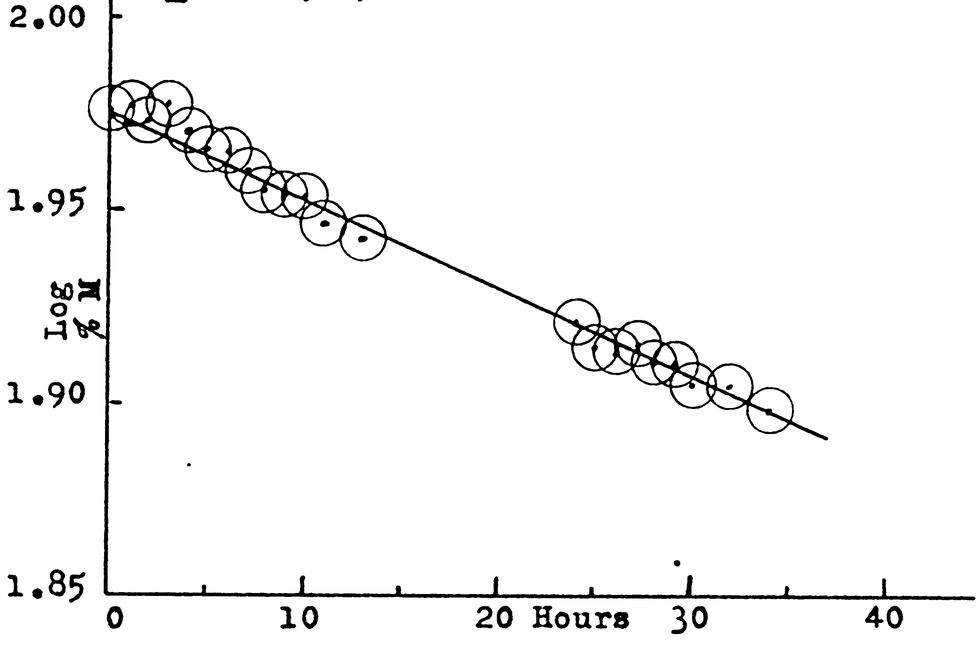
No appreciable polymerization occurred in any of these runs. The data is consistent within the experimental error.



Allylbutyrate

0.01477 m.f. benzoylperoxide

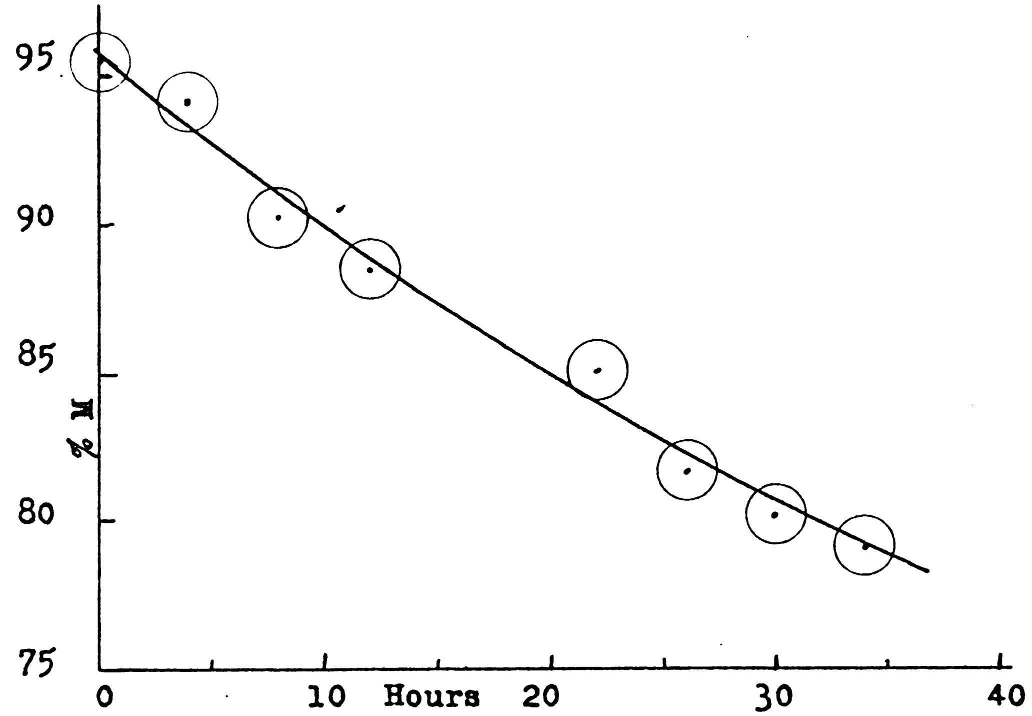
K = 0.00528/hr.



POLYMERIZATION: (1) Allylbutyrate with 0.01477 mol fraction of benzoylperoxide at 60°C.

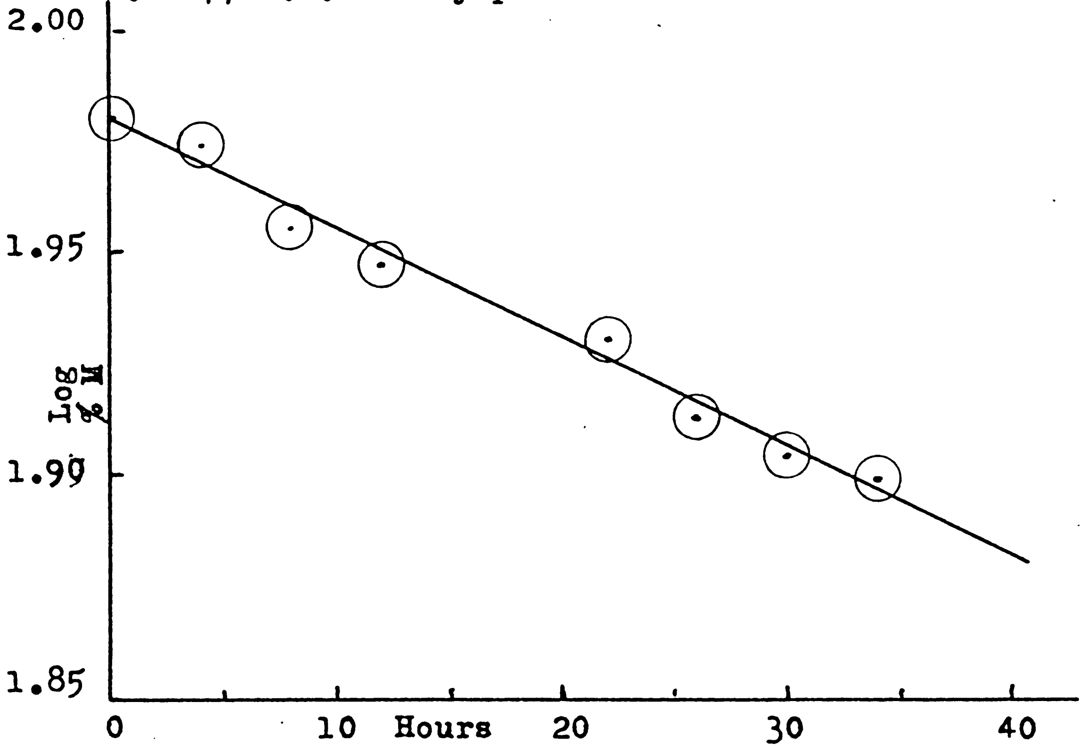
22.187 g. monomer
0.629 g. catalyst

Time hours	Sample weight grams	Ml.Br	Ml.TS	Titre	% M	Log % M	Remarks
0	0.5754	15.00	8.20	6.80	94.5	1.975	Clear colorless solution
1	0.5594	15.00	8.39	6.61	94.6	1.976	
2	0.5931	15.00	8.01	6.99	94.3	1.974	1 ml. aliquotes used of all samples.
3	0.5735	15.00	8.20	6.80	94.8	1.977	
4	0.5720	15.00	8.33	6.67	93.0	1.968	Reactor was not fired.
5	0.5415	15.00	8.75	6.25	92.3	1.965	
6	0.5772	15.00	8.35	6.65	92.1	1.964	No change of sample properties is apparent.
7	0.5452	15.00	8.79	6.21	91.2	1.960	
8	0.5765	15.00	8.47	6.53	90.3	1.955	
9	0.5382	15.00	8.97	5.03	90.04	1.954	
10	0.5010	15.00	9.38	5.62	90.0	1.954	
11	0.5486	15.00	8.97	6.03	88.3	1.946	
13	0.5330	15.00	9.17	5.83	87.5	1.942	
24	0.5852	15.00	8.87	6.13	83.4	1.921	
25	0.5880	15.00	8.92	6.08	82.7	1.917	
26	0.5315	15.00	9.57	5.43	81.8	1.913	
27	0.5546	15.00	9.30	5.70	82.2	1.915	
28	0.5653	15.00	9.33	5.67	81.6	1.911	
29	0.5674	15.00	9.22	5.78	81.3	1.910	
30	0.5494	15.00	9.47	5.53	80.3	1.905	
32	0.5554	15.00	9.42	5.58	80.2	1.904	
34	0.5339	15.00	9.72	5.28	79.2	1.898	



Allylbutyrate K = 0.00561

0.01477 m.f. benzoylperoxide



POLYMERIZATION: (1-a) Allylbutyrate with 0.01477 mol fraction of benzoylperoxide at 60°C.

12.809 g. monomer   0.3631 g. catalyst

Time hours	Sample weight grams	Ml.Br.	Ml.TS	Titre	% M	Log % M	Aliquot ml.
0	0.4483	15.00	9.66	5.34	95.5	1.980	1
4	0.4402	15.00	9.83	5.17	94.2	1.974	1
8	0.4190	15.00	10.28	4.72	90.2	1.955	1
12	0.3927	15.00	10.66	4.34	88.5	1.947	1
22	0.4084	15.00	10.66	4.34	85.1	1.930	1
26	0.2783	15.00	12.16	2.84	81.7	1.912	1
30	0.2322	15.00	12.68	2.32	80.2	1.904	1
34	0.2584	15.00	12.45	2.55	79.1	1.898	1

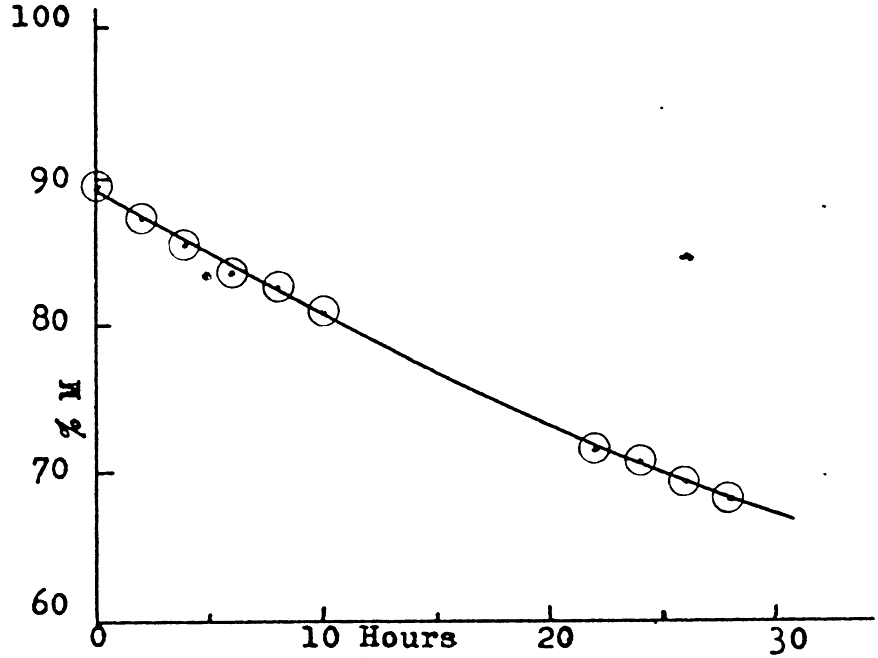
Remarks:

a. Reactants seemed to be a little more viscous after 34 hours.

b. The reactants formed a clear colorless solution throughout the run.

c. The polymer-pyridine solution was not colored.

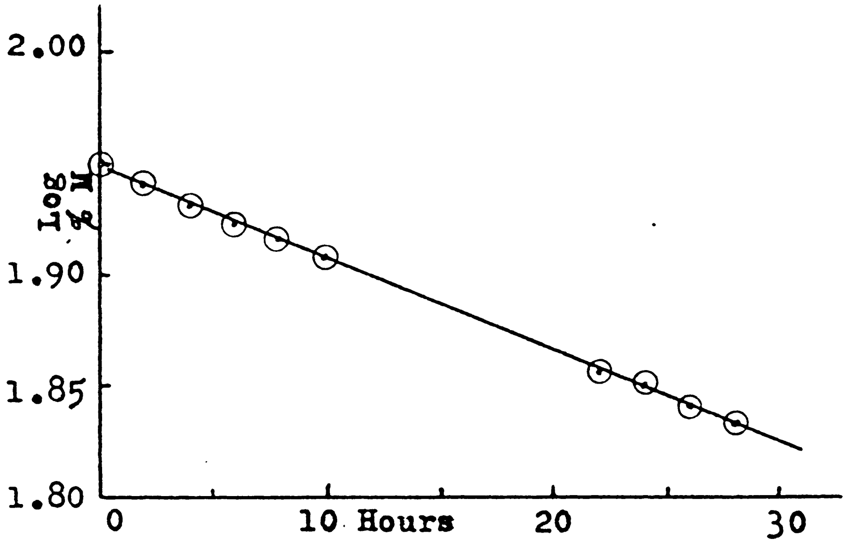
d. The reaction tube and distillation receiver were fired to remove any traces of water or impurities.



Diethyleneglycol bis(allylcarbonate)

0.01477 m.f. benzoylperoxide

K = 0.00948/hr.



POLYMERIZATION: (2) Diethyleneglycol bis(allylcarbonate) with 0.01477 mol fraction of benzoylperoxide at 60°C.

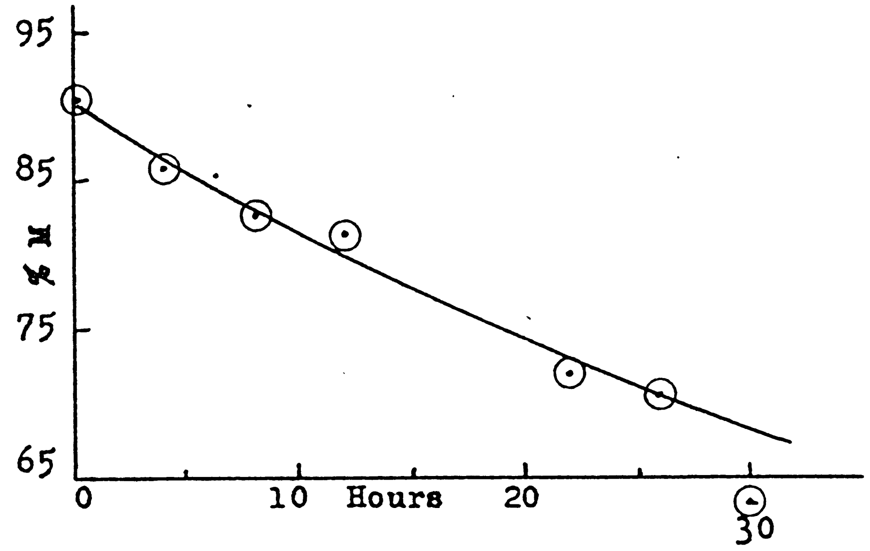
27.08 g. monomer 0.3585 g. catalyst

Time hours	Sample weight grams	Ml.Br	Ml.TS	Titre	% M	Log % M	Aliquot ml.
0	0.6133	15.00	8.62	6.38	89.2	1.9504	1
2	0.5950	15.00	8.97	6.03	87.1	1.940	1
4	0.5963	15.00	9.05	5.95	85.5	1.932	1
6	0.5235	15.00	9.90	5.10	83.5	1.922	1
8	0.5903	15.00	9.83	5.17	82.4	1.916	1
10	0.6210	15.00	9.13	5.87	80.8	1.907	1
22	0.6325	15.00	9.72	5.28	71.6	1.855	1
24	0.6117	15.00	9.92	5.08	70.9	1.850	1
26	0.6075	15.00	10.08	4.92	69.4	1.841	1
28	0.6290	15.00	10.00	5.00	68.1	1.833	1
48	Clear, colorless, rubbery jel; fractures easily.						

Remarks:

a. The sample was a heavy syrup after ten hours and a fragile jel after twenty-two hours.

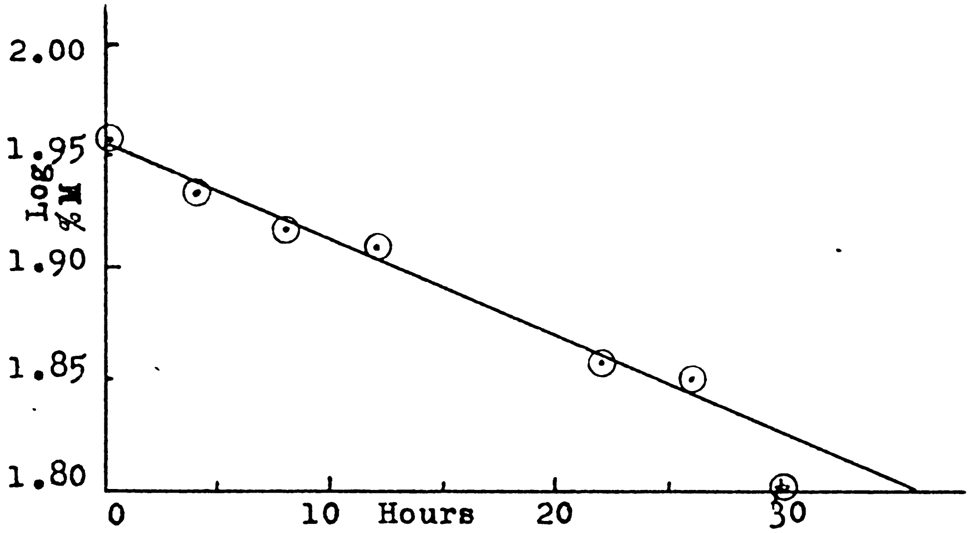
b. After standing for about a year in the air the polymer had turned a light yellow color.



Diethyleneglycol bis(allylcarbonate)

0.01477 m.f. benzoylperoxide

K = 0.00983



POLYMERIZATION: (2-a) Diethyleneglycol bis(allylcarbonate) with 0.01477 mol fraction of benzoylperoxide at 60°C.

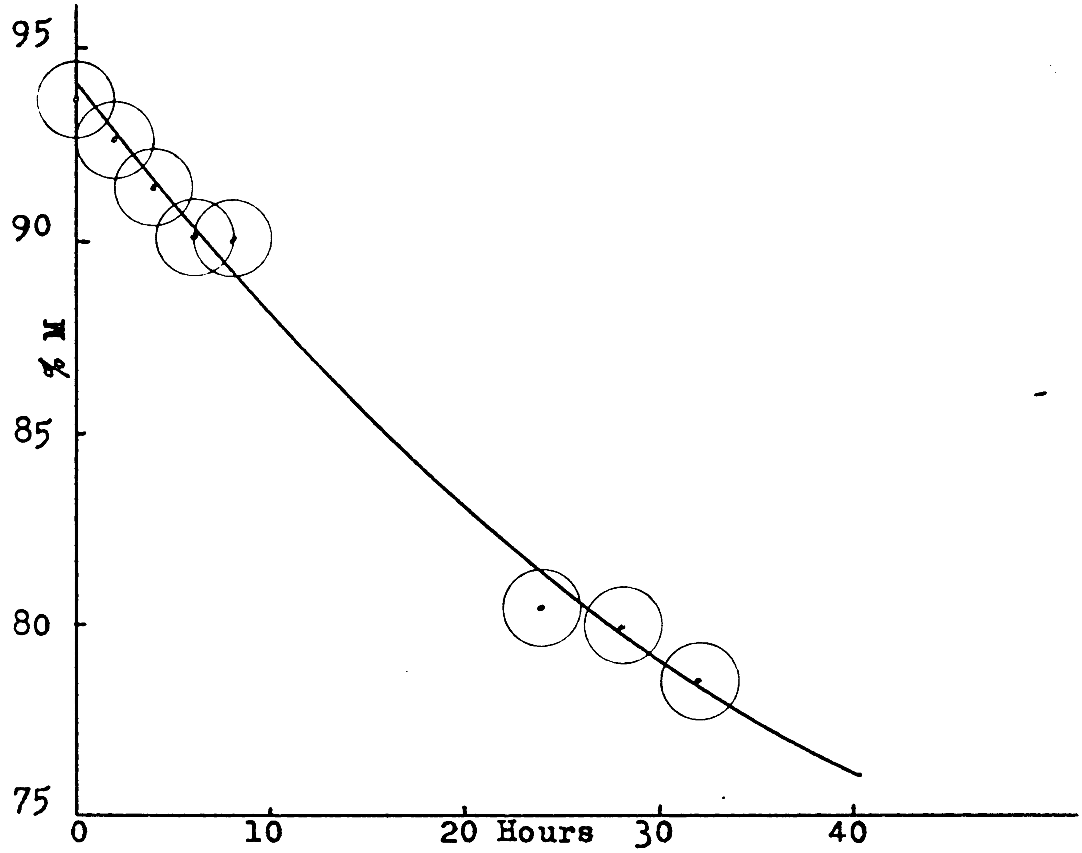
13.707 g. monomer 0.1815 g. catalyst

Time hours	Sample weight grams	Ml.Br.	Ml.TS	Titre	% M	Log % M	Aliquot ml.
0	0.2241	15.00	12.63	2.37	90.4	1.956	1
4	0.2688	15.00	12.31	2.69	85.9	1.934	1
8	0.2134	15.00	12.94	2.06	82.6	1.917	1
12	0.1894	15.00	6.00	9.00	81.3	1.910	5
22	0.2494	15.00	12.91	2.09	72.1	1.858	1
26	0.2562	15.00	12.88	2.12	70.8	1.850	1
30	0.1175	15.00	10.66	4.34	63.4	1.802	5
48	A fragile, clear, colorless, rubbery jel was produced.						

Remarks:

a. This run was made to check the reproducibility of these experiments. The agreement with the previous experiment is good.

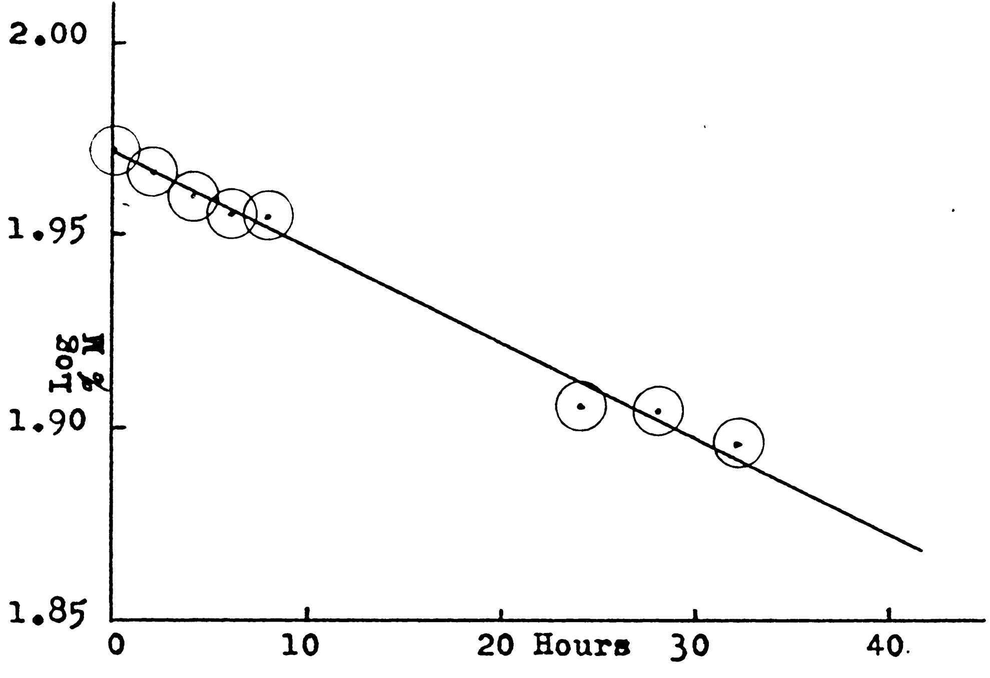
b. The last sample was evidently not completely soluble in pyridine, as indicated by its low unsaturation.



Triallylcitrate

0.01477 m.f. = benzoylperoxide

K = 0.00567/hr.



POLYMERIZATION: (3) Triallylcitrate with 0.01477 mol fraction of benzoylperoxide at 60°C.

10.828 g. monomer   0.1260 g. catalyst

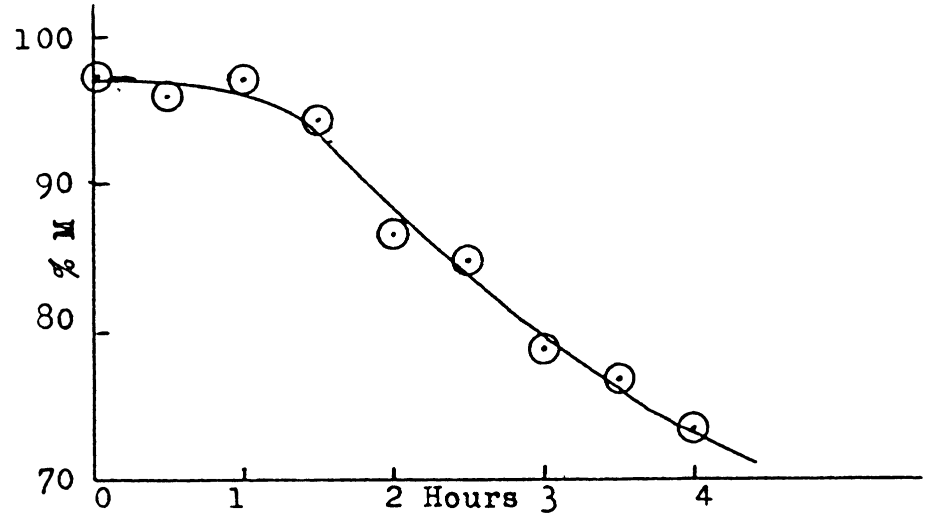
Time hours	Sample weight grams	Ml.Br	Ml.TS	Titre	% M	Log % M	Aliquot ml.
0	0.3002	15.00	10.67	4.33	93.7	1.972	1
2	0.3253	15.00	10.37	4.63	92.6	1.966	1
4	0.3194	15.00	10.52	4.48	91.3	1.960	1
6	0.2574	15.00	11.44	3.56	90.1	1.955	1
8	0.2455	15.00	11.61	3.39	90.0	1.954	1
24	0.2580	15.00	11.81	3.19	80.4	1.905	1
28	0.2820	15.00	11.53	3.47	79.9	1.903	1
32	0.1831	15.00	12.79	2.21	78.5	1.895	1

Remarks:

a. The monomer and the product were clear and colorless.

b. The solution was syrupy after 24 hours and a fragile jel after 32 hours.

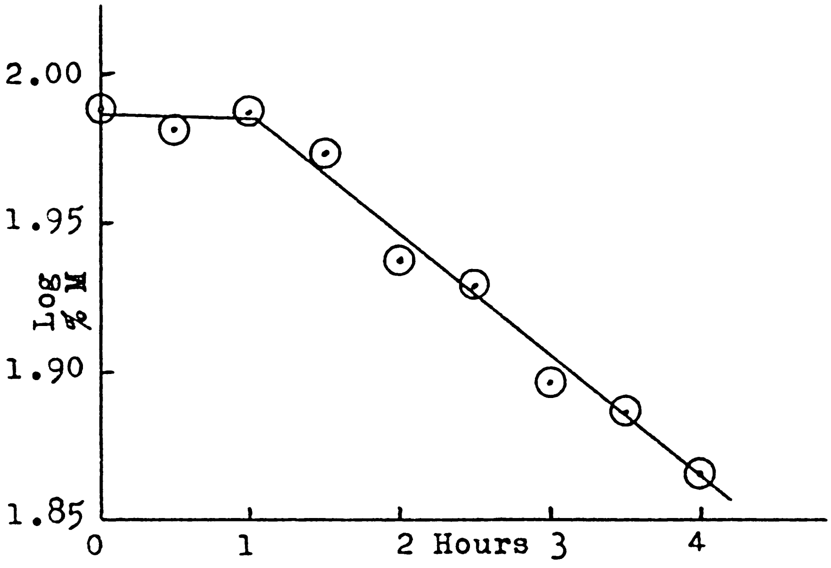
c. A sample was taken after 48 hours,however, it would not dissolve in pyridine or acetic acid and, consequently, could not be analyzed.



Isobutylmethacrylate

0.01477 m.f. benzoylperoxide

K = 0.0932/hr.



POLYMERIZATION: (4) Isobutylmethacrylate with 0.01477 mol fraction of benzoylperoxide at 60°C.

14.219 g. monomer   0.3631 g. catalyst

Time hours	Sample weight grams	Ml.Br	Ml.TS	Titre	% M	Log % M	Aliquot ml.
0	0.6298	20.00	13.10	6.90	97.3	1.988	1
0.5	0.7252	20.00	12.15	7.85	96.0	1.982	1
1.0	0.6634	20.00	12.75	7.25	97.0	1.987	1
1.5	0.7202	20.00	12.37	7.63	94.2	1.974	1
2.0	0.7200	20.00	12.98	7.02	86.6	1.937	1
2.5	0.7306	20.00	13.02	6.98	84.8	1.928	1
3.0	0.7285	20.00	13.53	6.47	78.8	1.896	1
3.5	0.5467	20.00	15.27	4.73	76.9	1.886	1
4.0	0.3918	20.00	16.76	3.24	73.3	1.865	1

Remarks:

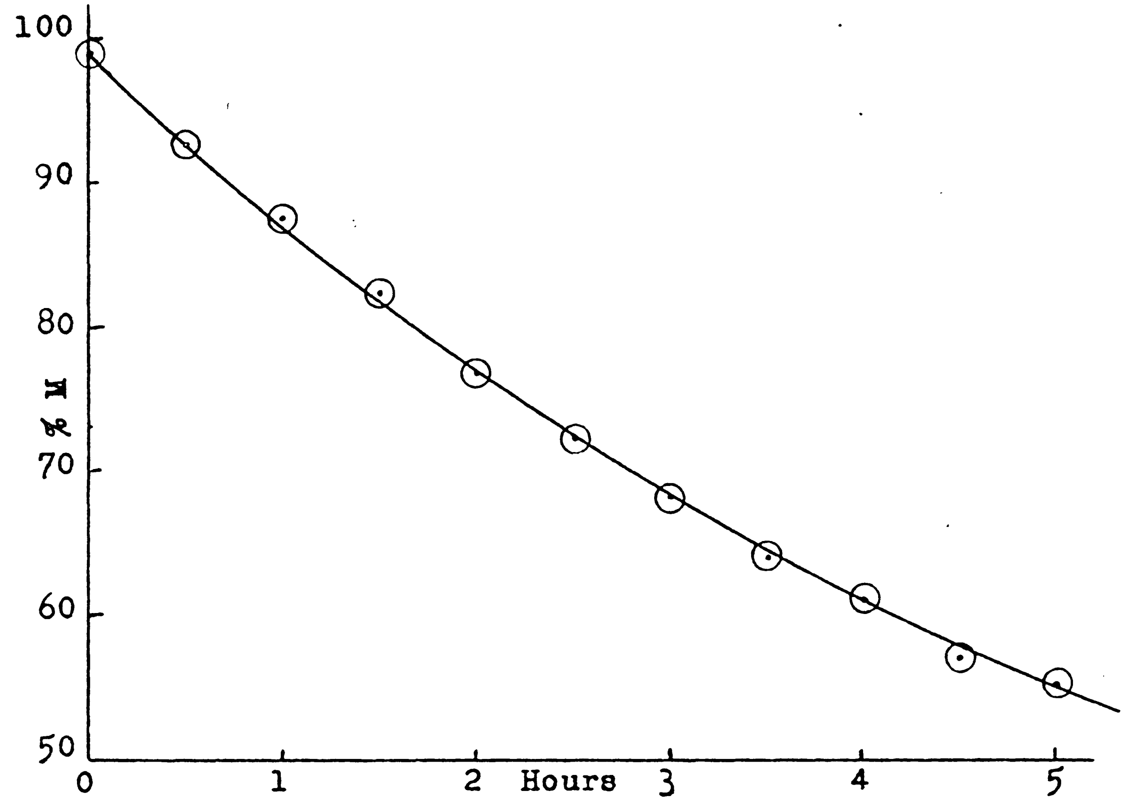
a. An induction period of about one hour occurred.

b. The sample was syrupy after 2.75 hours.

c. Samples could not be taken after 4 hours.

d. Reactants formed a clear, colorless, hard polymer. It softens with heat but cracks when fractured in the cold.

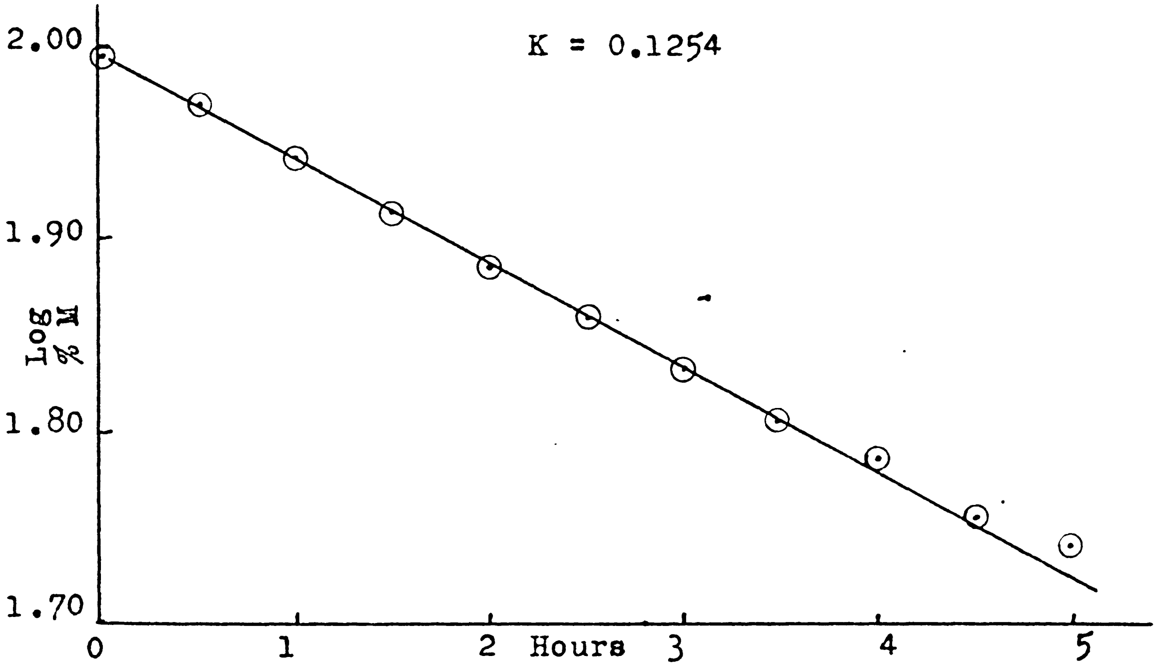
e. It was decided to repeat this run and try to avoid the induction period and to secure better analytical data.



Isobutylmethacrylate

0.01477 m.f. benzoylperoxide

K = 0.1254



POLYMERIZATION: (4-a) Isobutylmethacrylate with 0.01477 mol fraction of benzoylperoxide at 60°C.

14.219 g. monomer 0.3631 g. catalyst

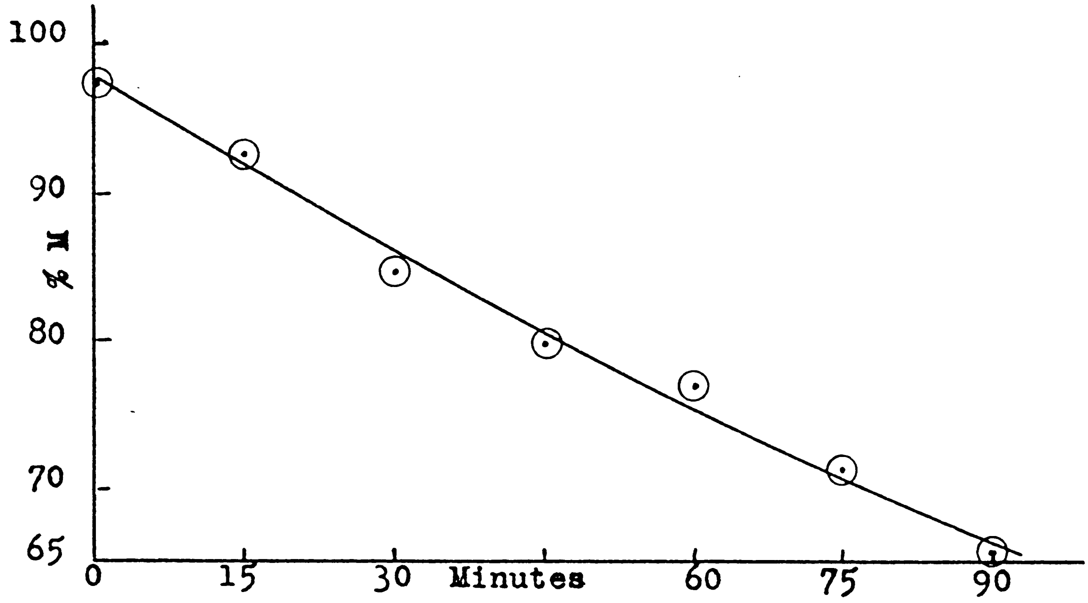
Time hours	Sample weight grams	Ml.Br	Ml.TS	Titre	% M	Log % M	Aliquot ml.
0	0.4654	15.00	9.82	5.18	99.0	1.995	1
½	0.3535	15.00	11.31	3.69	92.6	1.969	1
1	0.4281	15.00	10.78	4.22	87.5	1.942	1
1½	0.4052	15.00	11.26	3.74	82.1	1.914	1
2	0.3046	15.00	12.37	2.63	76.8	1.885	1
2½	0.2546	15.00	4.67	10.33	72.1	1.858	5
3	0.2385	15.00	5.84	9.16	68.2	1.834	5
3½	0.1737	15.00	8.75	6.25	64.0	1.806	5
4	0.1549	15.00	9.69	5.31	61.0	1.785	5
4½	0.1623	15.00	9.80	5.20	56.9	1.755	5
5	0.1577	15.00	10.16	4.84	54.7	1.738	5

Remarks:

a. Portions of the catalyst-monomer solution were sealed in 6 mm. glass tubes and then allowed to polymerize at 60°C. Each was withdrawn from the bath after a certain time and analyzed.

b. The solution was syrupy after 1½ hours, a solid gel after 2½ hours and was a fairly tough polymer after 5 hours.

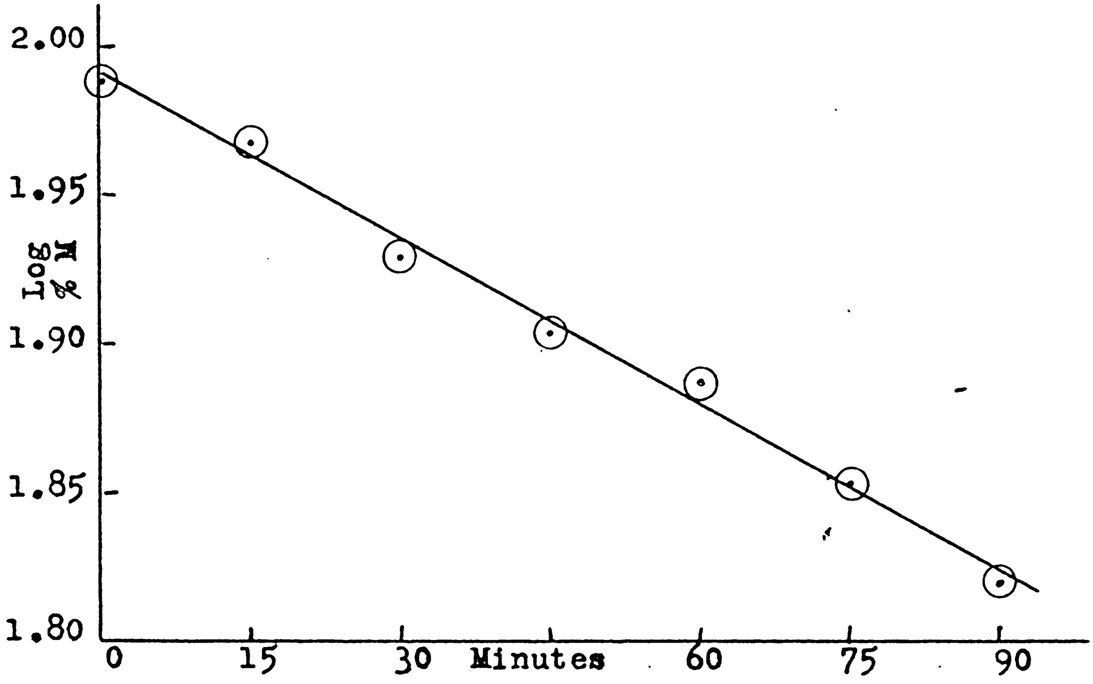
c. This reaction occurred about 30% faster than the previous, contaminated run.



Isobutylmethacrylate

0.02913 m.f. benzoylperoxide

K = 0.2582



POLYMERIZATION: (4-b) Isobutylmethacrylate with 0.02913 mol fraction of benzoylperoxide at 60°C.

14.219 g. monomer   0.7262 g. catalyst

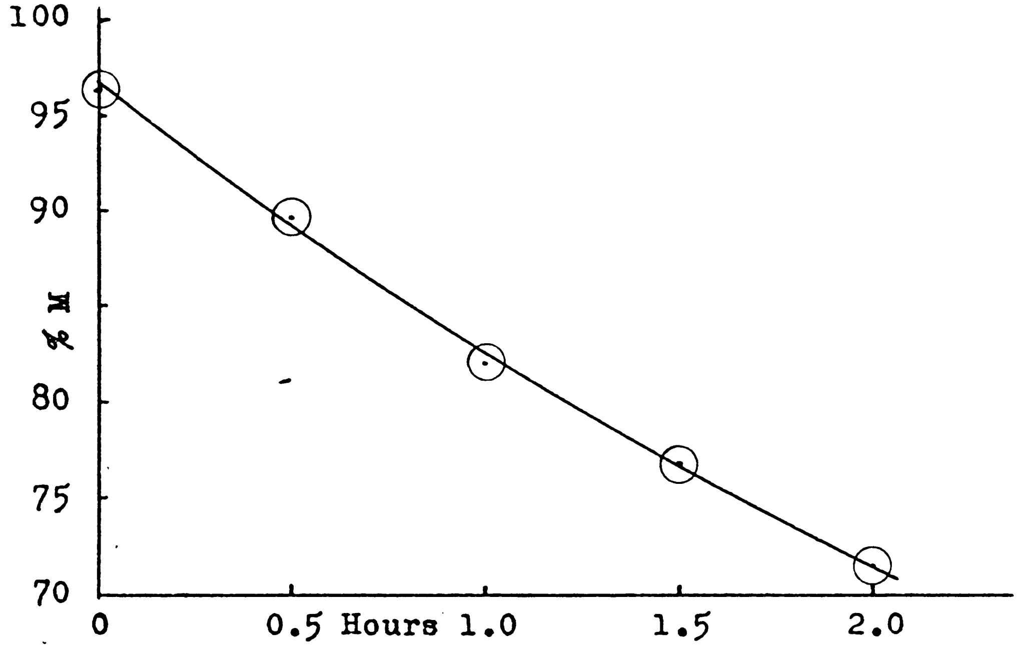
Time hours	Sample weight grams	Ml.Br.	Ml.TS	Titre	% M	Log % M	Aliquot ml.
0	0.3248	15.00	11.44	3.56	97.3	1.988	1
0.25	0.1569	15.00	6.81	8.19	92.7	1.967	5
0.50	0.2746	15.00	12.39	2.61	84.7	1.928	1
0.75	0.2214	15.00	5.04	9.96	79.8	1.902	5
1.00	0.1235	15.00	9.64	5.36	77.0	1.886	5
1.25	0.1382	15.00	9.46	5.54	71.2	1.852	5
1.50	0.1053	15.00	11.11	3.89	65.7	1.818	5

Remarks:

a. The reactants were mixed and portions sealed in 6 mm. glass tubes. They were all put in the 60°C. bath at the same time and withdrawn one at a time at 15 minute intervals for analysis.

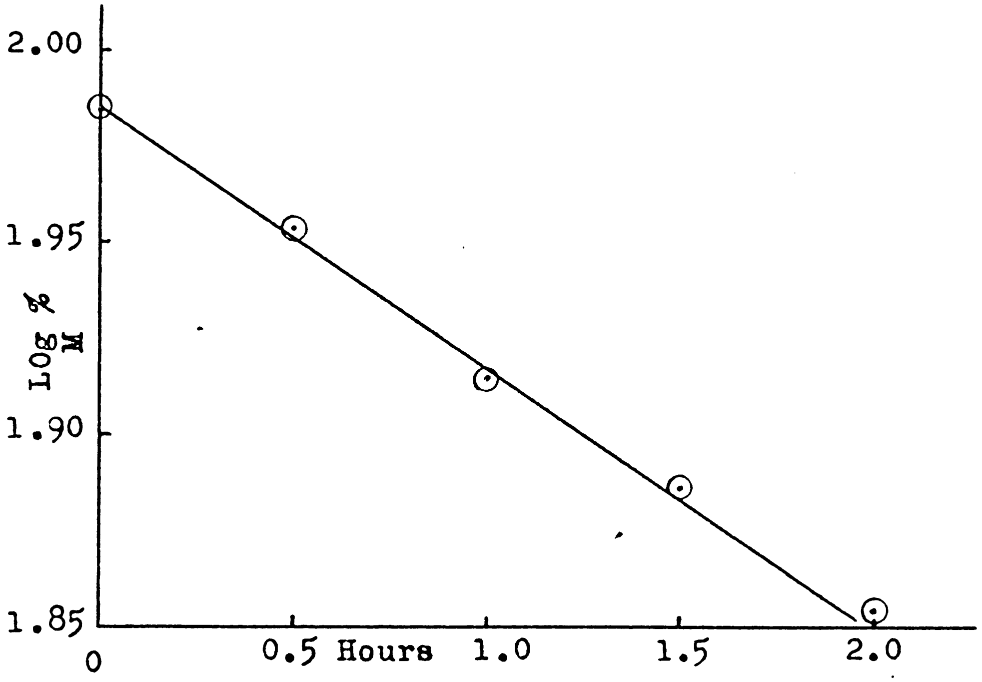
b. The cloudy reactant solution did not become clear.

c. The final polymer after 1.25 hours was hard and tough with no bubbles, but had a rough powdery surface and was not clear.



Glycoldimethacrylate with 0.01477 m.f. benzoylperoxide

K = 0.1575 / hr.



POLYMERIZATION: (5) Glycoldimethacrylate with 0.01477 mol fraction of benzoylperoxide at 60°C.

9.910 g. monomer 0.1815 g. catalyst

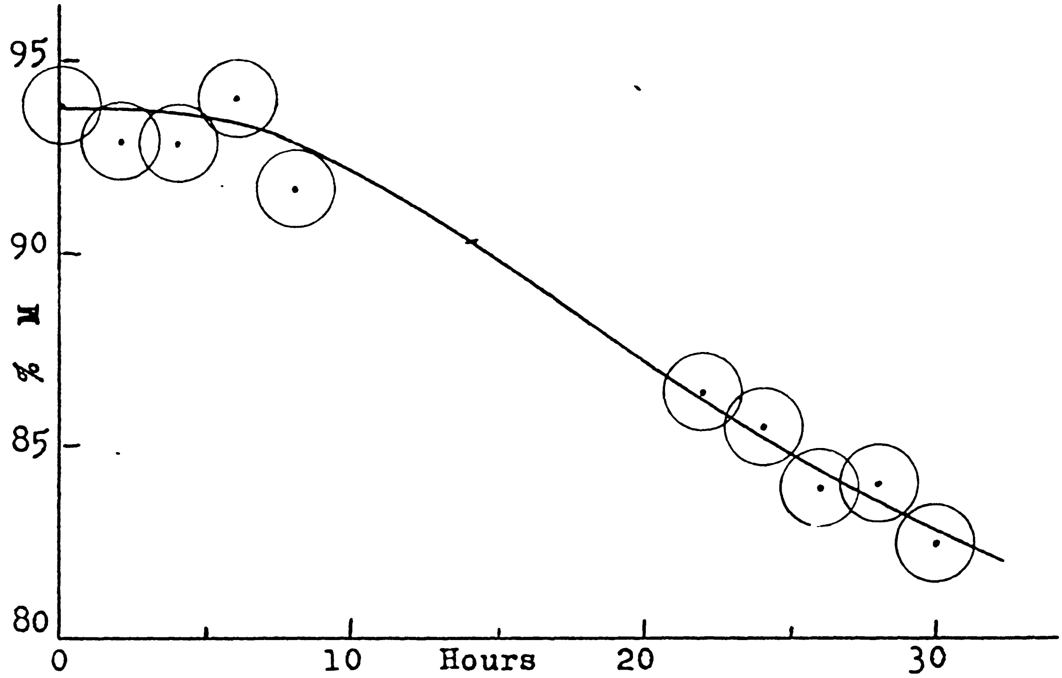
Time hours	Sample weight grams	Ml.Br	Ml.TS	Titre	% M	Log % M	Aliquot ml.
0	0.3172	15.00	10.06	4.94	96.4	1.984	1
½	0.2890	15.00	10.82	4.18	89.7	1.953	1
1	0.1641	15.00	12.82	2.18	82.1	1.914	1
1½	0.1452	15.00	5.97	9.03	76.9	1.886	5
2	0.1287	15.00	7.56	7.44	71.5	1.854	5

Remarks:

a. The sample had thickened appreciably after one hour and was an insoluble jel after two hours.

b. The product remained clear and colorless throughout the polymerization.

c. After 18 hours the polymer was very hard and brittle. An internal crack had developed while the sample was in the constant temperature bath. The polymer had shrunk so much during polymerization that it rattled about in the test tube.

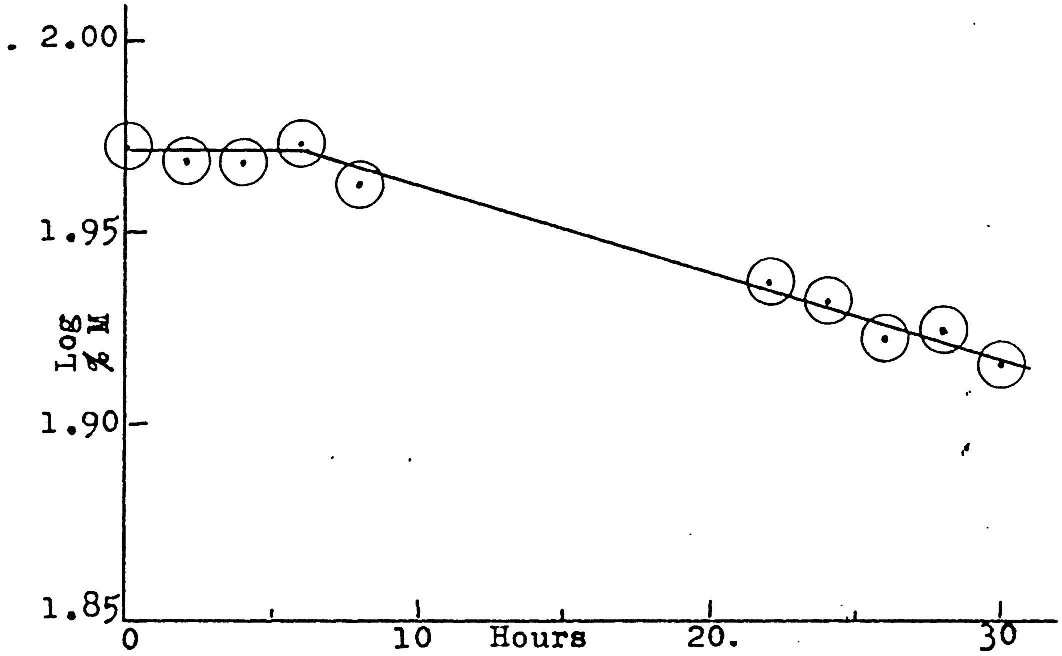


Allylbutyrate

0.0147 m.f. benzoylperoxide

0.0049 m.f. tetrachlorohydroquinone

K = 0.00516



POLYMERIZATION: (6) Allylbutyrate with 0.0147 mol fraction of benzoylperoxide and 0.0049 mol fraction of tetrachlorohydroquinone at 60°C.

12.809 g. monomer 0.3631 g. catalyst 0.1239 g. promoter

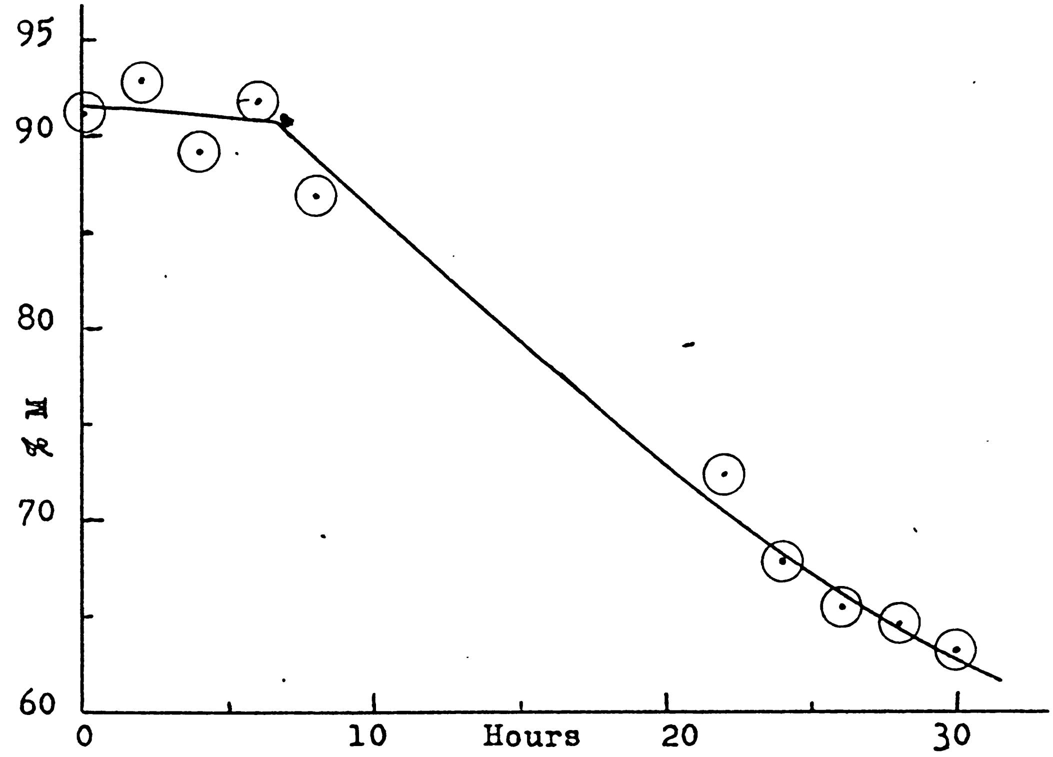
Time hours	Sample weight grams	Ml.Br	Ml.TS	Titre	% M	Log % M	Aliquot ml.
0	0.4207	15.00	10.07	4.93	93.8	1.972	1
2	0.3516	15.00	10.92	4.08	92.9	1.968	1
4	0.3177	15.00	11.31	3.69	92.8	1.968	1
6	0.2800	15.00	11.71	3.29	94.0	1.973	1
8	0.2969	15.00	11.60	3.40	91.7	1.9625	1
22	0.1538	15.00	6.68	8.32	86.5	1.937	5
24	0.1426	15.00	7.38	7.62	85.5	1.932	5
26	0.1557	15.00	6.85	8.15	83.8	1.923	5
28	0.1494	15.00	7.16	7.84	84.0	1.924	5
30	0.1489	15.00	7.33	7.67	82.4	1.916	5

Remarks:

a. The dark color of the sample-pyridine solution did not seem to change during the first eight hours, although it did change to a light yellow after twenty-two hours.

b. The monomer solution appeared to be slightly more viscous the second day.

c. A six to eight hour induction period was caused by the quinone.

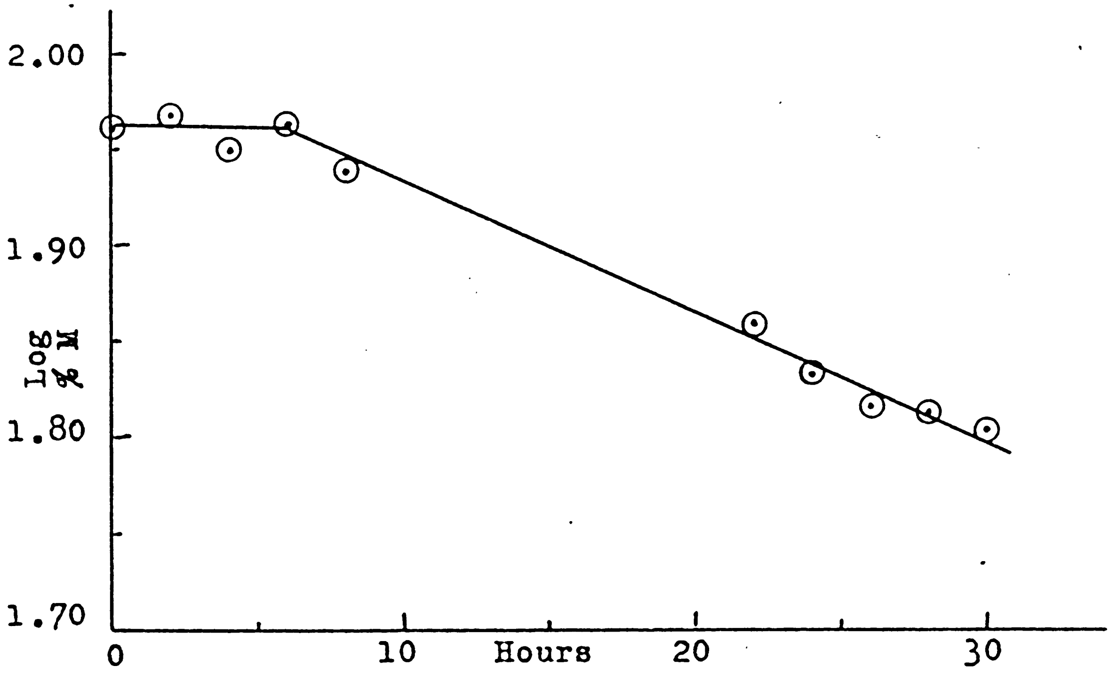


Diethyleneglycol bis(allylcarbonate)

0.0147 m.f. benzoylperoxide

0.0049 m.f. tetrachlorohydroquinone

K = 0.0159



POLYMERIZATION:(7) Diethyleneglycol bis(allylcarbonate) with 0.0147 mol fraction of benzoylperoxide and 0.0049 mol fraction of tetrachlorohydroquinone at 60°C.

13.707 g. monomer 0.1815 g. catalyst 0.0619 g. promoter

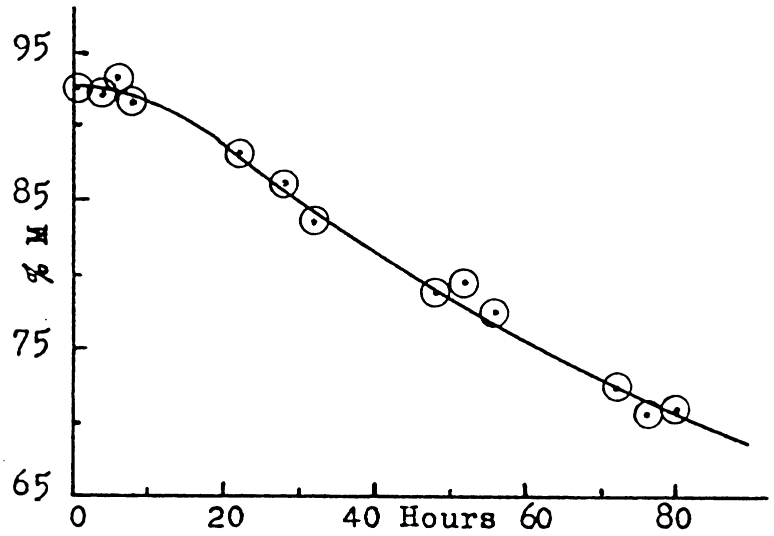
Time hours	Sample weight grams	Ml.Br	Ml.TS	Titre	% M	Log % M	Aliquot ml.
0	0.4000	15.00	10.74	4.26	91.2	1.960	1
2	0.3980	15.00	10.68	4.32	92.9	1.968	1
4	0.4262	15.00	10.57	4.43	89.1	1.950	1
6	0.3955	15.00	10.77	4.23	91.8	1.963	1
8	0.4178	15.00	10.77	4.23	86.9	1.939	1
22	0.1886	15.00	7.03	7.97	72.3	1.859	5
24	0.1577	15.00	8.76	6.24	67.8	1.831	5
26	0.1623	15.00	8.79	6.21	65.5	1.816	5
28	0.1001	15.00	11.22	3.78	64.8	1.812	5
30	0.1280	15.00	10.27	4.73	63.4	1.802	5
48	A clear, light-yellow, rubbery jel which fractures easily.						

Remarks:

a. A 5 to 7 hour induction period was caused by the quinone.

b. After starting, polymerization occurred at a slightly faster rate.

c. The pyridine-polymer solution remained colored much longer than in the acrylate systems. The color was a deeper brown which gradually changed to orange after about 6 to 8 hours, and remained constant thereafter.

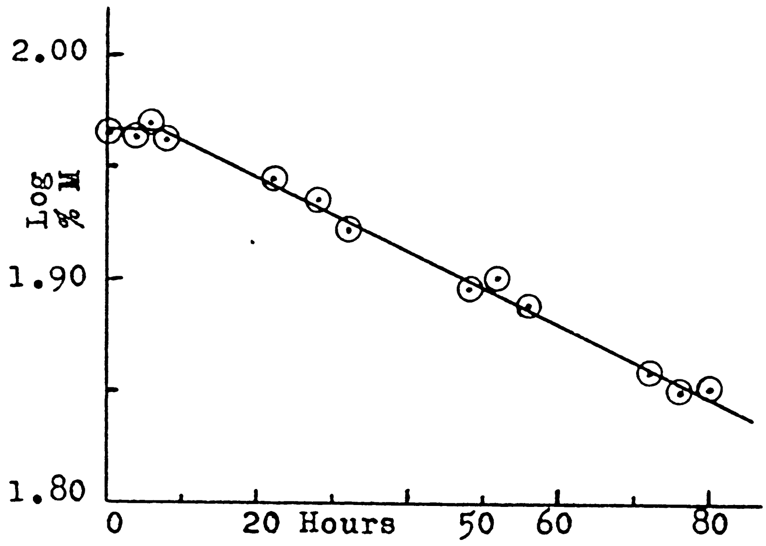


Triallylcitrate

0.0147 m.f. benzoylperoxide

0.0049 m.f. tetrachlorohydroquinone

K = 0.00386



POLYMERIZATION: (8) Triallylcitrate with 0.0147 mol fraction of benzoylperoxide and 0.0049 mol fraction of tetrachlorohydroquinone at 60°C.

15.615 g. monomer   0.1815 g. catalyst   0.0619 g. promoter

Time hours	Sample weight grams	Ml.Br	Ml.TS	Titre	% M	Log % M	Aliquot ml.
0	0.4047	15.00	9.23	5.77	92.9	1.968	1
4	0.3561	15.00	9.97	5.03	92.1	1.964	1
6	0.2818	15.00	10.97	4.03	93.2	1.969	1
8	0.2621	15.00	11.31	3.69	91.6	1.962	1
22	0.3557	15.00	10.18	4.82	88.1	1.945	1
28	0.3212	15.00	10.73	4.27	86.3	1.936	1
32	0.3016	15.00	11.12	3.88	83.6	1.922	1
48	0.2510	15.00	11.96	3.04	78.9	1.897	1
52	0.2612	15.00	11.81	3.19	79.5	1.900	1
56	0.2252	15.00	12.32	2.68	77.5	1.889	1
72	0.1979	15.00	3.98	11.01	72.3	1.859	5
76	0.1601	15.00	6.27	8.73	70.8	1.850	5
80	0.1656	15.00	5.96	9.04	71.0	1.851	5
96	A rubbery jel formed. No longer soluble in pyridine.						

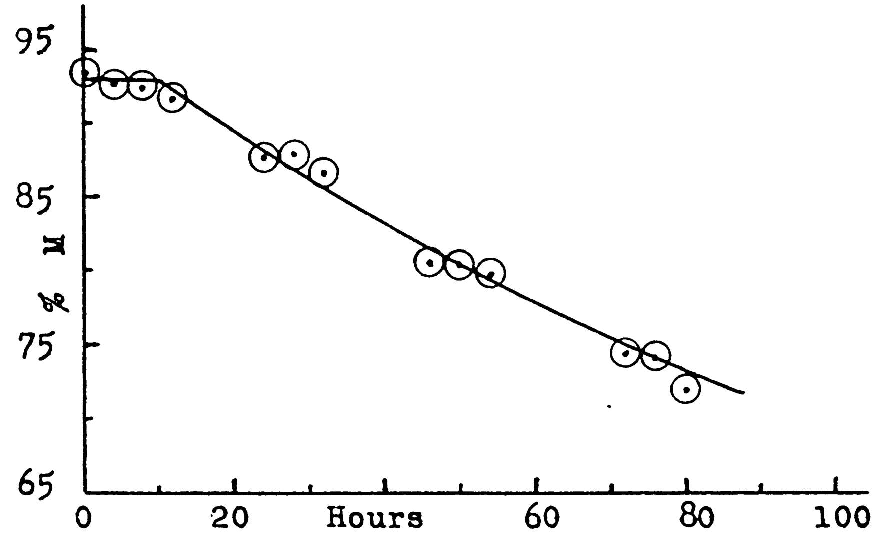
Remarks:

a. The color of the polymer-pyridine solution changed from tan to orange-yellow during the first eight hours of the reaction and remained constant thereafter.

b. Some chain transfer occurred.

c. The reaction rate was slower than when benzoyl peroxide was used alone.

d. The polymer-monomer solution was syrupy after about fifty hours reaction time.

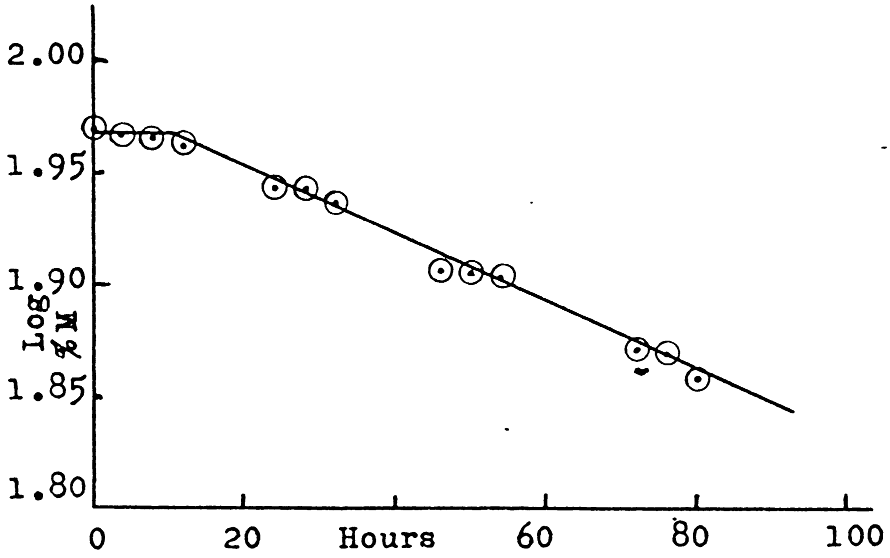


Triallylcitrate

0.0147 m.f. benzoylperoxide

0.0049 m.f. tetrachlorohydroquinone

K = 0.00347



POLYMERIZATION: (8-a) Triallylcitrate with 0.0147 mol fraction of benzoylperoxide and 0.0049 mol fraction of tetrachlorohydroquinone at 60°C.

15.615 g. monomer   0.1815 g. catalyst   0.0619 g. promoter

Time hours	Sample weight grams	Ml.Br	Ml.TS	Titre	% M	Log % M	Aliquot ml.
0	0.4171	15.00	9.02	5.98	93.3	1.971	1
4	0.4015	15.00	9.28	5.72	92.7	1.967	1
8	0.3658	15.00	9.81	5.19	92.3	1.965	1
12	0.3168	15.00	10.53	4.47	91.6	1.962	1
24	0.3895	15.00	9.75	5.25	87.7	1.943	1
28	0.3003	15.00	10.93	4.07	87.9	1.944	1
32	0.2487	15.00	11.69	3.31	86.5	1.937	1
46	0.2176	15.00	12.31	2.69	80.5	1.906	1
50	0.2344	15.00	12.10	2.90	80.3	1.905	1
54	0.2102	15.00	12.41	2.59	79.8	1.902	1
72	0.2363	15.00	12.30	2.70	74.3	1.871	1
76	0.1544	15.00	6.21	8.79	74.0	1.869	5
80	0.1273	15.00	7.95	7.05	72.0	1.857	5
96	Rubbery jel formed. No longer soluble in pyridine.						

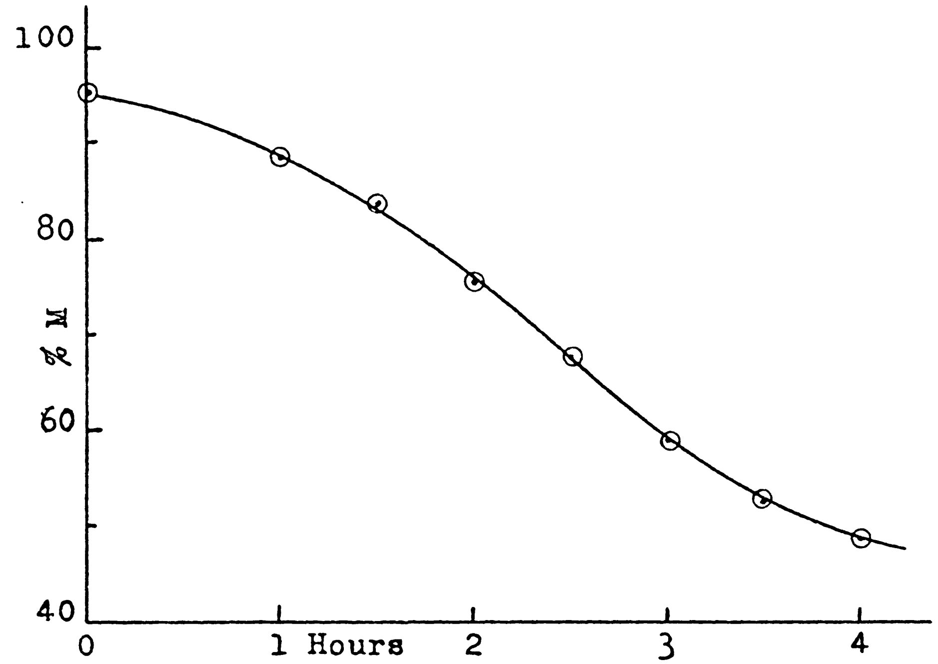
Remarks:

a. The tetrachlorohydroquinone was reprecipitated from acetic acid in an attempt to avoid the induction period of the previous run.

b. About a 10 hour induction period was indicated.

c. The reaction rate was about 10% slower than in the previous similar run.

d. No physical differences were noted in the polymerization reaction.

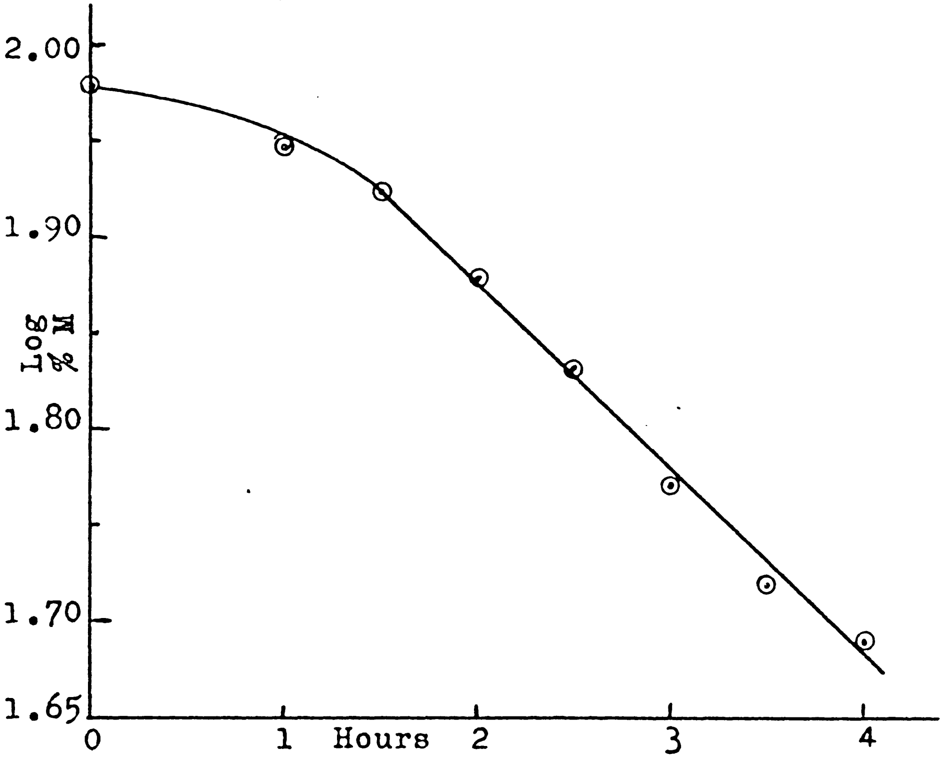


Isobutylmethacrylate

0.0147 m.f. benzoylperoxide

0.0049 m.f. tetrachlorohydroquinone

K = 0.2215



POLYMERIZATION: (9) Isobutylmethacrylate with 0.0147 mol fraction of benzoylperoxide and 0.0049 mol fraction of tetrachlorohydroquinone at 60°C.

14.219 g. monomer 0.3631 g. catalyst 0.1239 g. promoter

Time hours	Sample weight grams	Ml.Br	Ml.TS	Titre	% M	Log % M	Aliquot ml.
0	0.4948	15.00	9.70	5.30	95.2	1.978	1
1	0.4020	15.00	11.00	4.00	88.5	1.947	1
1½	0.4351	15.00	10.89	4.11	83.7	1.922	1
2	0.3728	20.00	4.20	15.80	75.3	1.877	5
2½	0.3427	20.00	6.90	13.10	67.8	1.831	5
3	0.3392	15.00	3.75	11.25	58.8	1.769	5
3½	0.4008	15.00	3.20	11.80	52.3	1.718	5
4	0.1563	15.00	10.70	4.30	48.7	1.687	5
4½	Polymer too hard to sample						
24	Clear, orange-yellow, hard polymer						

Remarks:

a. The reaction mixture was a cloudy, light yellow solution.

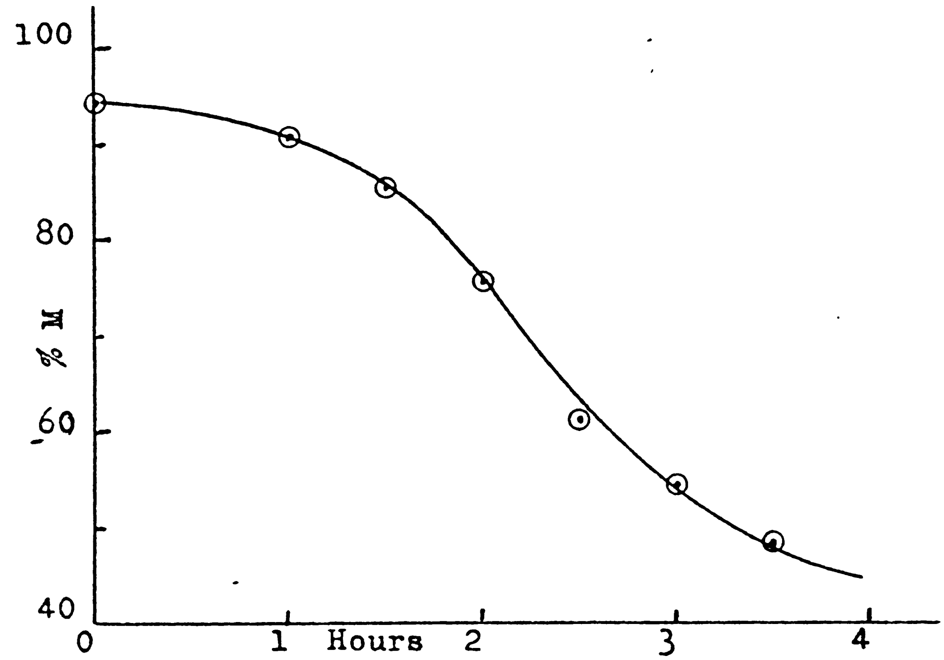
b. The quinone caused the pyridine-polymer solution to have a light brown color. No more lightening of the quinone color was noticed after 1½ hours of reaction.

c. The unsaturation of the starting material appears to be low.

d. The constancy of pyridine-quinone color begins at the break in the curve.

e. The low unsaturation at the jel stage might be ascribed to chain transfer.

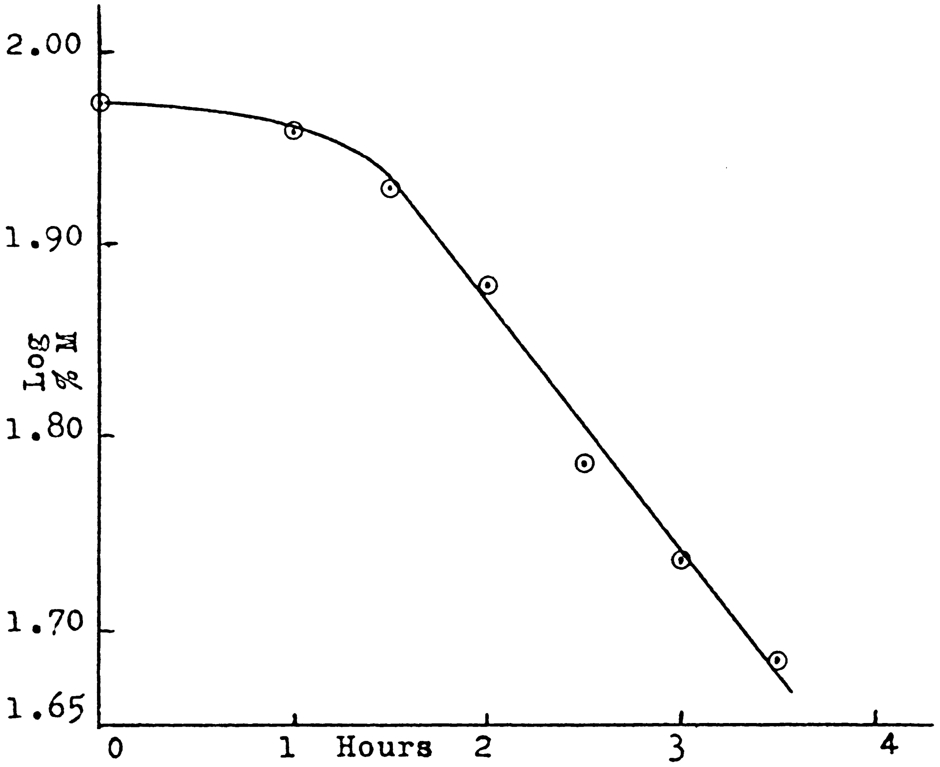
f. The polymer had a light yellow color.



Glycoldimethacrylate K = 0.293

0.0147 m.f. benzoylperoxide

0.0049 m.f. tetrachlorohydroquinone



POLYMERIZATION: (10) Glycoldimethacrylate with 0.0147 mol fraction of benzoylperoxide and 0.0049 mol fraction of tetrachlorohydroquinone at 60°C.

9.901 g. monomer 0.1815 g. catalyst 0.0619 promoter

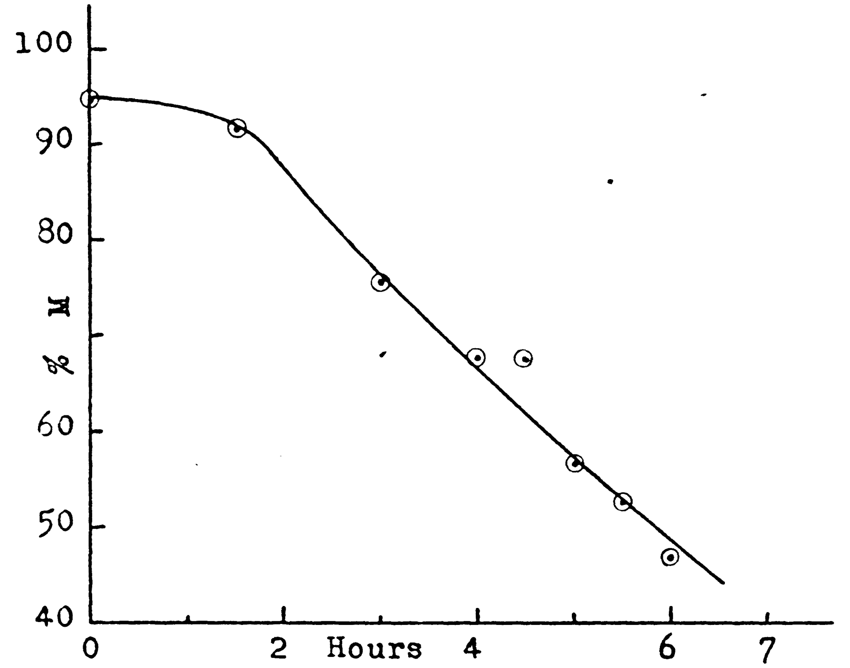
Time hours	Sample weight grams	Ml.Br	Ml.TS	Titre	% M	Log % M	Aliquot ml.
0	0.2614	15.00	11.02	3.98	94.2	1.974	1
1	0.2221	15.00	11.74	3.26	90.8	1.958	1
1½	0.1703	15.00	3.29	11.71	85.2	1.930	5
2	0.1568	15.00	5.44	9.56	75.5	1.878	5
2½	0.1633	15.00	6.94	8.06	61.1	1.786	5
3	0.1370	15.00	8.97	6.03	54.4	1.735	5
3½	0.1298	15.00	9.93	5.07	48.3	1.684	5

4 Stiff jel, can no longer be disolved in pyridine.

Remarks:

a. The color or the pyridine-polymer solutions changed gradually from a light tan to a yellowish-orange within the first 1.5 hours and remained constant thereafter.

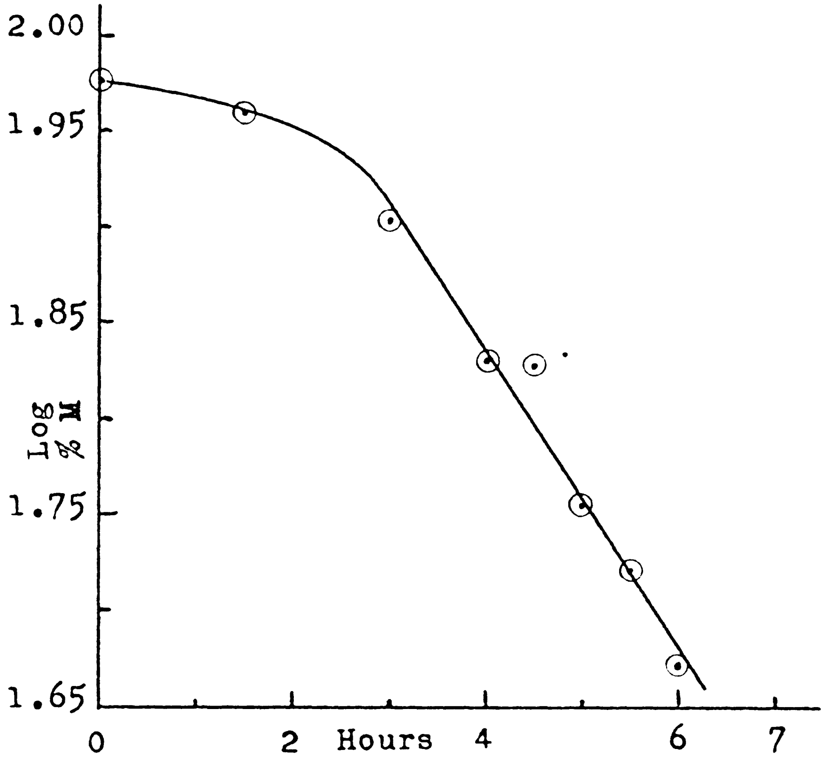
b. After polymerizing over night the sample was a hard, lusterous plastic which did not appear to be as brittle as the polymer from benzoylperoxide and glycoldimethacrylate. It had a faint yellow color.



Isobutylmethacrylate K = 0.1444

0.0147 m.f. benzoylperoxide

0.00975 m.f. tetrachlorohydroquinone



POLYMERIZATION: (11) Isobutylmethacrylate with 0.01462 mol fraction of benzoylperoxide and 0.00975 mol fraction of tetrachlorohydroquinone at 60°C.

14.219 g. monomer 0.3631 g. catalyst 0.2478 g. promoter

Time hours	Sample weight grams	Ml.Br	Ml.TS	Titre	% M	Log % M	Aliquot ml.
0	0.3987	20.00	15.75	4.25	94.6	1.976	1
1.5	0.4042	20.00	15.85	4.15	91.3	1.960	1
3.0	0.4004	20.00	16.59	3.41	75.4	1.877	1
4.0	0.3676	15.00	12.18	2.82	67.6	1.830	1
4.5	0.3412	15.00	12.41	2.59	67.5	1.829	1
5.0	0.3378	15.00	4.19	10.81	56.8	1.754	5
5.5	0.2480	15.00	7.65	7.35	52.5	1.720	5
6.0	0.2667	15.00	7.95	7.05	46.9	1.671	5
6.5	Polymer too hard to sample						
24	Clear, orange-yellow, hard polymer, somewhat brittle.						

Remarks:

a. The color of the pyridine-polymer solution changed from light brown to yellow during the first two hours of the run and appeared to be constant thereafter.

b. The polymer showed lower unsaturation than normal at the jel point.

c. It was decided to react benzoylperoxide with tetrachlorohydroquinone in the absence of monomer to determine whether bromine adds to either of these catalytic agents.

d. Reprecipitated tetrachlorohydroquinone was used in this experiment.

Reaction of 0.01462 mol fraction of benzoylperoxide and 0.00975 mol fraction of tetrachlorohydroquinone in acetic acid at 60°C., and determination of unsaturation of this mixture.

This experiment was carried out for two purposes:

1. To elucidate the nature of the reaction.
2. To determine whether an appreciable amount of bromine adds to these substances.

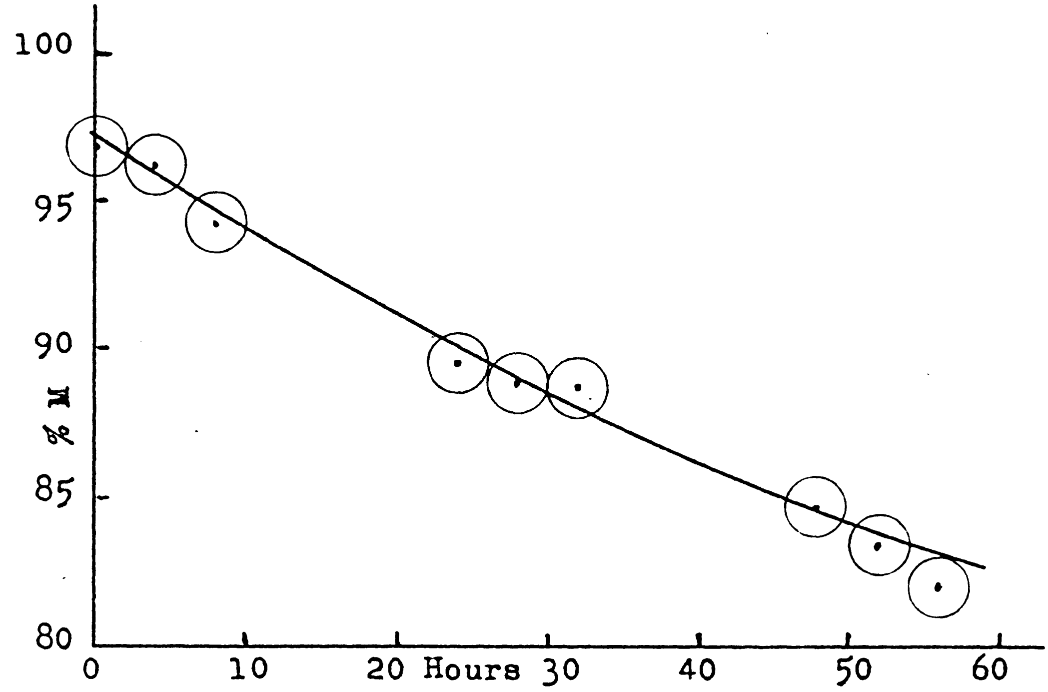
20.01 g. solvent 1.2104 g. peroxide 0.7435 g. quinone

Time hours	Sample weight grams	Ml.Br	Ml.TS	Titre	% M as isobutyl-methacrylate	Aliquot
0	0.4449	15.00	15.00	0.00	0.00	1
0.5	0.4116	15.00	15.06	0.06	0.25	5
1.0	0.3849	15.00	15.01	0.01	0.046	5
1.5	0.3890	15.00	15.05	0.05	0.22	5
2.0	0.3676	15.00	15.10	0.10	0.47	5
3.0	0.3223	15.00	15.02	0.02	0.11	5
4.0	0.3572	15.00	15.05	0.05	0.24	5

Remarks:

a. Bromine addition is less than the experimental error in determining acrylate unsaturation, hence it is felt that no correction need be made for in in the polymerization experiments.

b. No color was formed when the reactants were dissolved in pyridine. Either the acetic acid inhibited the color, or monomer is necessary for color formation.

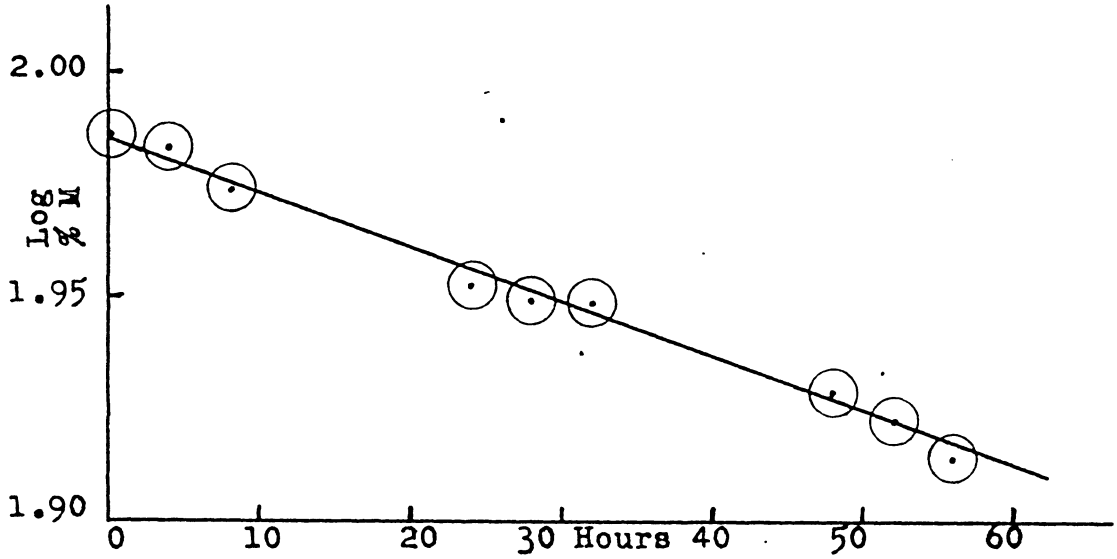


Allylbutyrate

0.0147 m.f. benzoylperoxide

0.0049 m.f. hydrazobenzene

K = 0.00278



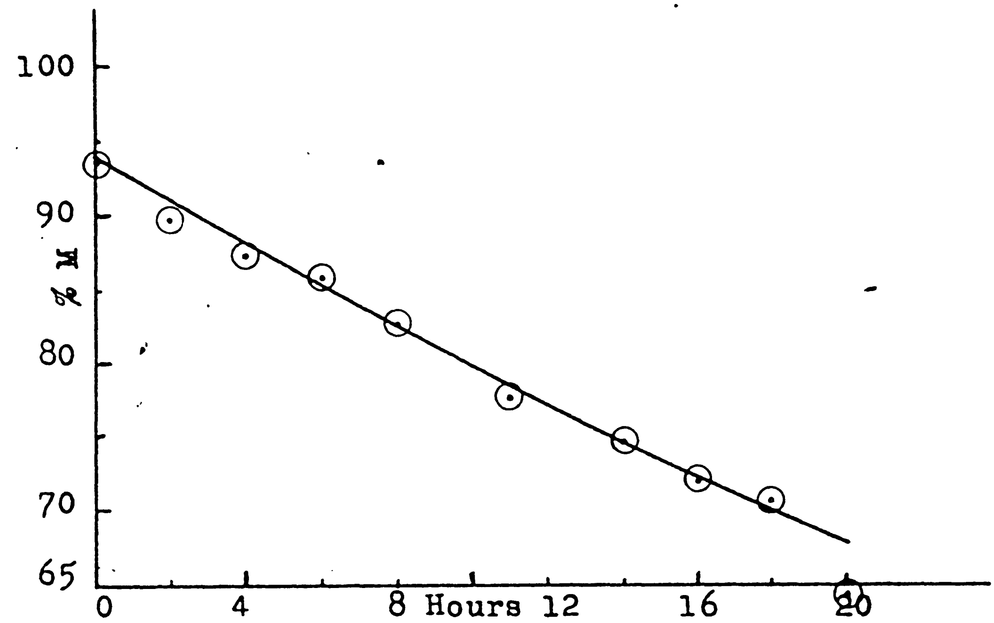
POLYMERIZATION: (12) Allylbutyrate with 0.0147 mol fraction of benzoylperoxide and 0.0049 mol fraction of hydrazobenzene at 60°C.

12.809 g. monomer 0.3631 g. catalyst 0.0921 g. promoter

Time hours	Sample weight grams	Ml.Br	Ml.TS	Titre	% M	Log % M	Aliquot ml.
0	0.2517	15.00	11.95	3.05	96.8	1.986	1
4	0.2640	15.00	11.83	3.17	96.2	1.983	1
8	0.2564	15.00	11.98	3.02	94.2	1.974	1
24	0.2397	15.00	12.32	2.68	89.5	1.952	1
28	0.2438	15.00	12.29	2.71	88.9	1.949	1
32	0.2023	15.00	3.79	11.21	88.7	1.948	5
48	0.1860	15.00	5.16	9.84	84.7	1.928	5
52	0.1968	15.00	4.75	10.25	83.4	1.921	5
56	0.1374	15.00	7.94	7.06	82.0	1.914	5

Remarks:

a. The pyridine-reactant mixtures formed yellow colored solutions.

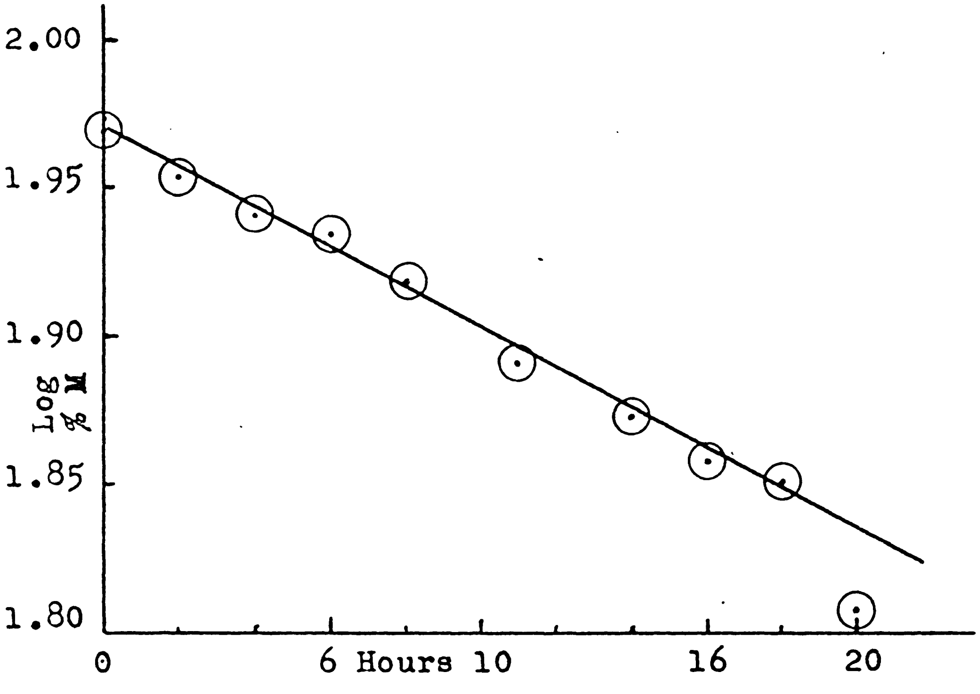


Diethyleneglycol bis(allylcarbonate)

0.0147 m.f. benzoylperoxide

0.0049 m.f. hydrazobenzene

K = 0.0153



POLYMERIZATION: (13) Diethyleneglycol bis(allylcarbonate) with 0.0147 mol fraction of benzoylperoxide and 0.0049 mol fraction of hydrazobenzene at 60°C.

13.707 g. monomer   0.1816 g. catalyst   0.0461 g. promoter

Time hours	Sample weight grams	Ml.Br	Ml.TS	Titre	% M	Log % M	Aliquot ml.
0	0.2989	15.00	11.73	3.27	93.8	1.972	1
2	0.3271	15.00	11.57	3.43	89.7	1.953	1
4	0.3530	15.00	11.41	3.59	87.1	1.940	1
6	0.3016	15.00	11.98	3.02	85.9	1.934	1
8	0.2798	15.00	12.29	2.71	82.8	1.918	1
0	0.3444	15.00	11.25	3.75	93.1	1.969	1
11	0.2165	15.00	13.03	1.97	77.8	1.891	1
14	0.1823	15.00	7.06	7.94	74.6	1.873	5
16	0.1517	15.00	8.63	6.37	72.0	1.857	5
18	0.1262	15.00	9.78	5.22	70.8	1.850	5
20	0.1384	15.00	9.81	5.19	64.3	1.808	5

Remarks:

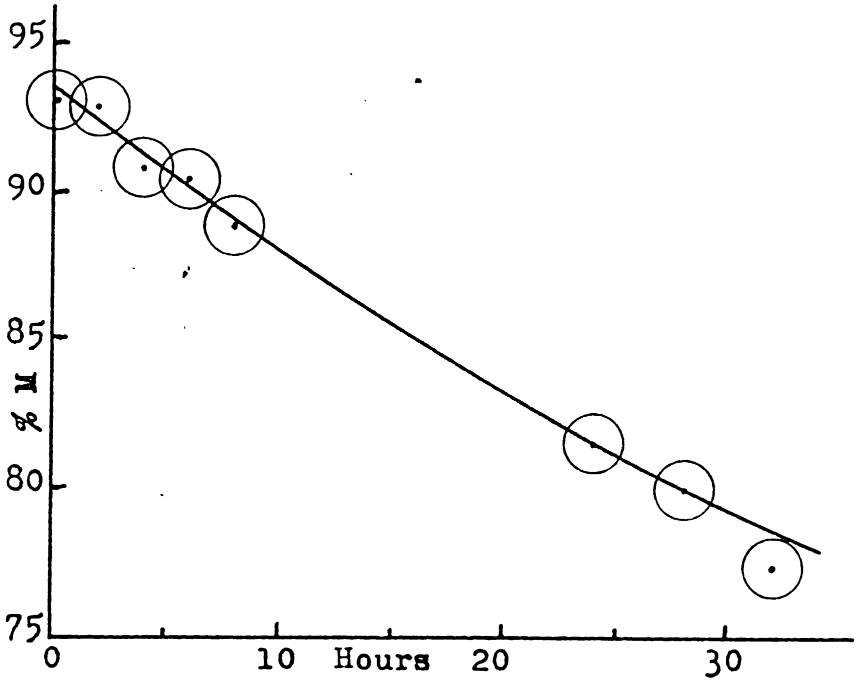
a. This experiment consisted of two polymerizations using the same amounts of reactants which were combined into one sequence. The first run hardened over night so that no morning samples could be taken. The second run was started at night so that sampling could be continued the next day until it hardened.

b. The last analysis figure was incorrect due to insolubility of the polymer in pyridine.

c. The reactants became syrupy after 8 to 10 hours.

d. The clear polymer had a brownish-red color.

e. The polymer-pyridine solution was colored yellow.

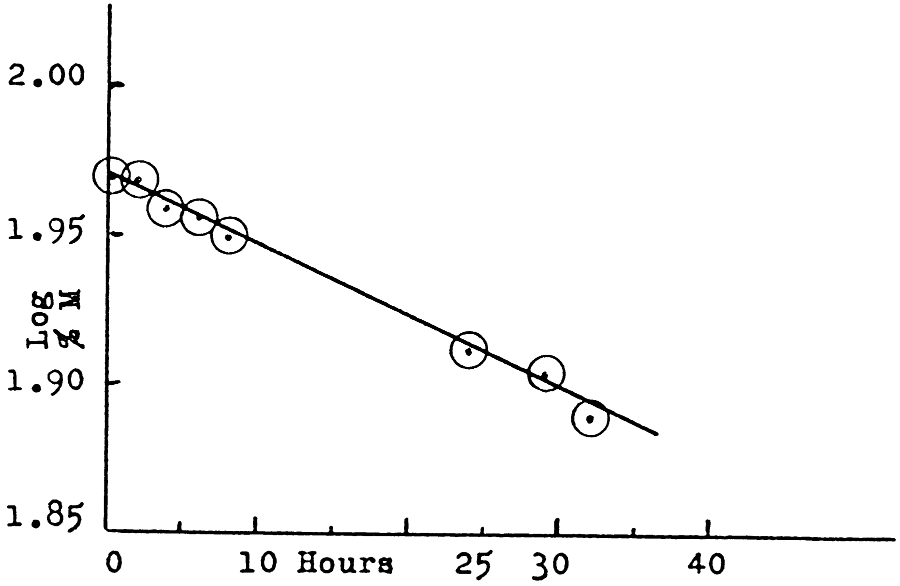


Triallylcitrate

0.0147 m.f. benzoylperoxide

0.0049 m.f. hydrazobenzene

k = 0.00545



POLYMERIZATION: (14) Triallylcitrate with 0.0147 mol fraction of benzoylperoxide and 0.0049 mol fraction of hydrazobenzene at 60°C.

15.615 g. monomer 0.1816 g. catalyst 0.0461 g. promoter

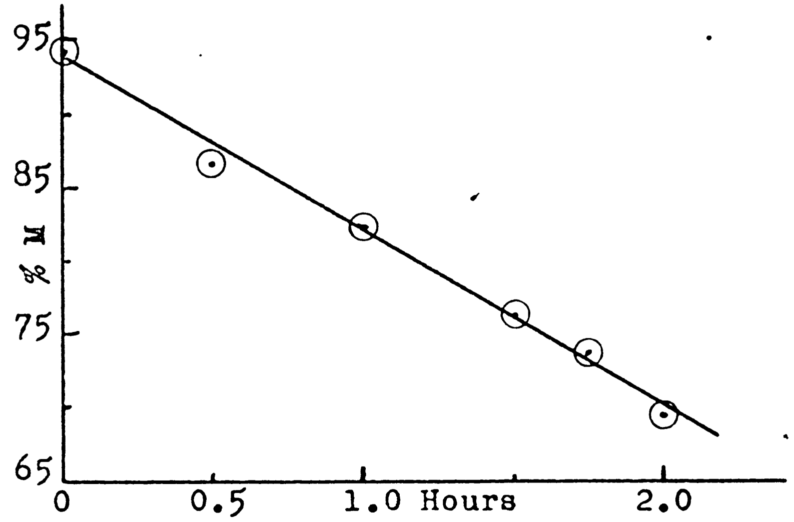
Time hours	Sample weight grams	Ml.Br	Ml.TS	Titre	% M	Log % M	Aliquot ml.
0	0.3374	15.00	10.17	4.83	93.1	1.969	1
2	0.2990	15.00	10.73	4.27	92.9	1.968	1
4	0.2711	15.00	11.21	3.79	90.8	1.958	1
6	0.2817	15.00	11.09	3.91	90.4	1.956	1
8	0.2524	15.00	11.55	3.45	88.9	1.949	1
24	0.1925	15.00	12.59	2.41	81.5	1.911	1
28	0.2849	15.00	11.49	3.51	80.0	1.903	1
32	0.1395	15.00	6.68	8.32	77.4	1.889	5
48	Reactants have formed a solid jel which was insoluble in pyridine.						

Remarks:

a. Reactants were syrupy after 28 to 32 hours.

b. A clear crystalline jel formed after 48 hours which had a light tan color.

c. The polymer-pyridine solutions were yellow when first mixed, but developed a red color after standing for an hour or so.

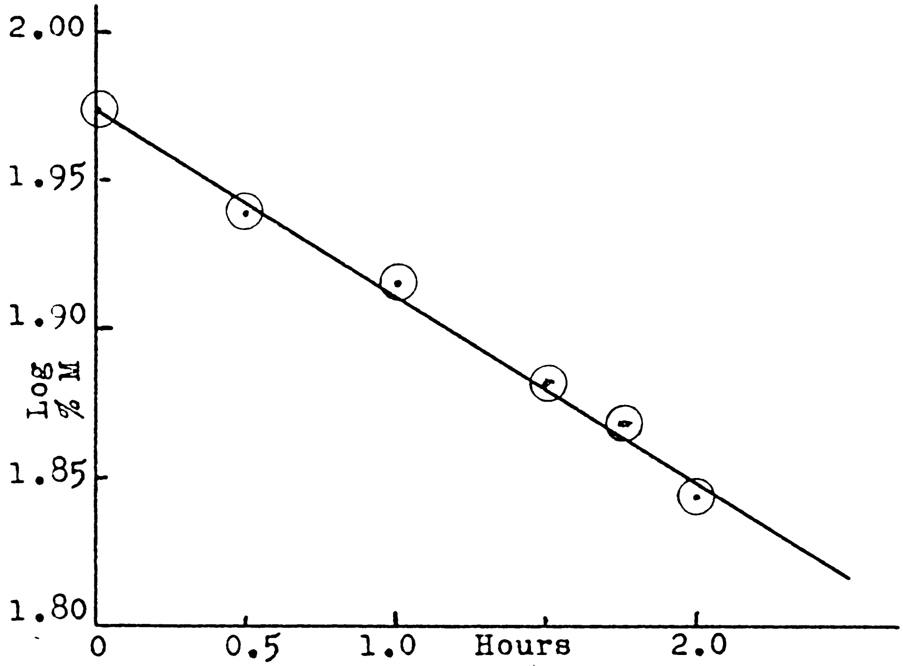


Isobutylmethacrylate

0.0147 m.f. benzoylperoxide

0.0049 m.f. hydrazobenzene

K = 0.1411



POLYMERIZATION: (15) Isobutylmethacrylate with 0.0147 mol fraction of benzoylperoxide and 0.0049 mol fraction of hydrazobenzene at 60°C.

14.219 g. monomer 0.3631 g. catalyst 0.0919 g. promoter

Time hours	Sample weight grams	Ml.Br	Ml.TS	Titre	% M	Log % M	Aliquot ml.
0	0.2457	15.00	12.40	2.60	94.1	1.974	1
0.5	0.2231	15.00	12.83	2.17	86.7	1.938	1
1.0	0.1795	15.00	6.70	8.30	82.2	1.915	5
1.5	0.1210	15.00	9.81	5.19	76.1	1.881	5
1.75	0.1056	15.00	10.60	4.40	73.8	1.868	5
2.0	0.1790	15.00	7.99	7.01	69.5	1.842	5

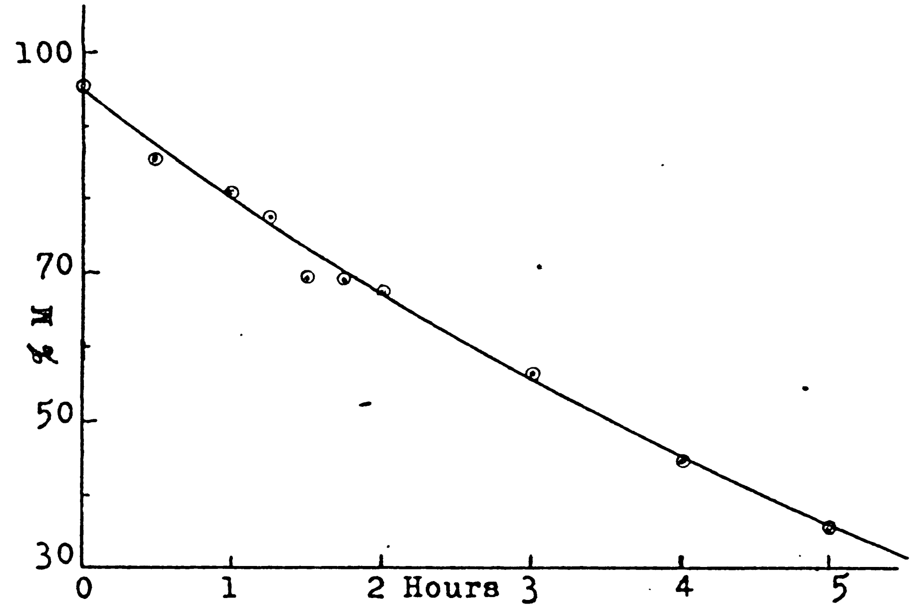
Remarks:

a. Reaction mixture was syrupy after one hour.

b. Reaction mixture was solid at two hours. The polymerization tube had to be broken in order to get the polymer for sampling.

c. The hydrazobenzene gave the polymer a light tan color which did not change hue during the reaction.

d. The hard polymer was clear and contained a few very small bubbles.

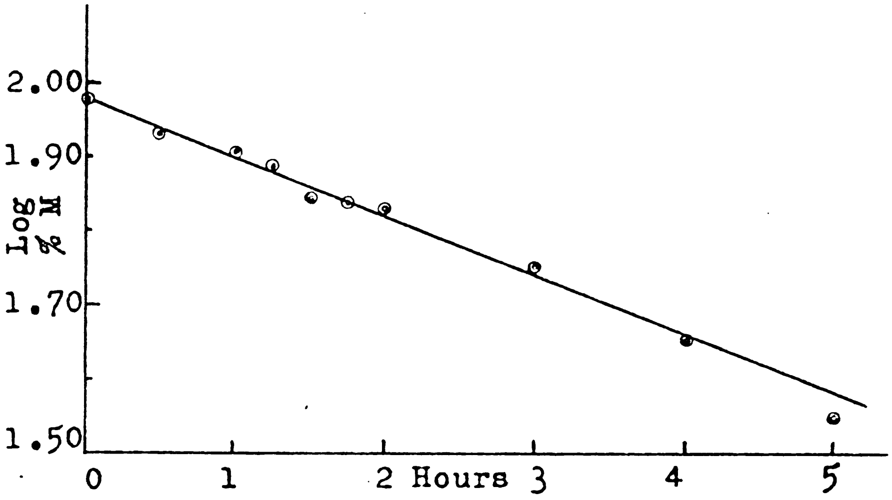


Isobutylmethacrylate

0.0147 m.f. benzoylperoxide

0.0049 m.f. hydrazobenzene

K = 0.1436



POLYMERIZATION: (15-a) Isobutylmethacrylate with 0.0147 mol fraction of benzoylperoxide and 0.0049 mol fraction of hydrazobenzene at 60°C.

14.219 g. monomer   0.3631 g. catalyst   0.0919 g. promoter

Time hours	Sample weight grams	Ml.Br	Ml.TS	Titre	% M	Log % M	Aliquot ml.
0	0.3526	15.00	11.21	3.79	95.4	1.979	1
0.5	0.2118	15.00	12.97	2.03	85.3	1.931	1
1.0	0.2816	15.00	12.44	2.56	80.7	1.907	1
1.25	0.2296	15.00	13.00	2.00	77.5	1.889	1
1.5	0.2530	15.00	13.03	1.97	69.2	1.840	1
1.75	0.1300	15.00	9.95	5.05	69.0	1.839	5
2.0	0.1824	15.00	8.06	6.94	67.7	1.831	5
3.0	0.1762	15.00	9.39	5.61	56.5	1.752	5
4.0	0.1071	15.00	12.29	2.71	44.8	1.651	5
5.0	0.1050	15.00	12.90	2.10	35.5	1.550	5

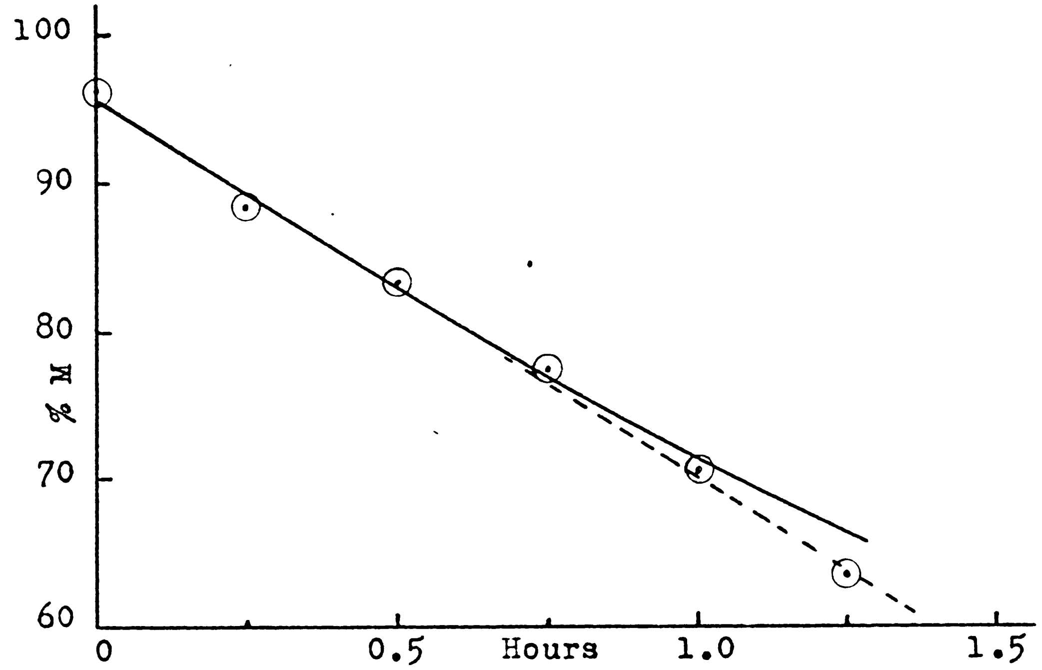
Remarks:

a. In this experiment the monomer solution was prepared in the cold and then portions of it sealed individually in 6 mm. diameter glass tubes. All the sealed samples were put in the bath together and each was then withdrawn at an appropriate interval for analysis. This was done in order to carry sampling beyond the jel stage.

b. The reaction mixture formed a hard polymer after 1.75 hours.

c. A clear, light tan colored plastic was formed.

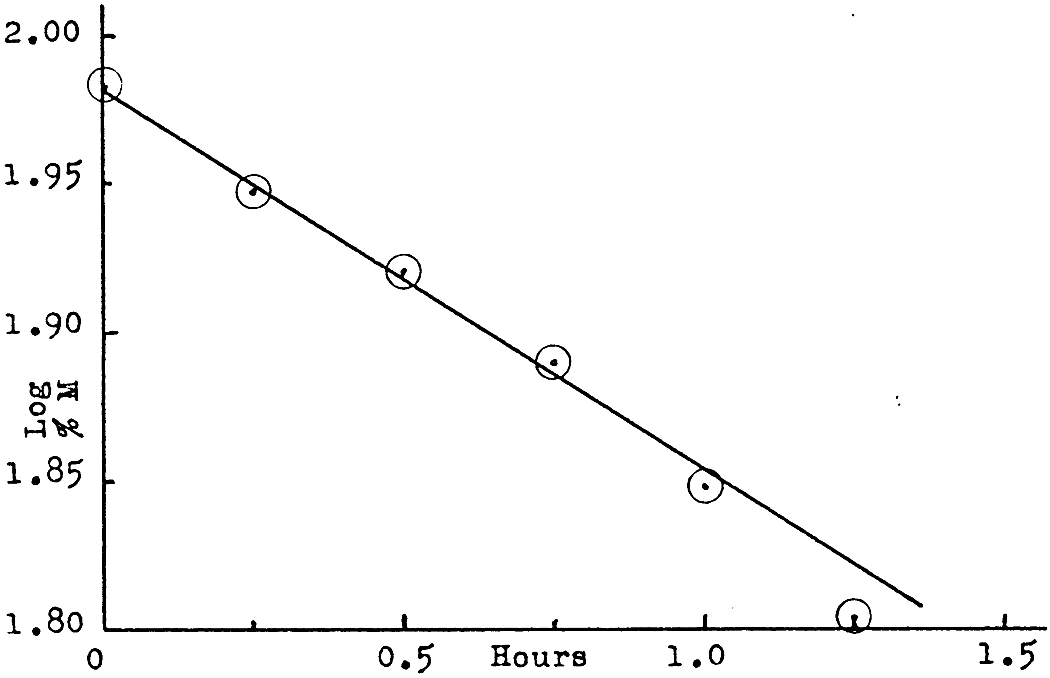
d. A definite % vs time curve was formed in this experiment which was not evidenced in the previous two hour run. The reaction was first order.



Glycoldimethacrylate K = 0.2946

0.0147 m.f. benzoylperoxide

0.0049 m.f. hydrazobenzene



POLYMERIZATION: (16) Glycoldimethacrylate with 0.0147 mol fraction of benzoylperoxide and 0.0049 mol fraction of hydrazobenzene at 60°C.

9.901 g. monomer   0.1815 g. catalyst   0.0461 g. promoter

Time hours	Sample weight grams	Ml.Br	Ml.TS	Titre	% M	Log % M	Aliquot ml.
0	0.3088	15.00	10.20	4.80	96.2	1.983	1
0.25	0.2229	15.00	11.81	3.19	88.5	1.947	1
0.50	0.1843	15.00	12.52	2.48	83.2	1.920	1
0.75	0.1486	15.00	5.71	9.29	77.4	1.889	5
1.00	0.1309	15.00	7.54	7.46	70.5	1.848	5
1.25	0.1312	15.00	8.27	6.73	63.5	1.803	5
2.00	Sample no longer soluble in pyridine.						

Remarks:

a. The reaction mixture was made up and portions of it sealed into 6 mm. glass tubes. These tubes were then inserted in the constant temperature bath and withdrawn at intervals for analysis.

b. The sample taken after 1.25 hours did not dissolve completely in the pyridine. As a result the unsaturation analysis was low.

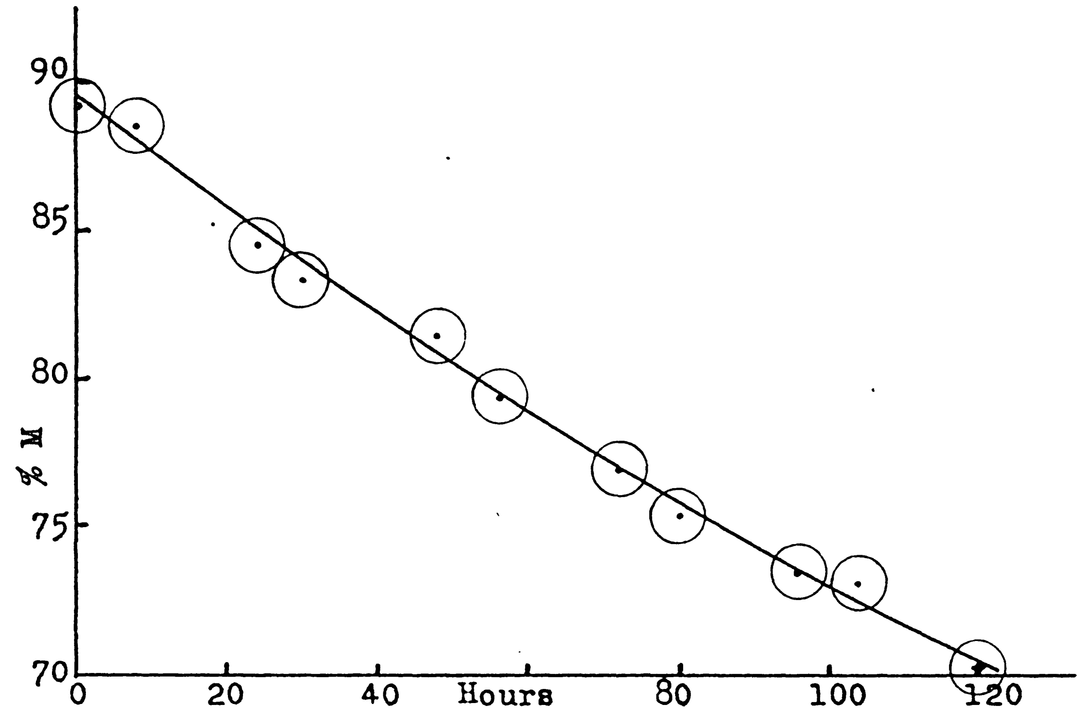
c. The polymer was a clear, light yellow colored plastic.

POLYMERIZATION: (17) Allylbutyrate with 0.01477 mol fraction of 1-hydroxycyclohexylhydroperoxide-1 at 60°C.

12.809 g. monomer   0.1982 g. catalyst

Remarks:

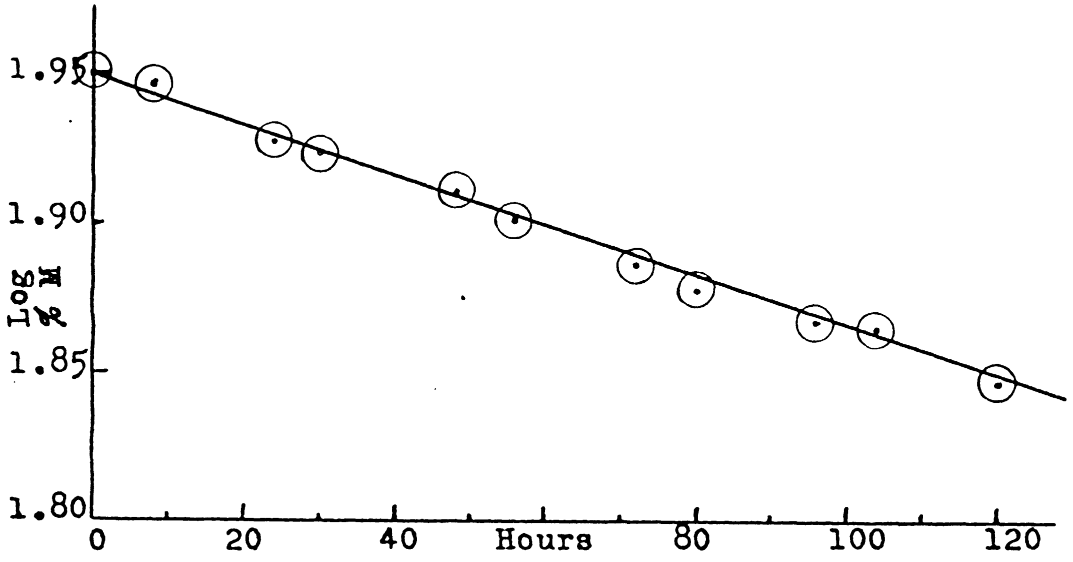
Several runs of this material were made but a continuous polymerization was not realized. Induction periods of several days were found. Induction periods also occurred after sampling. It was felt that this reaction rate was probably too slow to be measured by our technique.



Diethyleneglycol bis(allylcarbonate)

0.01477 m.f 1-hydroxycyclohexylhydroperoxide-1

K = 0.00193



POLYMERIZATION: (18) Diethyleneglycol bis(allylcarbonate) with 0.01477 mol fraction of 1-hydroxycyclohexylhydroperoxide-1 at 60°C.

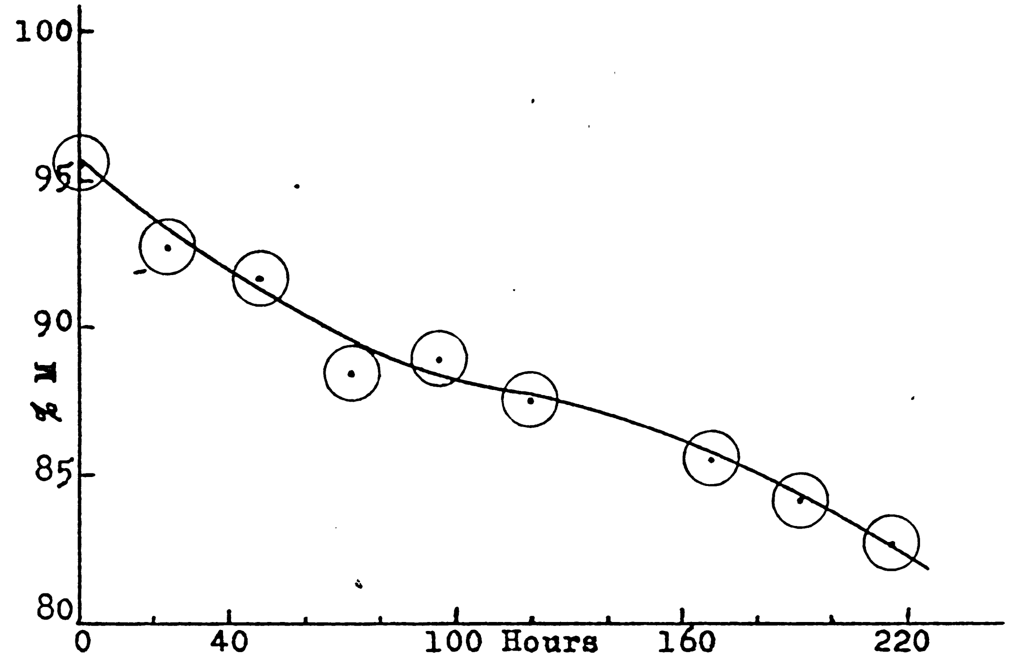
13.707 g. monomer 0.1982 g. catalyst

Time hours	Sample weight grams	Ml.Br	Ml.TS	Titre	% M	Log % M	Aliquot ml.
0	0.4254	15.00	10.57	4.43	89.2	1.950	1
8	0.3657	15.00	11.22	3.78	88.5	1.947	1
24	0.2948	15.00	12.09	2.91	84.5	1.927	1
30	0.3426	15.00	11.65	3.35	83.8	1.923	1
48	0.2324	15.00	12.79	2.21	81.5	1.911	1
56	0.1456	15.00	8.25	6.75	79.4	1.900	5
72	0.2392	20.00	9.26	10.74	76.9	1.886	5
80	0.2537	20.00	8.86	11.14	75.3	1.877	5
96	0.1789	15.00	7.33	7.67	73.4	1.866	5
104	0.1243	15.00	9.69	5.31	73.1	1.864	5
120	0.1475	15.00	8.97	6.03	70.2	1.846	5

Remarks:

a. The reactants became syrupy after 56 hours and formed a clear colorless jel which was insoluble in pyridine after 120 hours.

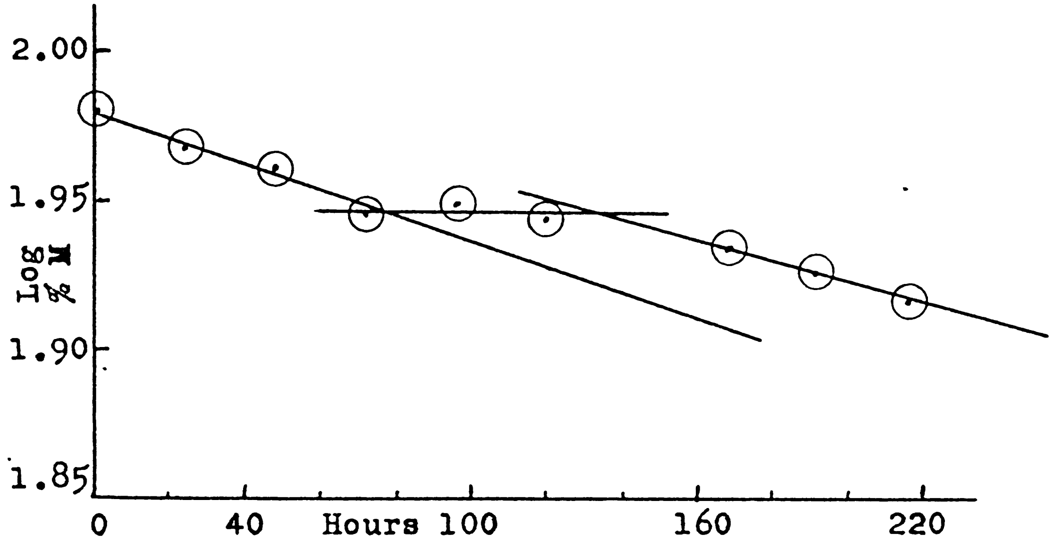
b. Samples were made less frequently than usual to avoid the chance of contamination.



Triallylcitrate

0.01477 m.f. 1-hydroxycyclohexylhydroperoxide-1

K = 0.00101



POLYMERIZATION (19) Triallylcitrate with 0.01477 mol fraction of 1-hydroxycyclohexylhydroperoxide-1 at 60°C.

15.615 g. monomer   0.0991 g. catalyst

Time hours	Sample weight grams	Ml.Br	Ml.TS	Titre	% M	Log % M	Aliquot ml.
0	0.2119	15.00	11.89	3.11	95.5	1.980	1
24	0.2394	15.00	11.59	3.41	92.7	1.967	1
48	0.2910	15.00	10.90	4.10	91.6	1.961	1
72	0.2362	15.00	11.79	3.21	88.3	1.946	1
96	0.1860	15.00	12.46	2.54	88.9	1.949	1
120	0.1495	15.00	4.93	10.07	87.5	1.942	5
168	0.1399	15.00	5.80	9.20	85.5	1.932	5
192	0.1841	15.00	3.10	11.90	84.1	1.925	5
216	0.1196	15.00	7.40	7.60	82.6	1.917	5

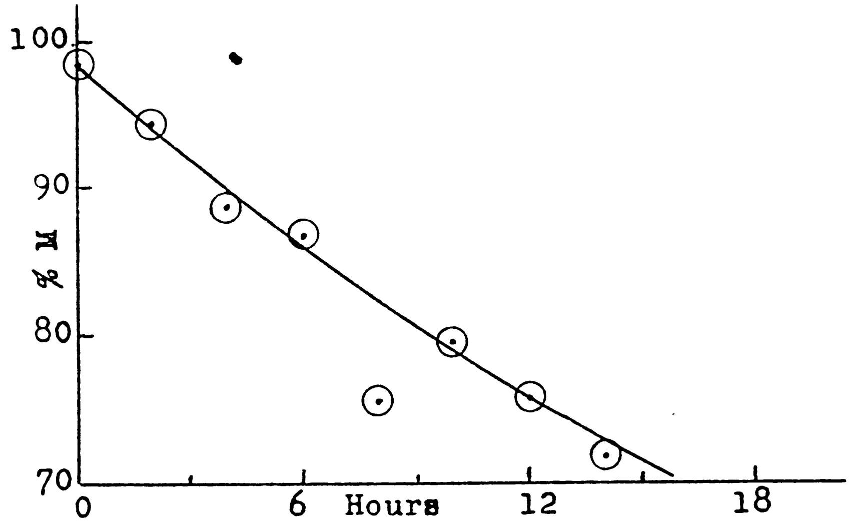
Remarks:

a. The reaction occurred so slowly that the minute impurities introduced in sampling caused induction periods of several days. This was the best of several runs.

b. The constant was calculated for the first slope.

c. It was felt that this data is only qualitative at best.

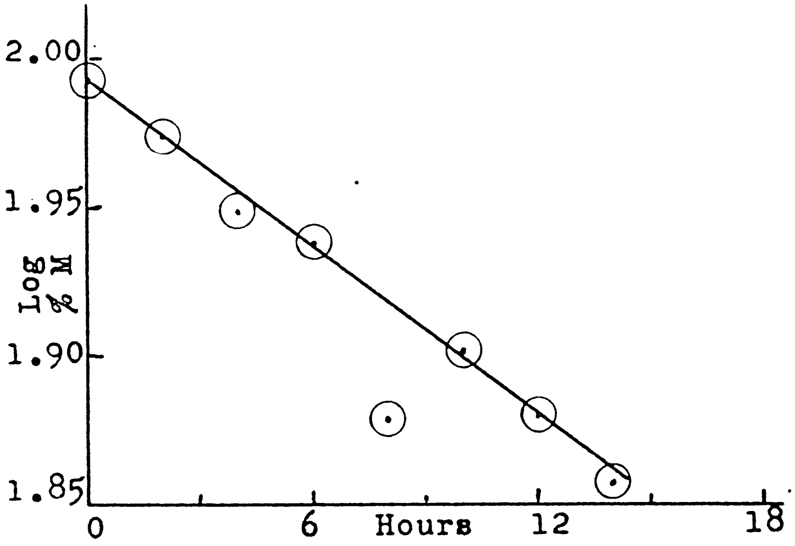
d. The clear, colorless reaction product was just beginning to get syrupy after 216 hours.



Isobutylmethacrylate

0.01477 m.f. 1-hydroxycyclohexylhydroperoxide-1

K = 0.0218



POLYMERIZATION: (20) Isobutylmethacrylate with 0.01477 mol fraction of 1-hydroxycyclohexylhydroperoxide-1 at 60°C.

14.219 g. monomer 0.1982 g. catalyst

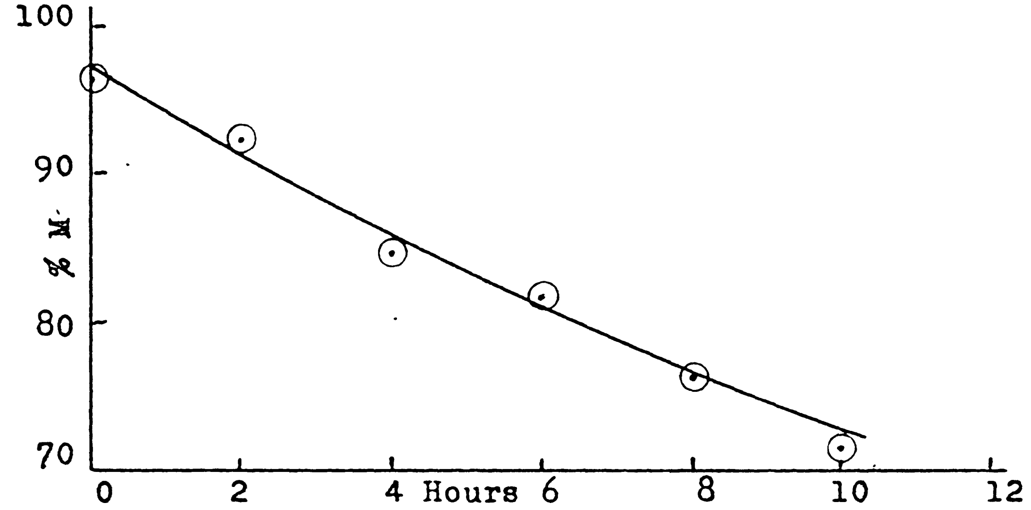
Time hours	Sample weight grams	Ml.Br	Ml.TS	Titre	% M	Log % M	Aliquot ml.
0	0.2318	15.00	12.43	2.57	98.4	1.993	1
2	0.2621	15.00	12.22	2.78	94.2	1.974	1
4	0.2521	15.00	12.48	2.52	88.7	1.948	1
6	0.2594	15.00	12.47	2.53	86.7	1.938	1
8	0.3010	15.00	12.44	2.56	75.5	1.878	1
10	0.2376	15.00	12.87	2.13	79.6	1.901	1
12	0.1652	15.00	7.95	7.05	75.7	1.879	5
14	0.1079	15.00	10.63	4.37	71.9	1.857	5

Remarks:

a. A hard, clear, colorless plastic was formed, which contained a few large bubbles.

b. The reaction tube had to be broken to take the 14 hour sample.

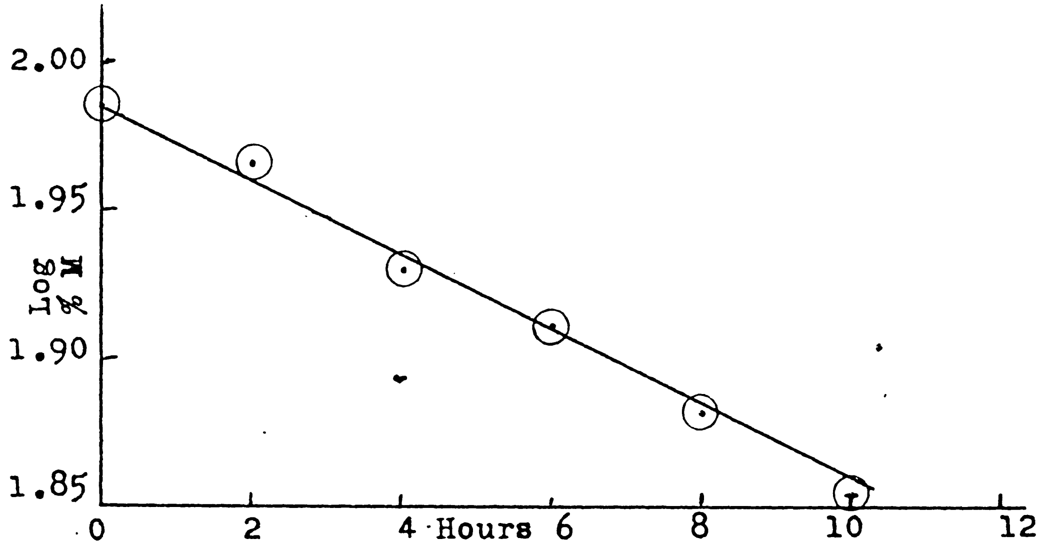
c. The 8 hour analysis was obviously incorrect.



Glycoldimethacrylate

0.01477 m.f. 1-hydroxycyclohexylhydroperoxide-1

K = 0.0287



POLYMERIZATION: (21) Glycoldimethacrylate with 0.01477 mol fraction of 1-hydroxycyclhexylhydroperoxide-1 at 60°C.

9.910 g. monomer 0.0991 g. catalyst

Time hours	Sample weight grams	Ml.Br	Ml.TS	Titre	% M	Log % M	Aliquot ml.
0	0.2299	15.00	11.42	3.58	96.4	1.984	1
2	0.1603	15.00	12.61	2.39	92.3	1.965	1
4	0.1932	15.00	12.35	2.65	84.7	1.928	1
6	0.2423	15.00	11.80	3.20	81.7	1.912	1
8	0.1221	15.00	7.48	7.52	76.2	1.882	5
10	0.1201	15.00	8.07	6.93	71.5	1.854	5
12	Reactants have formed an insoluble jel.						

Remarks:

a. Reactants were syrupy after 4 hours.

b. The product was clear and colorless.

c. After 24 hours the polymer was hard and brittle. It had shrunk considerably.

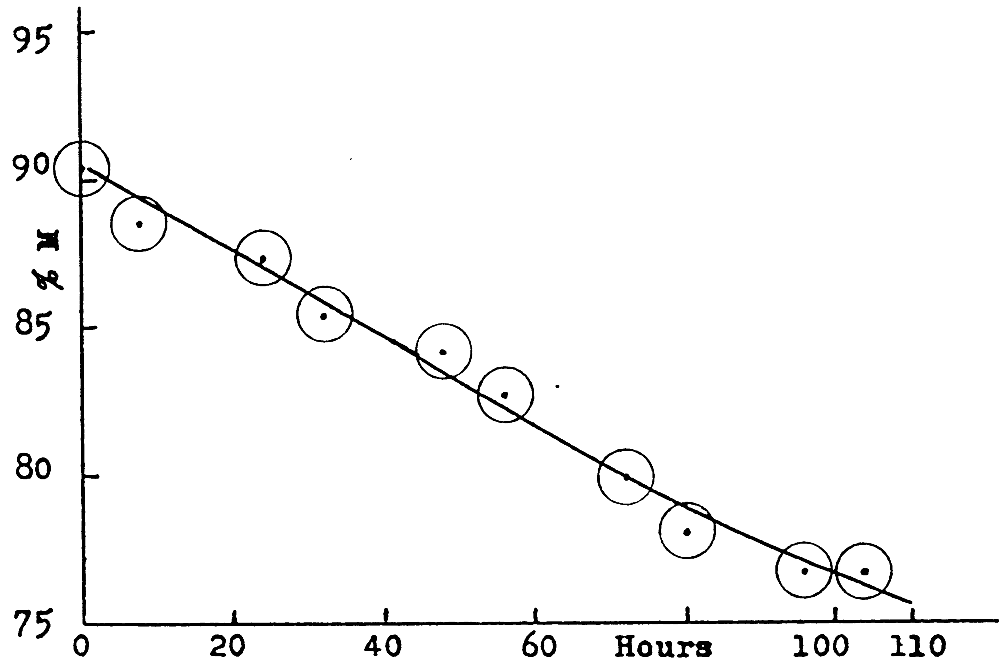
d. The pyridine-polymer solution was clear and colorless.

POLYMERIZATION: (22) Allylbutyrate with 0.01477 mol fraction of ditertiarybutyldiperphthalate at 60°C.

12.809 g. monomer   0.4655 g. catalyst

The reaction occurred so slowly that it was impossible to measure. Induction periods caused by introduction of minute impurities during sampling made the data discontinuous and meaningless. Two straight runs were made without success. A third run was made by sealing portions of the reactants in 6 mm. glass tubes and then polymerizing them. However, the data was still discontinuous.

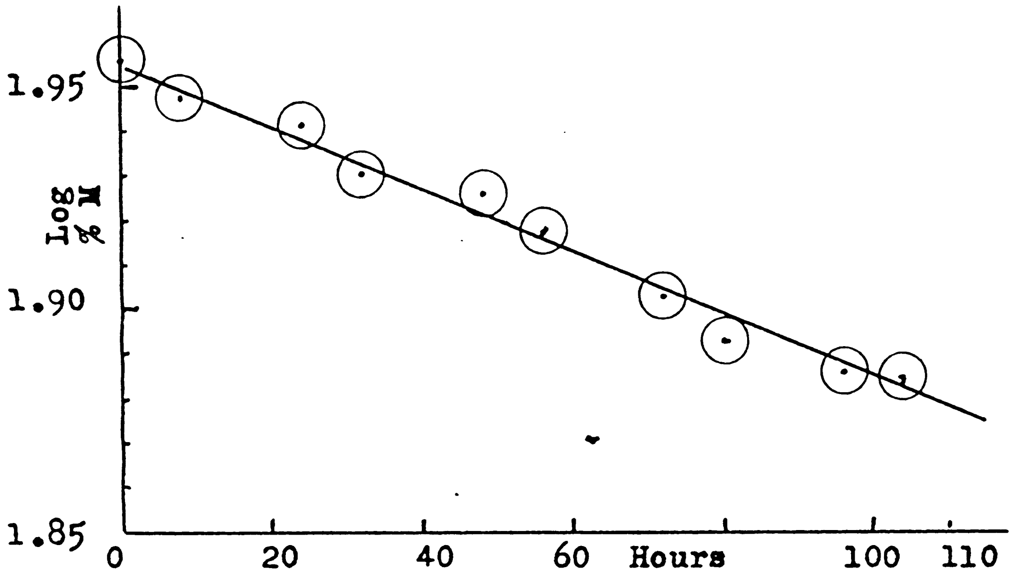
Crystallized catalyst was used in this experiment.



Diethyleneglycol bis(allylcarbonate)

0.01477 m.f. ditertiarybutyldiperphthalate

K = 0.00159



POLYMERIZATION: (23) Diethyleneglycol bis(allylcarbonate) with 0.01477 mol fraction of ditertiarybutyldiperphthalate at 60°C.

13.707 g. monomer   0.2327 g. catalyst

Time hours	Sample weight grams	Ml.Br	Ml.TS	Titre	% M	Log % M	Aliquot ml.
0	0.4462	15.00	10.29	4.71	90.4	1.956	1
8	0.3726	15.00	11.15	3.85	88.5	1.947	1
24	0.2471	15.00	12.48	2.52	87.3	1.941	1
32	0.3586	15.00	11.43	3.57	85.3	1.931	1
48	0.3179	15.00	11.88	3.12	84.1	1.925	1
56	0.2597	15.00	12.50	2.50	82.6	1.917	1
72	0.2021	15.00	5.59	9.41	79.8	1.902	5
80	0.1355	15.00	8.73	6.27	78.0	1.892	5
96	0.1584	15.00	7.91	7.09	76.7	1.885	5
104	0.1214	15.00	9.57	5.43	76.6	1.884	5

Remarks:

a. The reactants became syrupy after about 56 hours.

b. An insoluble jel formed before the 120 hour sample was taken.

c. A clear, colorless jel was formed which contained no bubbles.

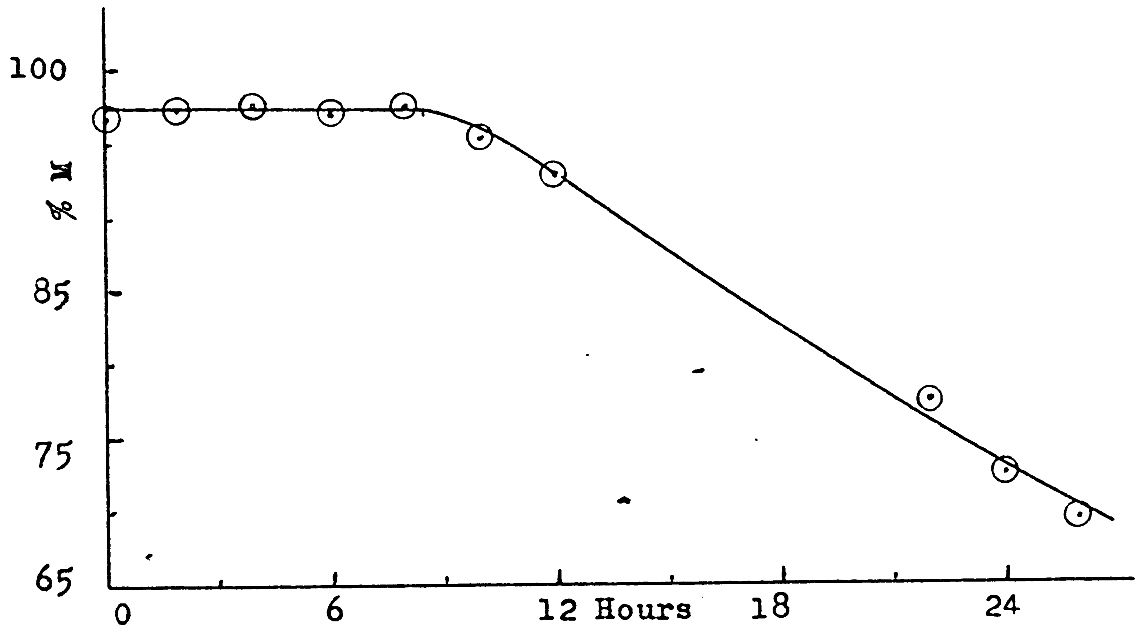
d. Crystallized catalyst was used in this experiment.

POLYMERIZATION: (24) Triallylcitrate with 0.01477 mol fraction of ditertiarybutyldiperphthalate at 60°C.

15.615 g. monomer 0.2327 g. catalyst

Three runs were made. The data was inconsistent. The reaction rate was so slow that impurities introduced when sampling created long induction periods.

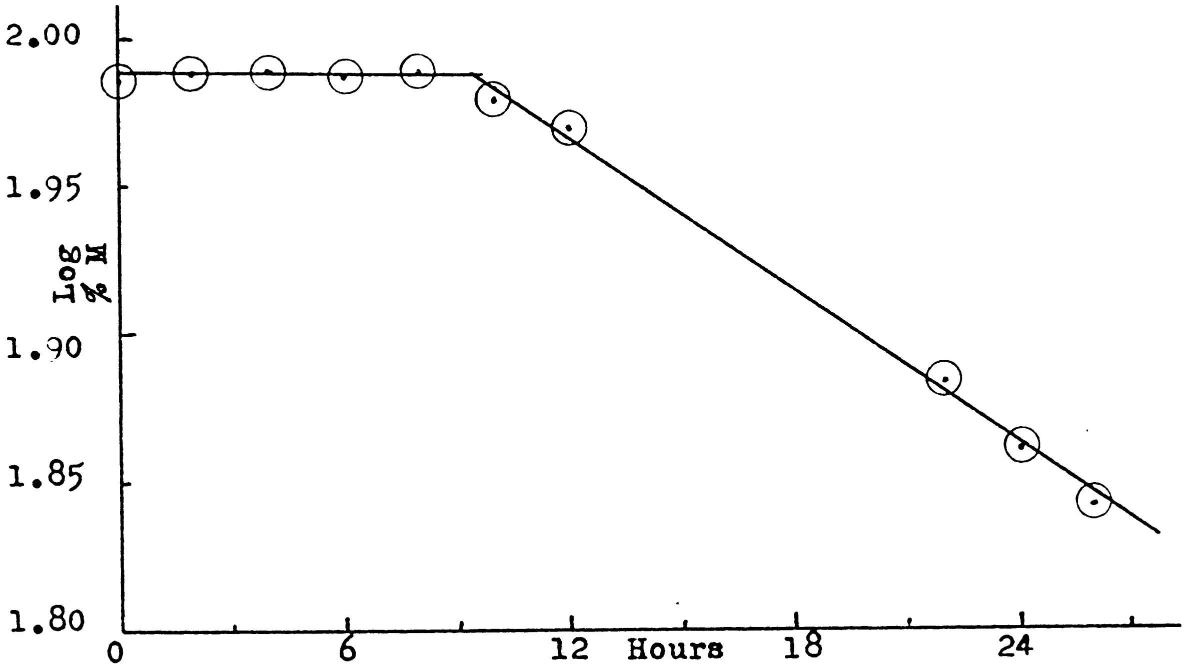
Crystallized catalyst was used in these experiments



Isobutylmethacrylate

0.01477 m.f. ditertiarybutyldiperphthalate

K = 0.0198



POLYMERIZATION: (25) Isobutylmethacrylate with 0.01477 mol fraction of ditertiarybutyldiperphthalate at 60°C.

14.219 g. monomer 0.4655 g. catalyst

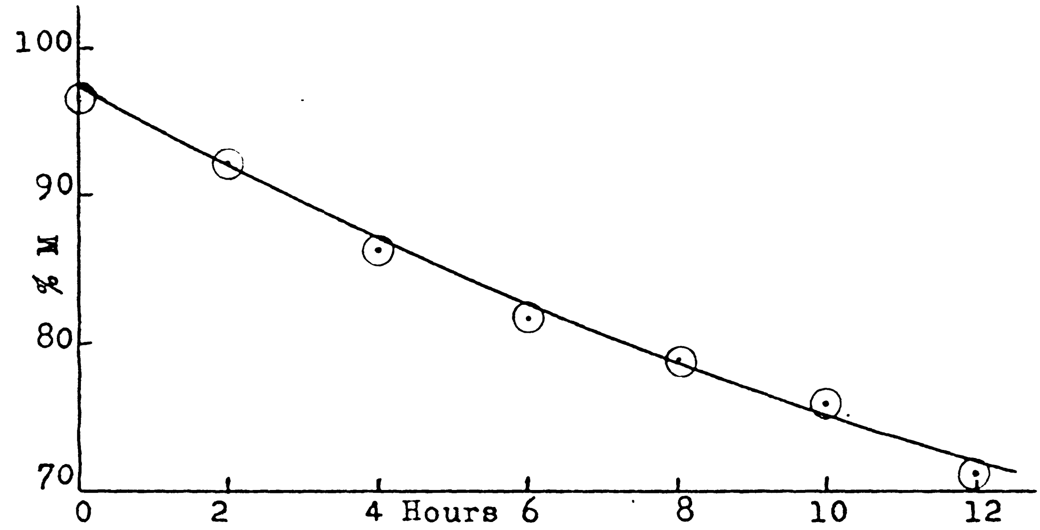
Time hours	Sample weight grams	Ml.Br	Ml.TS	Titre	% M	Log % M	Aliquot ml.
0	0.2621	15.00	12.14	2.86	96.8	1.986	1
2	0.2722	15.00	12.02	2.98	97.2	1.988	1
4	0.2868	15.00	11.85	3.15	97.5	1.989	1
6	0.2202	15.00	12.59	2.41	97.0	1.987	1
8	0.2118	15.00	12.68	2.32	97.3	1.988	1
10	0.2189	15.00	12.66	2.34	95.1	1.978	1
12	0.1636	15.00	6.43	8.57	92.9	1.968	5
22	0.1251	15.00	9.63	5.37	76.2	1.882	5
24	0.1432	15.00	9.16	5.84	72.3	1.859	5
26	0.1400	15.00	9.54	5.46	69.3	1.841	5

Remarks:

a. About a 9 hour induction period was found.

b. The catalyst is a was like substance which dissolved very readily in the monomer. It left a dirty grey precipitate in the reaction tube after dissolving.

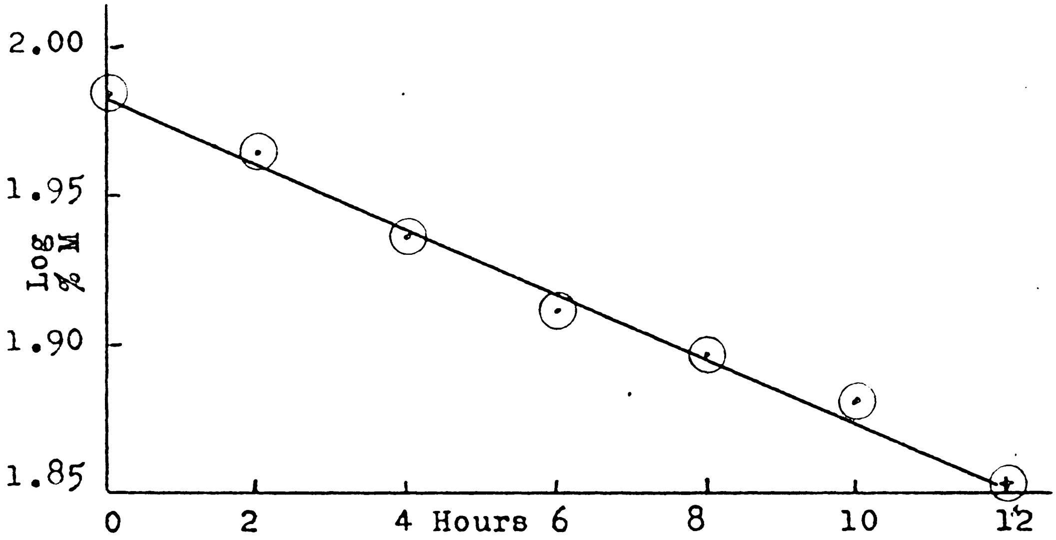
c. The reaction tube had to be broken in order to take the 26 hour sample.



Isobutylmethacrylate

0.01477 m.f. ditertiarybutyldiperphthalate

K = 0.0250



POLYMERIZATION: (25-a) Isobutylmethacrylate with 0.01477 mol fraction of ditertiarybutyldiperphthalate at 60°C.

14.219 g. monomer 0.4655 g. catalyst

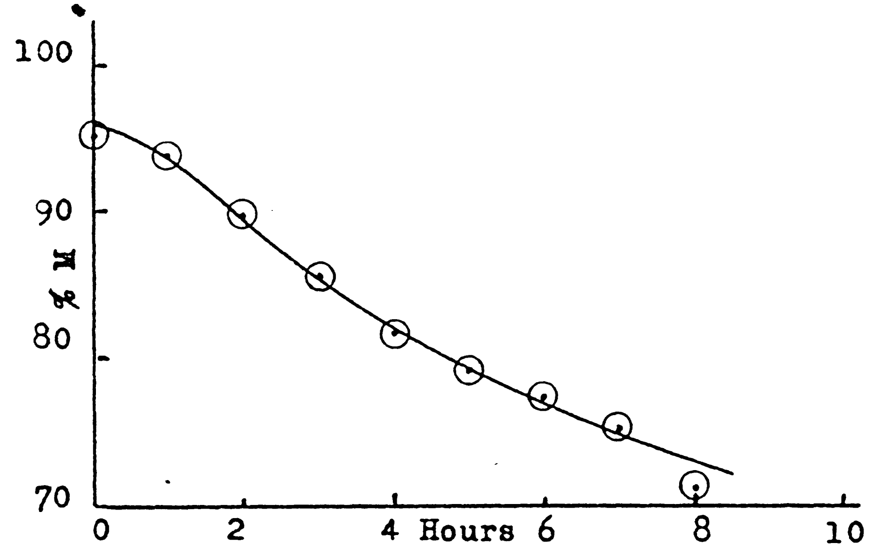
Time hours	Sample weight grams	Ml.Br	Ml.TS	Titre	% M	Log % M	Aliquot ml.
0	0.3492	15.00	11.21	3.79	96.4	1.984	1
2	0.3731	15.00	11.13	3.87	92.0	1.964	1
4	0.3665	15.00	11.44	3.56	86.3	1.936	1
6	0.2185	15.00	12.99	2.01	81.7	1.912	1
8	0.2810	15.00	12.50	2.50	78.9	1.897	1
10	0.1944	15.00	6.68	8.32	76.0	1.881	5
12	0.2242	15.00	5.98	9.02	71.3	1.853	5
24	Hard, clear, colorless plastic						

Remarks:

a. This run was made with catalyst which had been crystallized from methanol.

b. The induction period was eliminated and a slightly faster reaction rate was observed.

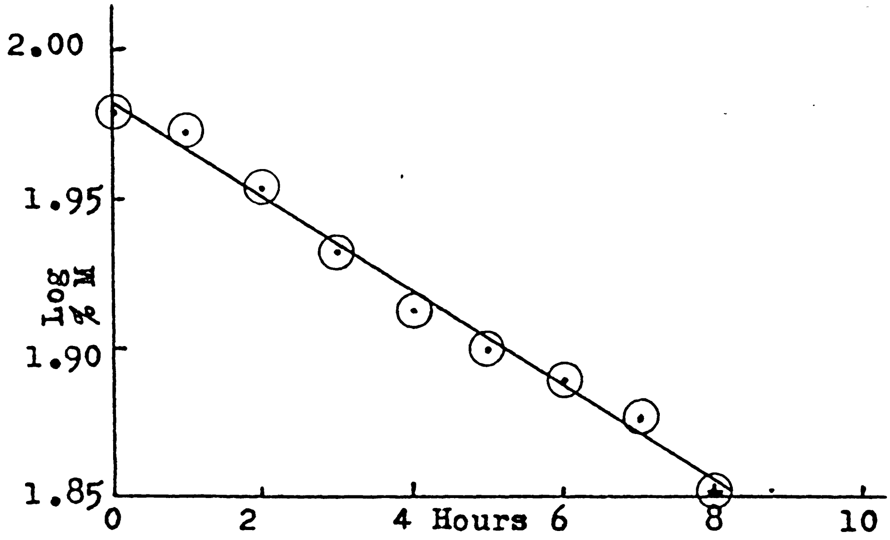
c. The pyridine-polymer solution was colorless.



Glycoldimethacrylate

0.01477 m.f. ditertiarybutyldiperphthalate

K = 0.0364



POLYMERIZATION: (26) Glycoldimethacrylate with 0.01477 mol fraction of ditertiarybutyldiperphthalate at 60°C.

19.821 g. monomer 0.4655 g. catalyst

Time hours	Sample weight grams	Ml.Br	Ml.TS	Titre	% M	Log % M	Aliquot ml.
0	0.2975	15.00	10.43	4.57	95.1	1.978	1
1	0.2551	15.00	11.13	3.87	93.8	1.972	1
2	0.3351	15.00	10.13	4.87	89.7	1.953	1
3	0.2111	15.00	12.08	2.92	85.5	1.932	1
4	0.3029	15.00	11.00	4.00	81.7	1.912	1
5	0.2985	15.00	11.18	3.82	79.2	1.899	1
6	0.1820	20.00	8.63	11.37	77.3	1.888	5
7	0.1069	15.00	8.51	6.49	75.2	1.876	5
8	0.1051	15.00	8.97	6.03	71.1	1.852	5

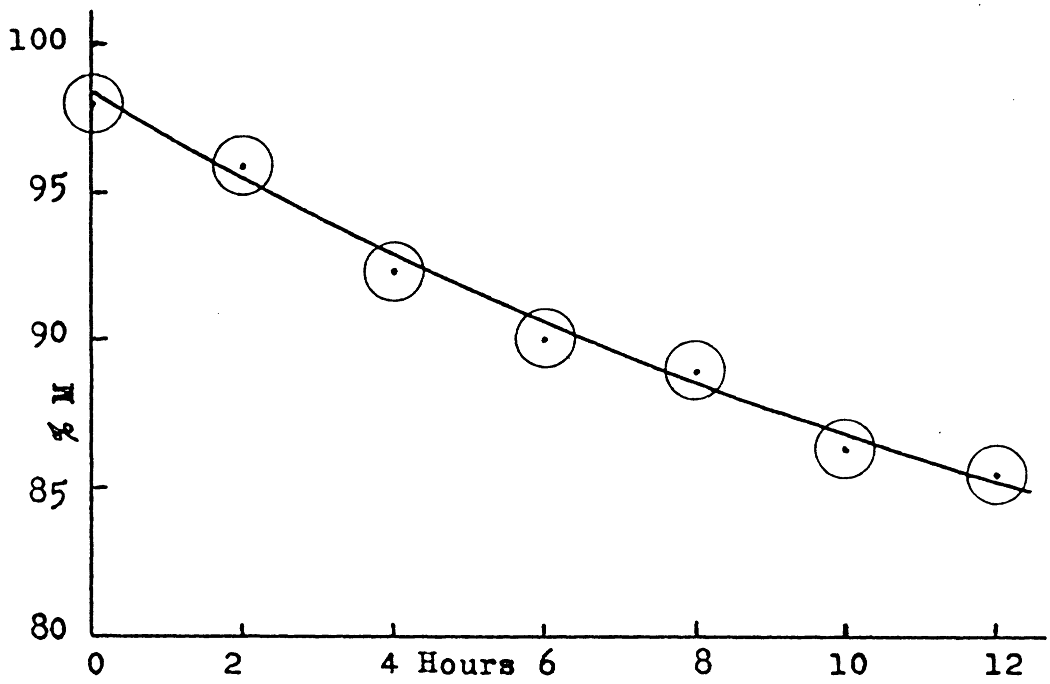
Remarks:

a. The reactants became syrupy after 3 hours.

b. The reaction tube had to be broken to take the 8 hour sample.

c. The polymer was clear and colorless.

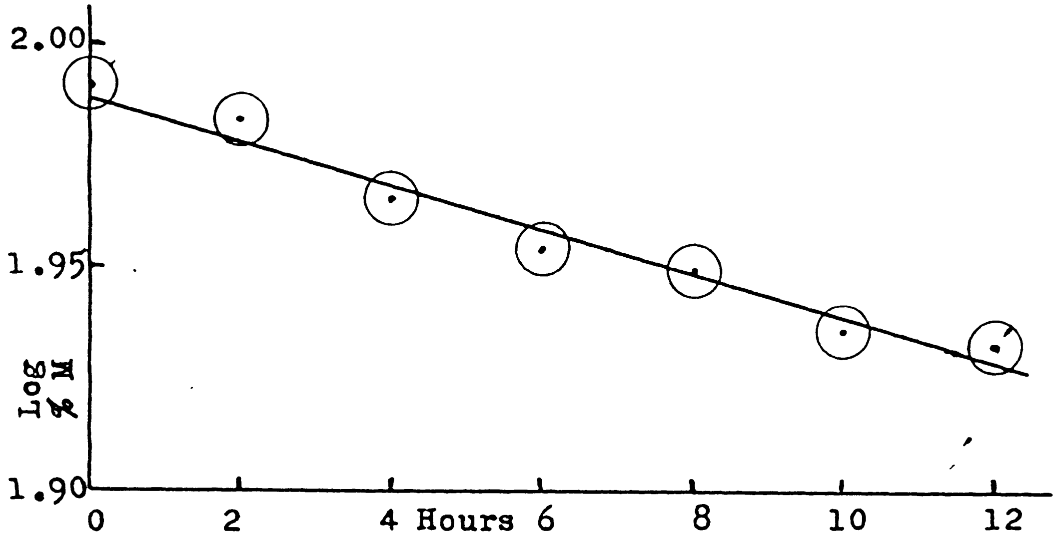
d. Recrystallized catalyst was used in this experiment.



Allylbutyrate

0.01477 m.f. diazoaminobenzene

K = 0.0113



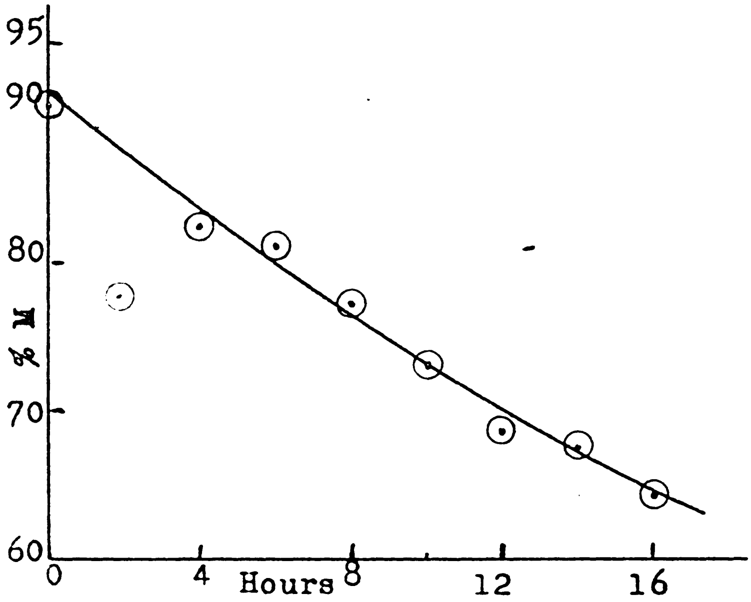
POLYMERIZATION: (27) Allylbutyrate with 0.01477 mol fraction of diazoaminobenzene at 60°C.

12.809 g. monomer 0.2958 g. catalyst

Time hours	Sample weight grams	Ml.Br	Ml.TS	Titre	% M	Log % M	Aliquot ml.
0	0.2489	15.00	11.95	3.05	98.0	1.991	1
2	0.2033	15.00	12.57	2.43	95.9	1.982	1
4	0.3184	15.00	11.32	3.68	92.3	1.965	1
6	0.1221	15.00	8.13	6.87	90.0	1.954	5
8	0.1153	15.00	8.58	6.42	88.9	1.949	5
10	0.1471	15.00	7.06	7.94	86.3	1.936	5
12	0.1197	15.00	8.61	6.39	85.5	1.932	5

Remarks:

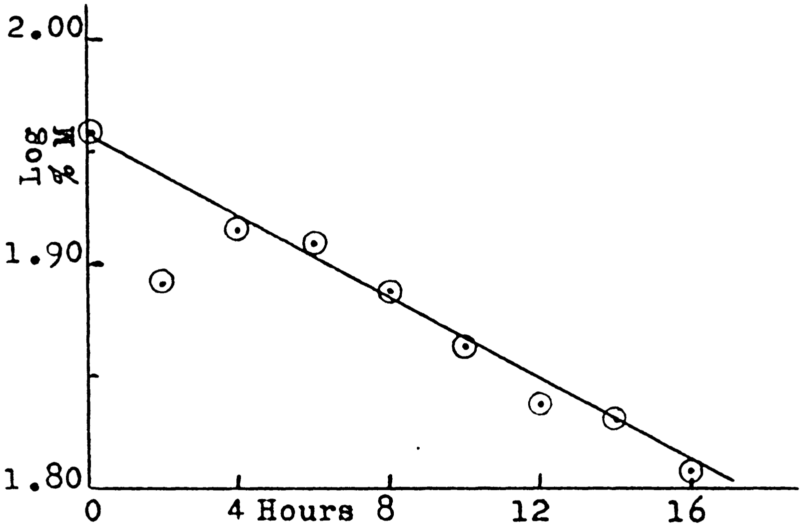
a. The reactants were a clear light tan colored liquid.



Diethyleneglycol bis(allylcarbonate)

0.01477 m.f. diazoaminobenzene

K = 0.0208



POLYMERIZATION: (28) Diethyleneglycol bis(allylcarbonate) with 0.01477 mol fraction of diazoaminobenzene at 60°C.

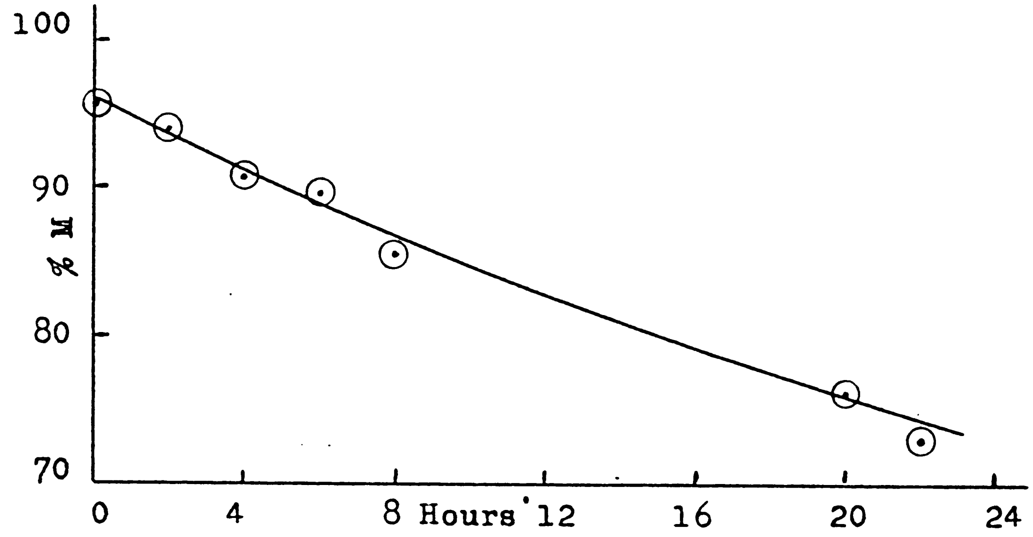
13.707 g. monomer 0.1479 g. catalyst

Time hours	Sample weight grams	Ml.Br	Ml.TS2	Titre	% M	Log % M	Aliquot ml.
0	0.2979	15.00	11.84	3.16	90.8	1.958	1
2	0.2414	15.00	12.81	2.19	77.8	1.891	1
4	0.2817	15.00	12.29	2.71	82.4	1.916	1
6	0.1506	15.00	7.88	7.12	81.1	1.909	5
8	0.1384	15.00	8.77	6.23	77.1	1.887	5
10	0.1673	15.00	8.87	6.13	73.0	1.863	5
12	0.2203	15.00	6.18	8.82	68.5	1.836	5
14	0.1114	15.00	10.61	4.39	67.6	1.830	5
16	0.1788	15.00	8.31	6.69	64.1	1.807	5

Remarks:

a. This experiment consists of two runs, each made with the same amount of reactants. The second run was set up in the evening when it was seen that the first was not going to solidify within 10 hours.

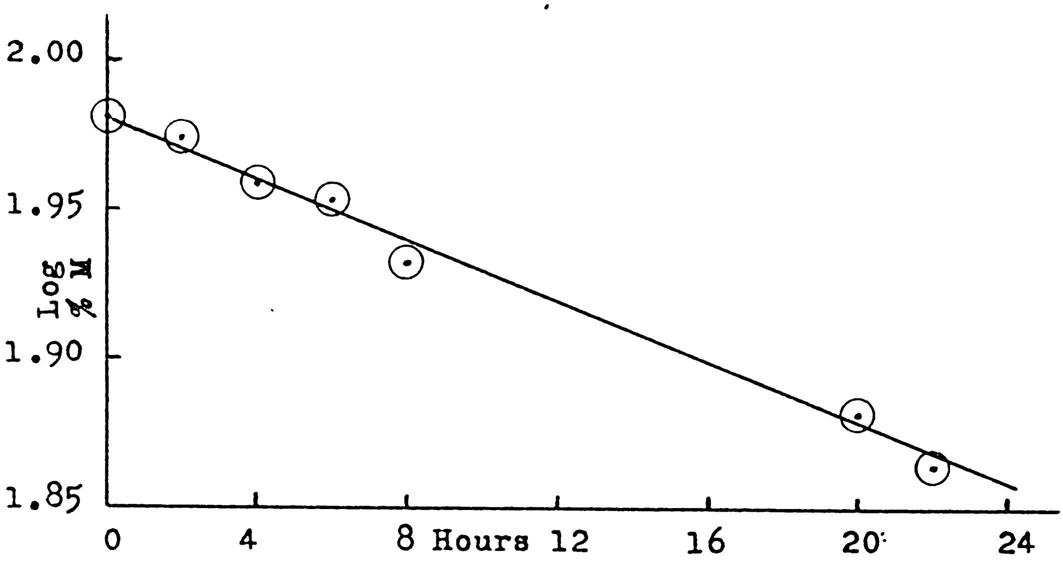
b. The clear, light tan colored reaction mixture became syrupy after about 10 hours and formed an insoluble jel just after 16 hours.



Triallylcitrate

0.01477 m.f. diazoaminobenzene

K = 0.0117



POLYMERIZATION: (29) Triallylcitrate with 0.01477 mol fraction of diazoaminobenzene at 60°C.

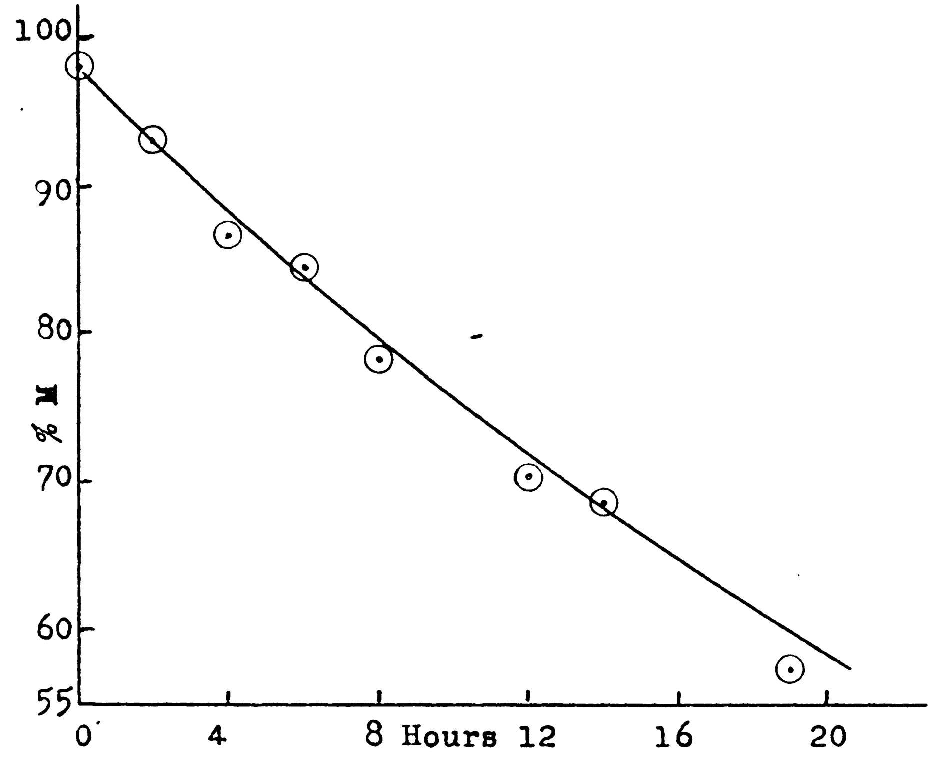
15.615 g. monomer 0.1479 g. catalyst

Time hours	Sample weight grams	Ml.Br	Ml.TS	Titre	% M	Log % M	Aliquot ml.
0	0.2256	15.00	11.69	3.31	95.7	1.981	1
2	0.3234	15.00	10.33	4.67	94.0	1.973	1
4	0.3090	15.00	10.68	4.32	90.8	1.958	1
6	0.3018	15.00	10.84	4.16	89.7	1.953	1
8	0.1136	15.00	7.57	7.43	85.5	1.932	5
20	0.1249	15.00	7.68	7.32	76.2	1.882	5
22	0.1384	15.00	7.22	7.78	73.1	1.864	5
24	Jel insoluble in pyridine.						

Remarks:

a. The reactants formed a clear, light tan colored solution.

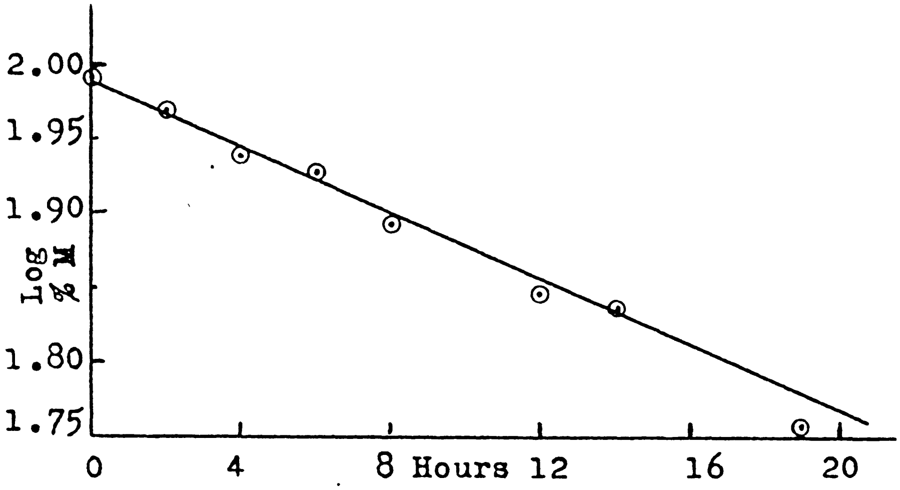
b. The reaction was started at noon, allowed to continue during the night and was completed the following morning.



Isobutylmethacrylate

0.01477 m.f. diazoaminobenzene

K = 0.0279



POLYMERIZATION: (30) Isobutylmethacrylate with 0.01477 mol fraction of diazoaminobenzene at 60°C.

14.219 g. monomer 0.2958 g. catalyst

Time hours	Sample weight grams	Ml.Br	Ml.TS	Titre	% M	Log % M	Aliquot ml.
0	0.2564	15.00	12.17	2.83	98.0	1.991	1
2	0.2253	15.00	12.64	2.36	93.1	1.969	1
4	0.1526	15.00	13.51	1.49	86.7	1.938	1
6	0.2075	15.00	5.12	9.88	84.5	1.927	5
8	0.1239	15.00	9.54	5.46	78.2	1.893	5
12	0.1463	15.00	9.22	5.78	70.2	1.846	5
14	0.1142	15.00	10.58	4.42	68.6	1.836	5
19	0.1079	15.00	11.53	3.47	57.2	1.757	5

Remarks:

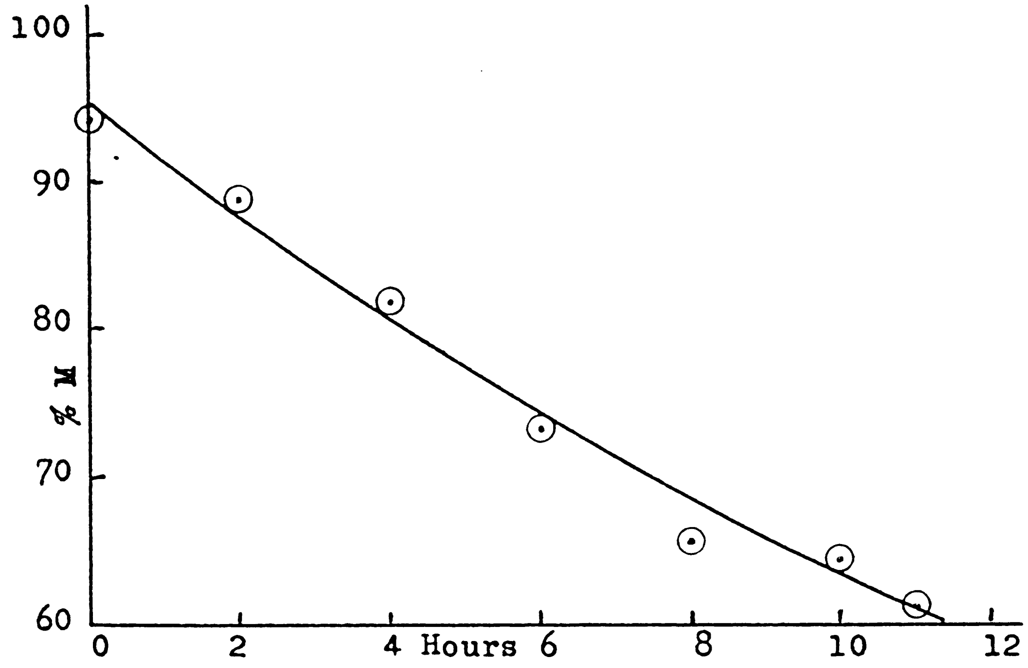
a. The reaction solution was a clear, light tan liquid which formed a light tan colored polymer.

b. The reactants had not solidified after 14 hours. Another run was started the next evening and stopped after 19 hours, the solidification point.

c. The reactants were syrupy after 12 hours.

d. Some chain transfer had occurred.

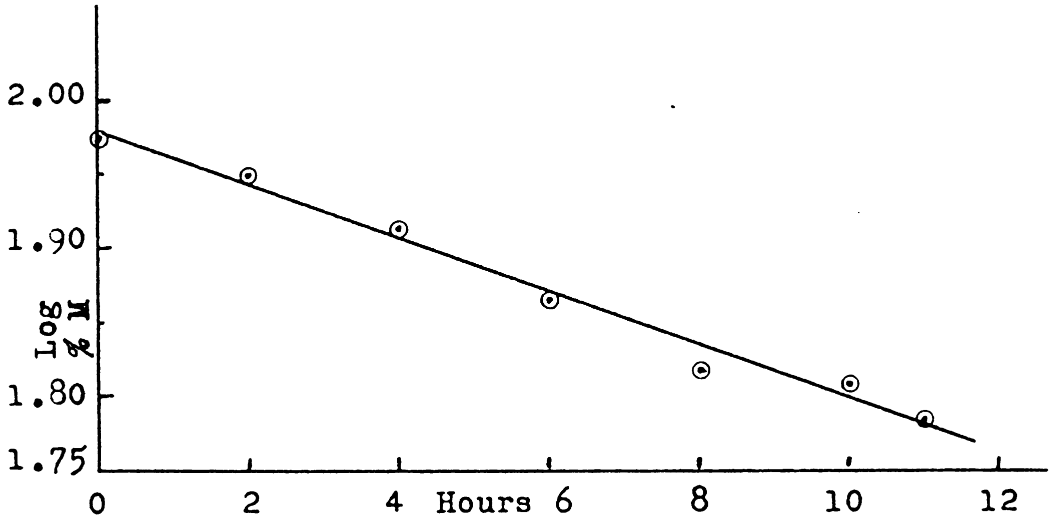
e. Some gas bubbles were caught in the polymer.



Glycoldimethacrylate

0.01477 m.f. diazoaminobenzene

K = 0.0412



POLYMERIZATION: (31) Glycoldimethacrylate with 0.01477 mol fraction of diazoaminobenzene at 60°C.

19.821 g. monomer   0.2958 g. catalyst

Time hours	Sample weight grams	Ml.Br	Ml.TS	Titre	% M	Log % M	Aliquot ml.
0	0.2605	15.00	11.04	3.96	94.2	1.974	1
2	0.2304	15.00	11.69	3.31	88.9	1.949	1
4	0.2529	15.00	11.66	3.34	81.8	1.913	1
6	0.1301	15.00	7.32	7.68	73.1	1.864	5
8	0.1589	15.00	6.59	8.41	65.6	1.817	5
10	0.1873	15.00	5.26	9.74	64.3	1.808	5
11	0.1363	15.00	8.27	6.73	61.1	1.786	5
12	Jel insoluble in pyridine.						

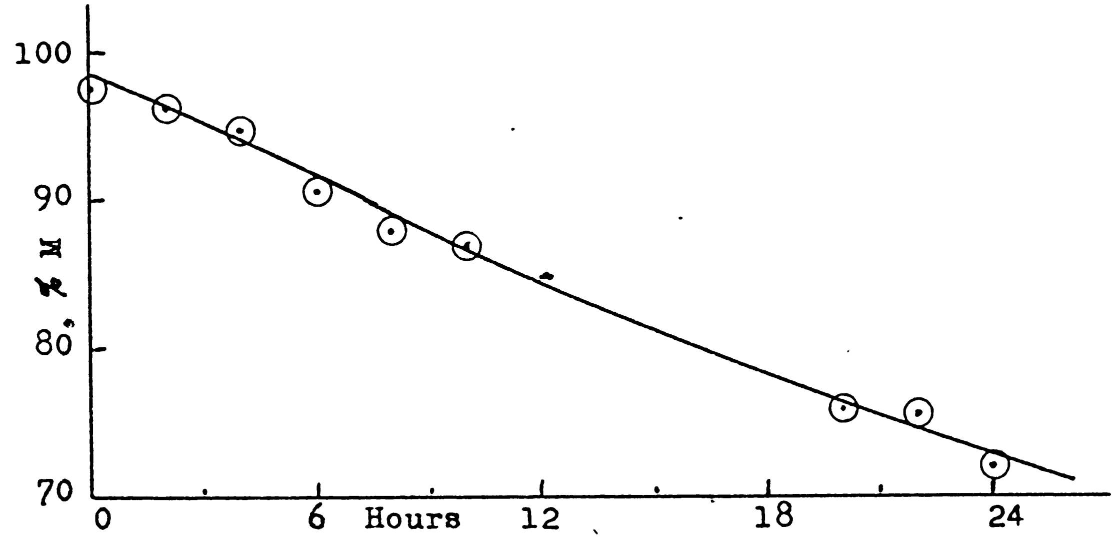
Remarks:

a. The reactants formed a clear light tan colored liquid.

b. The reactants became syrupy after 6 hours.

c. The low unsaturation at the jel point indicates a chain transfer reaction.

d. The jel was a clear tan color and contained a few small bubbles.

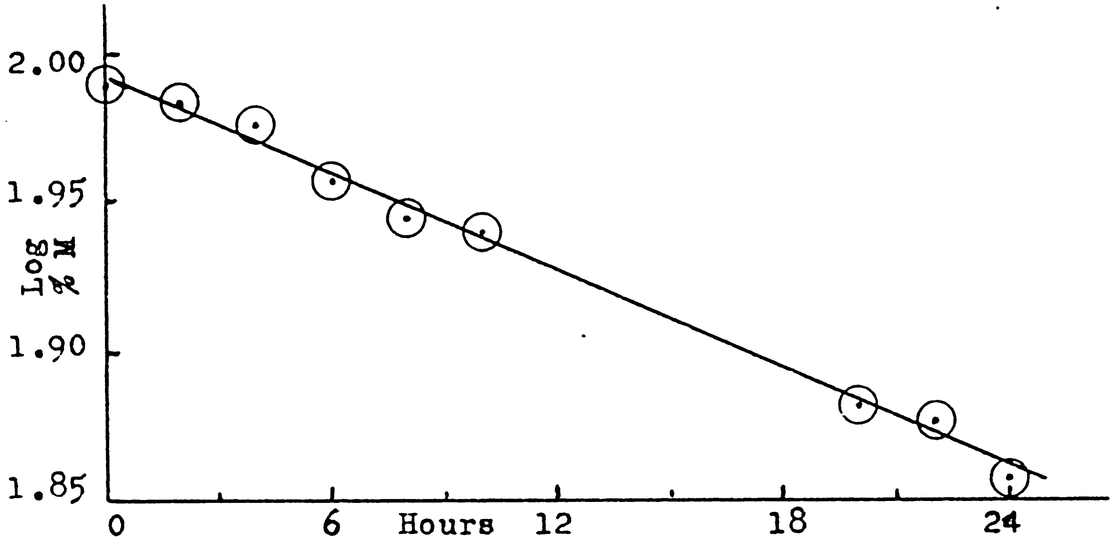


Allylbutyrate

0.0049 m.f. diazoaminobenzene

0.0147 m.f. benzoylperoxide

K = 0.0125



POLYMERIZATION: (32) Allylbutyrate with 0.0147 mol fraction of benzoylperoxide and 0.0049 mol fraction of diazoaminobenzene at 60°C.

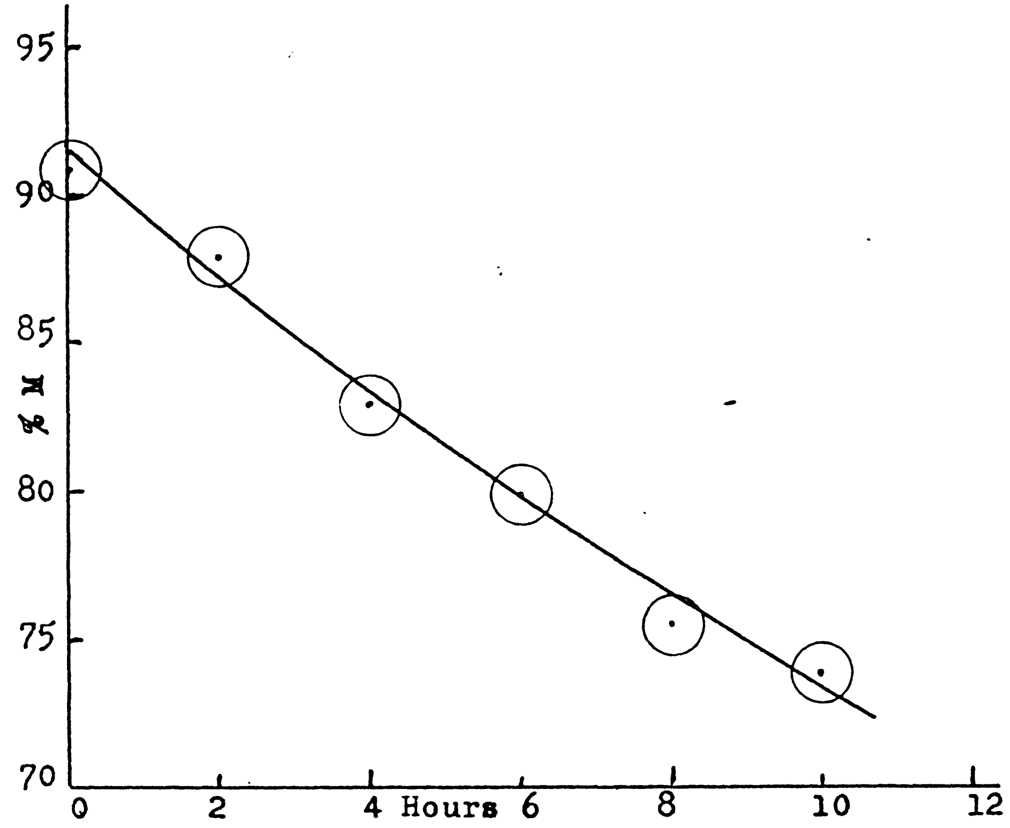
12.809 g. monomer 0.3631 g. catalyst 0.0986 g. promoter

Time hours	Sample weight grams	Ml.Br	Ml.TS	Titre	% M	Log % M	Aliquot ml.
0	0.3827	15.00	10.33	4.67	97.5	1.989	1
2	0.2795	15.00	11.64	3.36	96.2	1.983	1
4	0.1471	15.00	13.26	1.74	94.6	1.976	1
6	0.1850	15.00	4.53	10.47	90.6	1.957	5
8	0.1876	15.00	4.69	10.31	87.9	1.944	5
10	0.1444	15.00	7.15	7.85	86.9	1.939	5
22	0.1158	15.00	9.55	5.45	75.3	1.877	5
24	0.1132	15.00	9.91	5.09	72.0	1.857	5

Remarks:

a. The light tan color of the clear reaction liquor darkened somewhat after 24 hours.

b. The reactants were slightly more viscous after 24 hours.

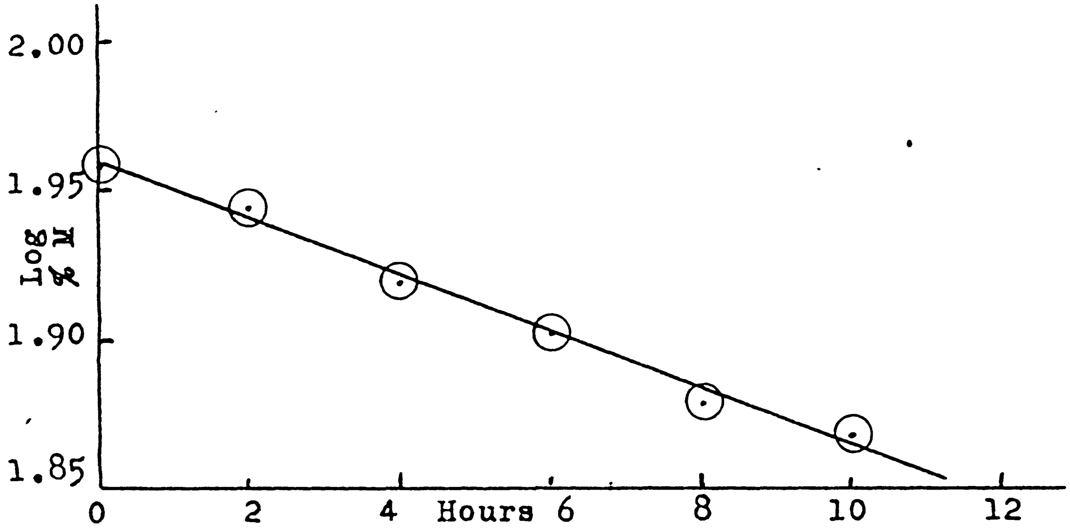


Diethyleneglycol bis(allylcarbonate)

0.0147 m.f. benzoylperoxide

0.0049 m.f. diazoaminobenzene

K = 0.0219



POLYMERIZATION: (33) Diethyleneglycol bis(allylcarbonate) with 0.0147 mol fraction of benzoylperoxide and 0.0049 mol fraction of diazoaminobenzene at 60°C.

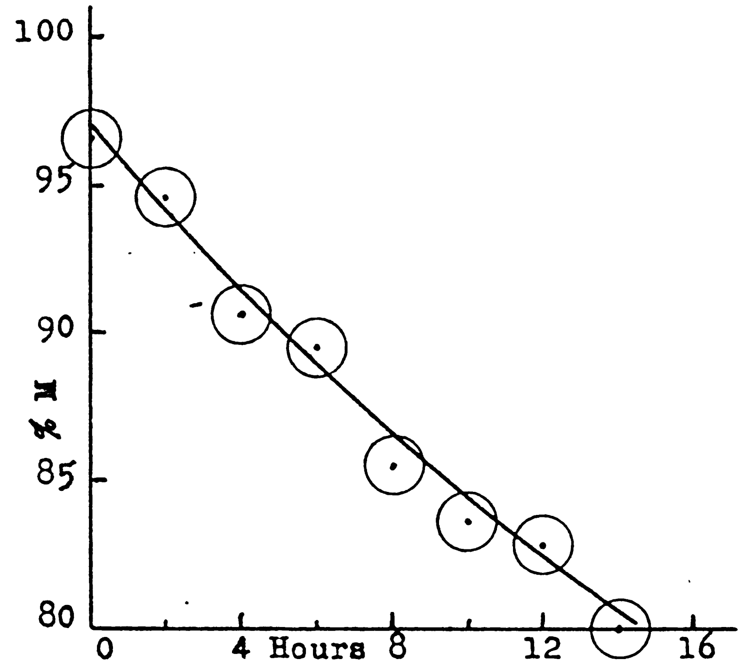
13.707 g. monomer 0.1815 g. catalyst 0.0493 g. promoter

Time hours	Sample weight grams	Ml.Br	Ml.TS	Titre	% M	Log % M	Aliquot ml.
0	0.2054	15.00	12.82	2.18	90.8	1.958	1
2	0.2601	15.00	12.33	2.67	87.9	1.944	1
4	0.2853	15.00	12.24	2.76	82.8	1.918	1
6	0.1655	15.00	7.29	7.71	79.8	1.902	5
8	0.1352	15.00	9.03	5.97	75.5	1.878	5
10	0.1021	15.00	10.61	4.39	73.8	1.868	5
12	Jel was insoluble in pyridine.						

Remarks:

a. The reactants formed a clear light yellow solution which darkened to a bright reddish-brown after polymerizatioh.

b. Many large bubbles were dispersed in the polymer.

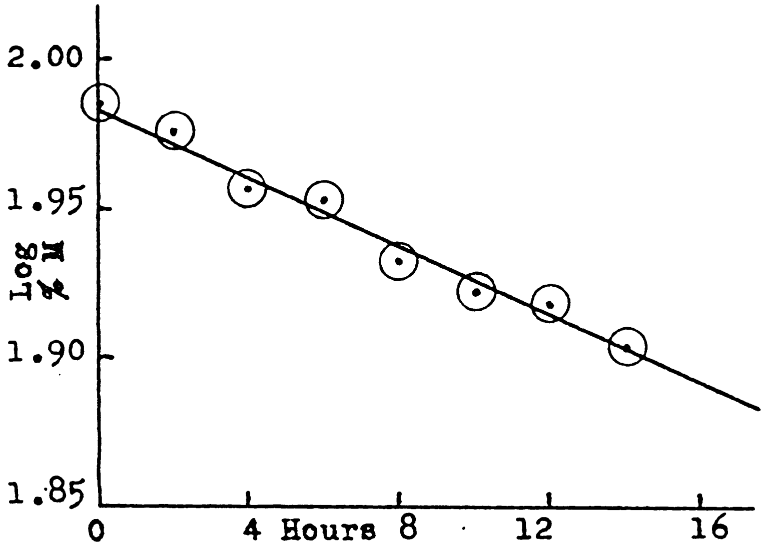


Triallylcitrate

0.0147 m.f. benzoylperoxide

0.0049 m.f. diazoaminobenzene

K = 0.01314



POLYMERIZATION:(34) Triallylcitrate with 0.0147 mol fraction of benzoylperoxide and 0.0049 mol fraction of diazoaminobenzene at 60°C.

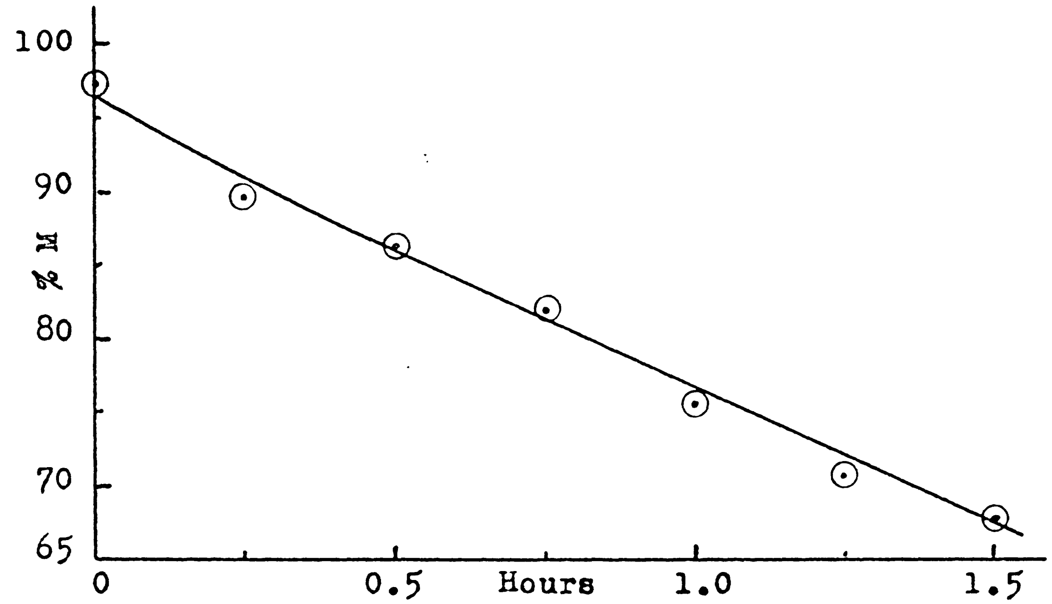
15.615 g. monomer 0.1815 g. catalyst 0.0493 g. promoter

Time hours	Sample weight grams	Ml.Br	Ml.TS	Titre	% M	Log % M	Aliquot ml.
0	0.2702	15.00	10.98	4.02	96.6	1.985	1
2	0.1628	15.00	12.63	2.37	94.6	1.976	1
4	0.1254	15.00	6.26	8.74	90.6	1.957	5
6	0.1833	15.00	12.47	2.53	89.5	1.952	1
8	0.1781	15.00	12.66	2.34	85.5	1.932	1
10	0.1982	15.00	12.45	2.55	83.6	1.922	1
12	0.1987	15.00	12.47	2.53	82.8	1.918	1
14	0.1625	15.00	13.00	2.00	80.0	1.903	1
24	Firm jel, insoluble in pyridine, has many bubbles.						

Remarks:

a. The monomer solution was a clear yellowish-brown liquid.

b. The reactants were almost solid after 14 hours. It was felt that they were probably a solid jel after about 15-16 hours.

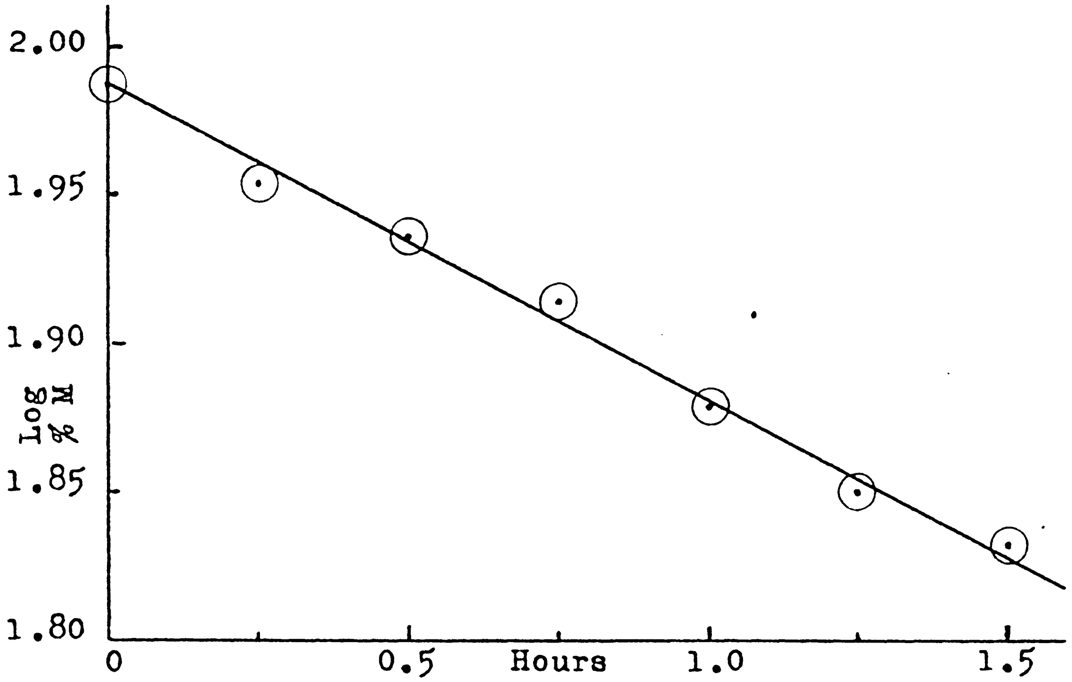


Isobutylmethacrylate

0.0147 m.f. benzoylperoxide

0.0049 m.f. diazoaminobenzene

K = 0.2512



POLYMERIZATION: (35) Isobutylmethacrylate with 0.0147 mol fraction of benzoylperoxide and 0.0049 mol fraction of diazoaminobenzene at 60°C.

14.219 g. monomer 0.3631 g. catalyst 0.0986 g. promoter

Time hours	Sample weight grams	Ml.Br	Ml.TS	Titre	% M	Log % M	Aliquot ml.
0	0.2872	15.00	11.85	3.15	97.3	1.988	1
0.25	0.2550	15.00	12.42	2.58	89.7	1.953	1
0.50	0.1835	15.00	6.07	8.93	86.3	1.936	5
0.75	0.2234	15.00	4.70	10.30	81.8	1.913	5
1.00	0.1730	15.00	7.64	7.36	75.5	1.878	5
1.25	0.1084	15.00	10.68	4.32	70.6	1.849	5
1.50	0.1236	15.00	10.28	4.72	67.8	1.831	5

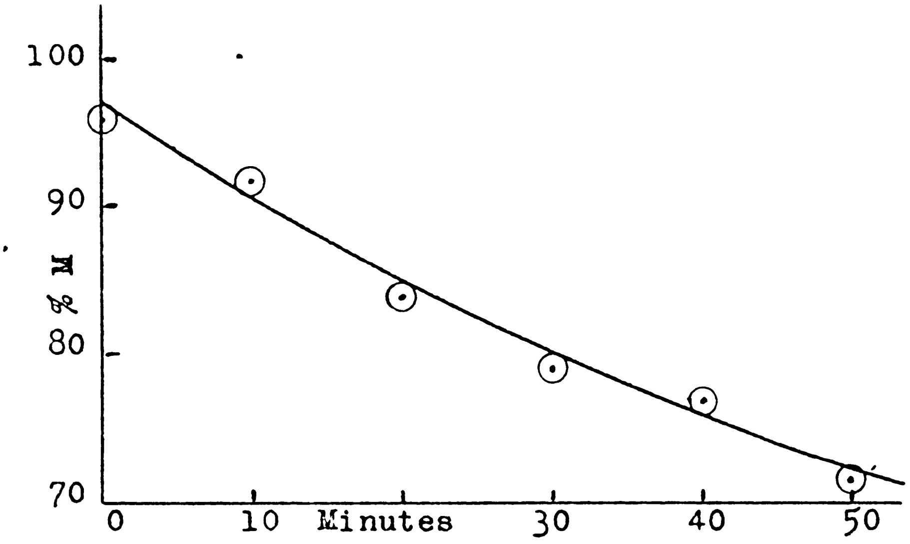
Remarks:

a. The sample tube had to be broken to take the last sample because the reactants had solidified.

b. The reactant solution was a clear light tan liquid; however, it turned to a deep reddish brown after the reactants had solidified.

c. The bubbles in the polymer were probably due to free nitrogen.

d. This appeared to be almost a zero order reaction.

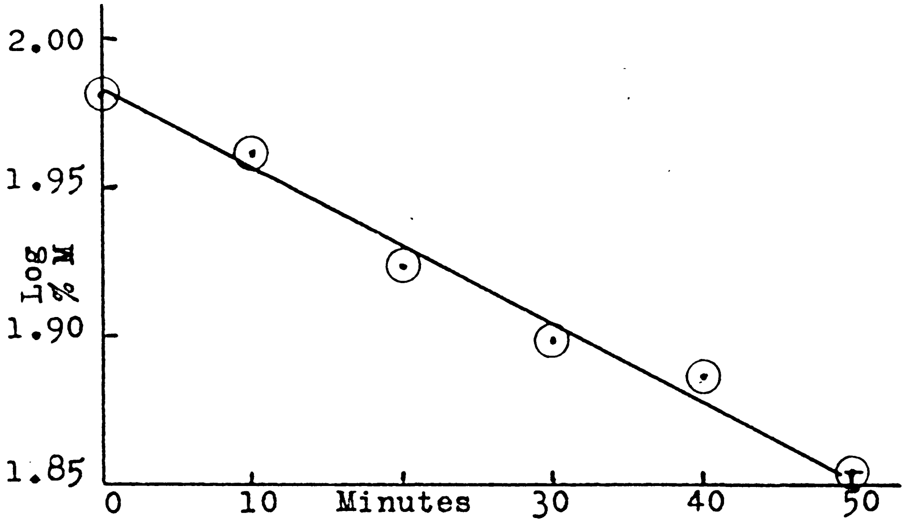


Glycoldimethacrylate

0.0147 m.f. benzoylperoxide

0.0049 m.f. diazoaminobenzene

K = 0.3606



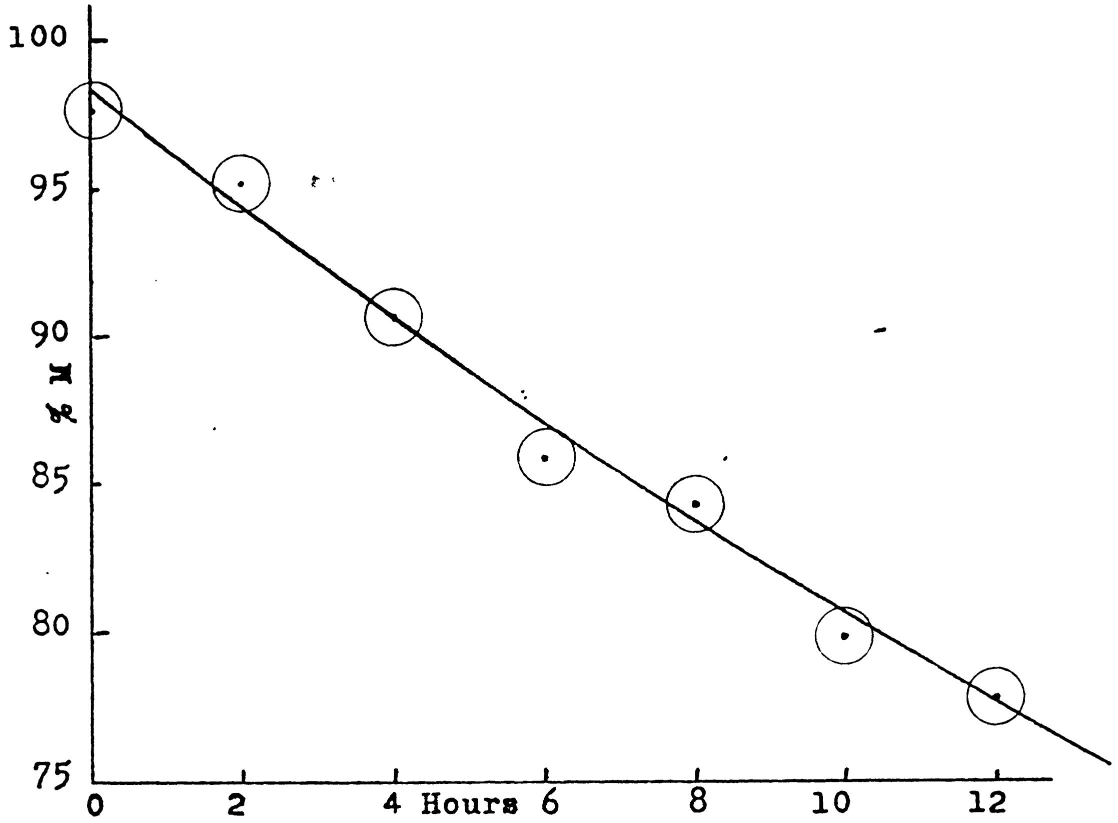
POLYMERIZATION: (36) Glycoldimethacrylate with 0.0147 mol fraction of benzoylperoxide and 0.0049 mol fraction of diazoaminobenzene at 60°C.

19.821 g. monomer 0.3631 g. catalyst 0.0986 g. promoter

Time minutes	Sample weight grams	Ml.Br	Ml.TS	Titre	% M	Log % M	Aliquot ml.
0	0.2885	15.00	10.53	4.47	95.8	1.981	1
10	0.1840	15.00	12.27	2.73	91.7	1.962	1
20	0.1624	15.00	12.81	2.19	83.7	1.923	1
30	0.2508	15.00	11.80	3.20	79.0	1.898	1
40	0.1235	15.00	7.33	7.67	76.9	1.886	5
50	0.1186	15.00	8.16	6.84	71.5	1.854	5
60	Pliable jel, insoluble in pyridine.						
240	Hard brittle reddish-brown colored plastic containing bubbles.						

Remarks:

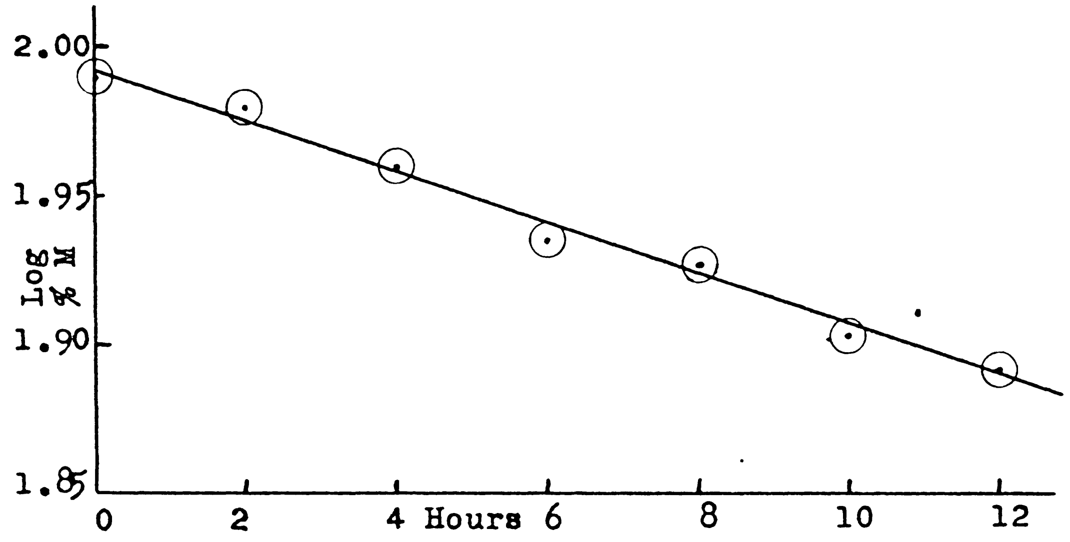
a. The reactants were mixed in the cold and portions sealed individually in 6 mm. glass tubes. The tubes were put in the bath together and withdrawn at definite intervals for analysis.



Allylbutyrate

0.01477 m.f. benzylhyponitrite

K = 0.0196



POLYMERIZATION: (37) Allylbutyrate with 0.01477 mol fraction of benzylhyponitrite at 60°C.

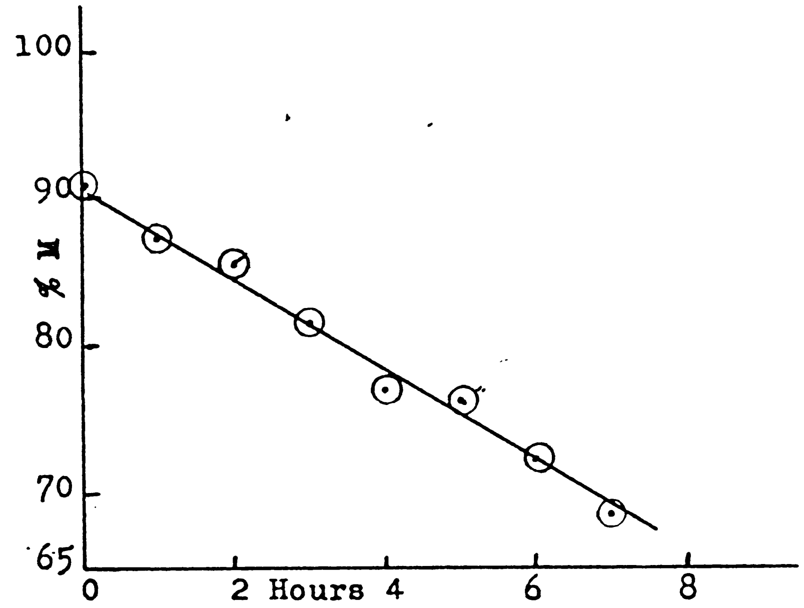
12.809 g. monomer 0.3634 g. catalyst

Time hours	Sample weight grams	Ml.Br	Ml.TS	Titre	% M	Log % M	Aliquot ml.
0	0.2519	15.00	11.93	3.07	97.6	1.989	1
2	0.1869	15.00	12.78	2.22	95.2	1.979	1
4	0.1605	15.00	5.90	9.10	90.7	1.958	5
6	0.1754	15.00	5.57	9.43	85.9	1.934	5
8	0.1343	15.00	7.91	7.09	84.4	1.926	5
10	0.1628	15.00	6.86	8.14	79.9	1.902	5
12	0.1760	15.00	6.44	8.56	77.8	1.891	5

Remarks:

a. The reactants formed a clear colorless liquid.

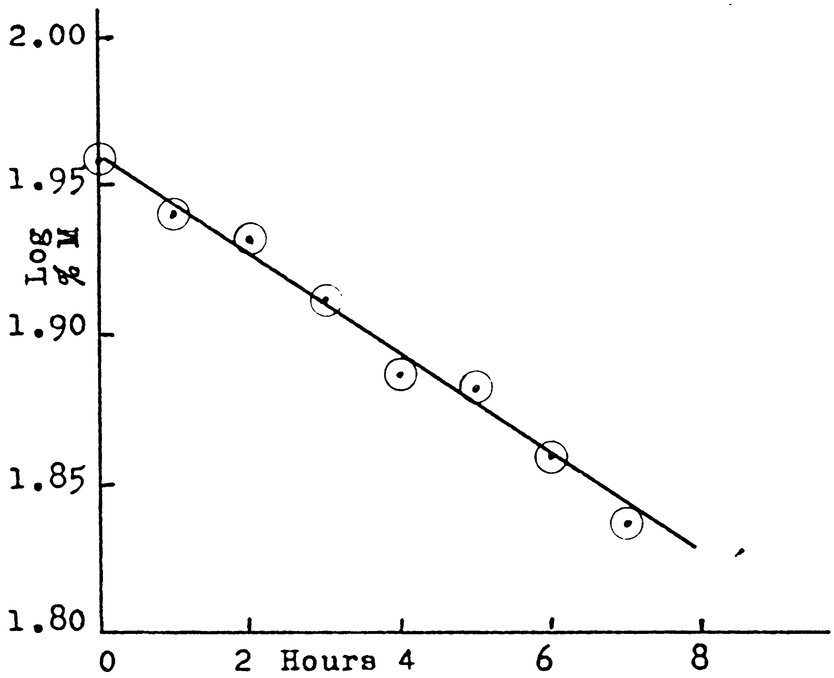
b. They were slightly more viscous after 12 hours.



Diethyleneglycol bis(allylcarbonate)

0.01477 m.f. benzylhyponitrite

K = 0.0387



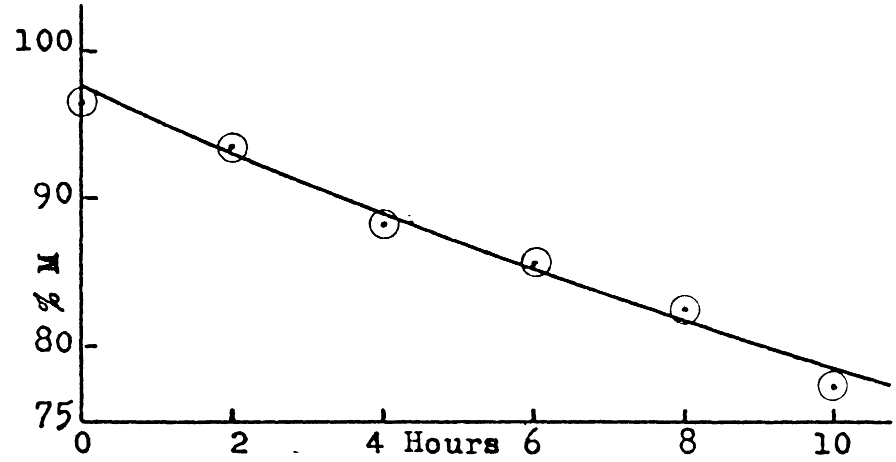
POLYMERIZATION: (38) Diethyleneglycol bis(allylcarbonate) with 0.01477 mol fraction of benzylhyponitrite at 60°C.

13.707 g. monomer   0.1817 g. catalyst

Time hours	Sample weight grams	Ml.Br	Ml.TS	Titre	% M	Log % M	Aliquot ml.
0	0.1971	15.00	12.91	2.09	90.8	1.958	1
1	0.2583	15.00	12.37	2.63	87.1	1.940	1
2	0.2038	15.00	12.97	2.03	85.4	1.932	1
3	0.1621	15.00	7.28	7.72	81.5	1.911	5
4	0.1463	15.00	8.43	6.57	77.0	1.887	5
5	0.1285	15.00	9.28	5.72	76.2	1.882	5
6	0.1174	15.00	10.05	4.95	72.2	1.859	5
7	0.1243	15.00	10.02	4.98	68.6	1.836	5
8	Jel insoluble in pyridine, contains many bubbles.						

Remarks:

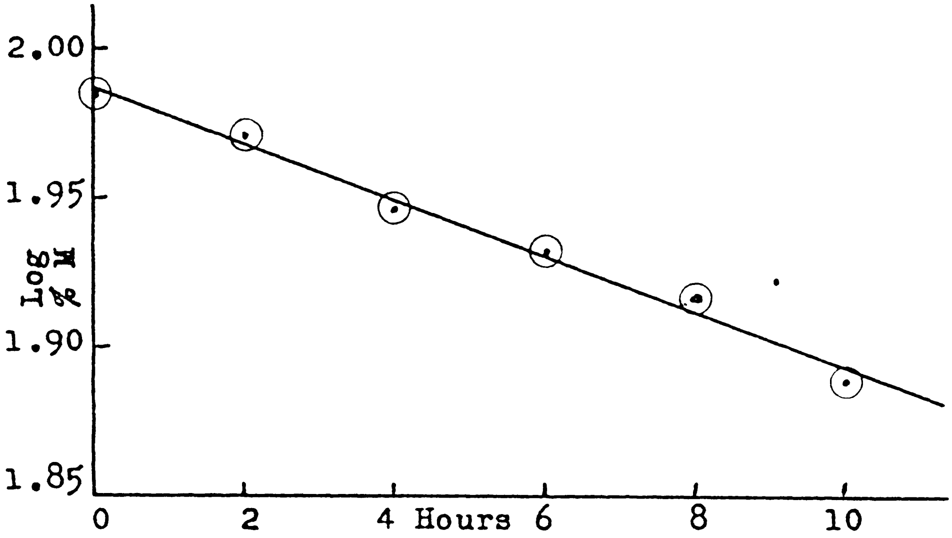
a. A clear, colorless jel formed.



Allylcitrate

0.01477 m.f. benzylhyponitrite

K = 0.0239



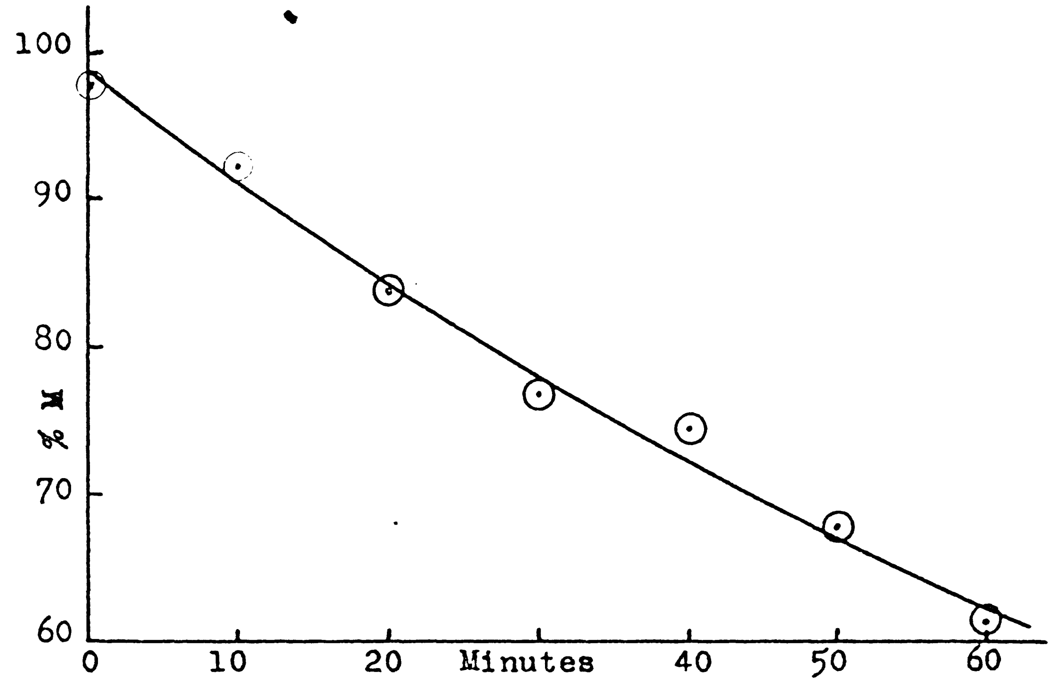
POLYMERIZATION: (39) Triallylcitrate with 0.01477 mol fraction of benzylhyponitrite at 60°C.

15.615 g. monomer 0.1817 g. catalyst

Time hours	Sample weight grams	Ml.Br	Ml.TS	Titre	% M	Log % M	Aliquot ml.
0	0.2954	15.00	10.62	4.38	96.4	1.984	1
2	0.2137	15.00	11.93	3.07	93.5	1.971	1
4	0.1501	15.00	4.84	10.16	88.2	1.946	5
6	0.1288	15.00	6.53	8.47	85.6	1.932	5
8	0.1361	15.00	6.32	8.68	82.7	1.917	5
10	0.1174	15.00	8.02	6.98	77.3	1.888	5
12	Jel insoluble in pyridine, clear colorless, many bubbles.						

Remarks:

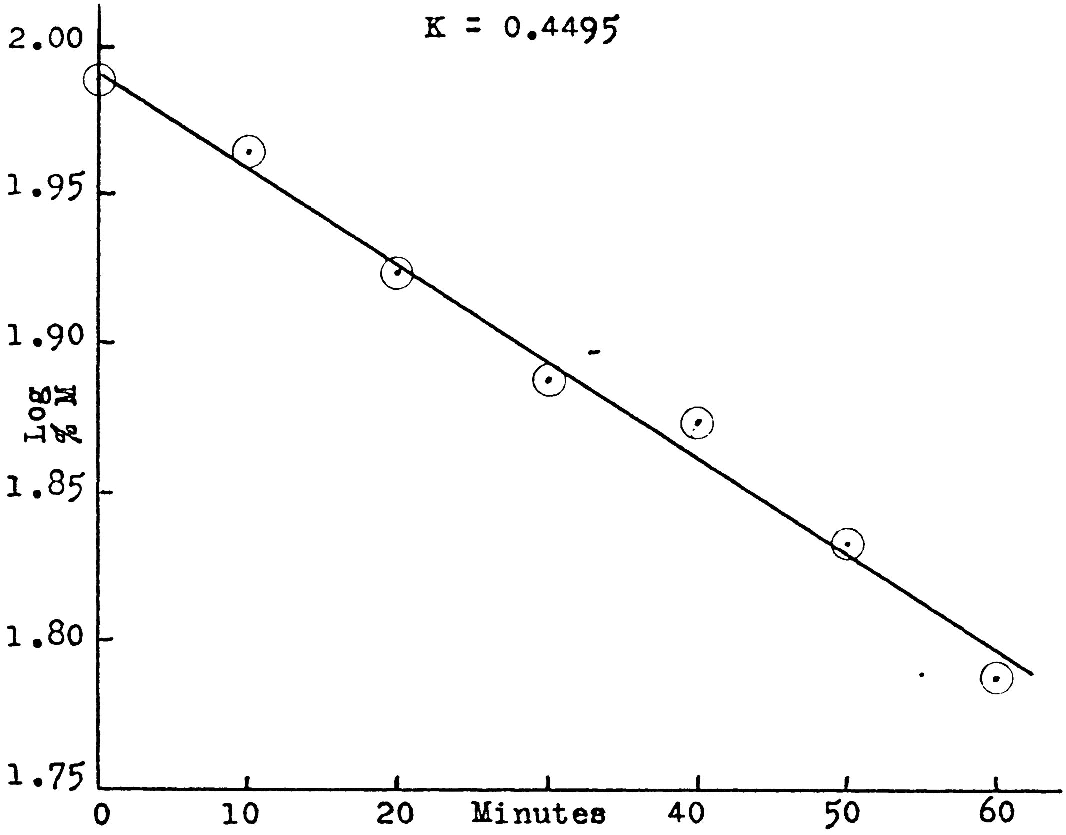
a. Reactants were syrupy after about 6 hours.



Isobutylmethacrylate

0.01477 m.f. benzylhyponitrite

K = 0.4495



POLYMERIZATION: (40) Isobutylmethacrylate with 0.01477 mol fraction of benzylhyponitrite at 60°C.

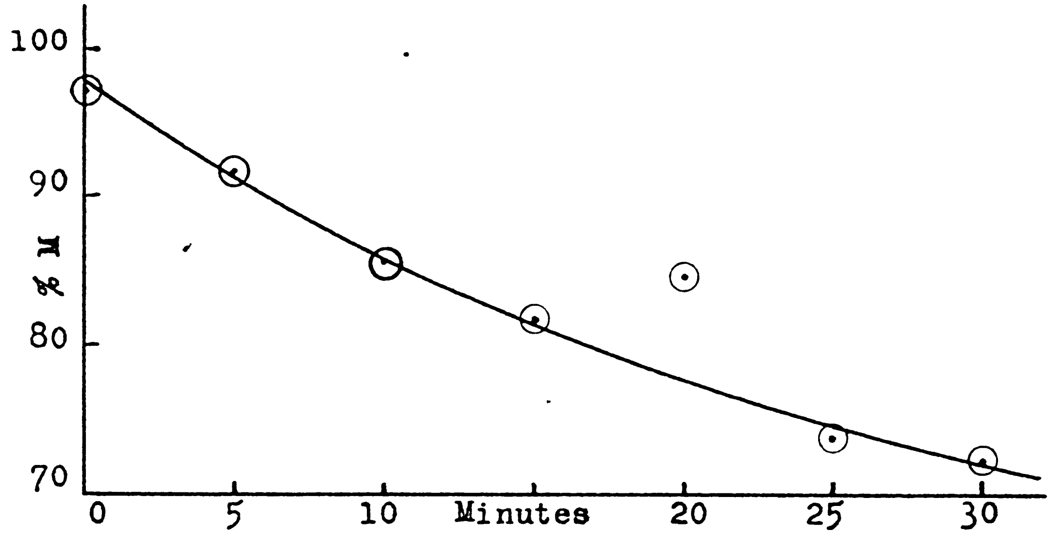
14.219 g. monomer   0.3634 g. catalyst

Time minutes	Sample weight grams	Ml.Br	Ml.TS	Titre	% M	Log % M	Aliquot ml.
0	0.2092	15.00	12.70	2.30	97.6	1.989	1
10	0.1719	15.00	13.22	1.78	92.1	1.964	1
20	0.1796	15.00	6.55	8.45	83.7	1.923	5
30	0.1549	15.00	8.28	6.72	77.0	1.887	5
40	0.1684	15.00	7.92	7.08	74.7	1.873	5
50	0.1124	15.00	10.70	4.30	67.9	1.832	5
60	0.1253	15.00	10.68	4.32	61.2	1.787	5
240	A clear, colorless plastic with large bubbles. Sticks tenaciously to glass test tube, slightly rubbery.						

Remarks:

a. The catalyst was dissolved in the monomer and the solution sealed in 6 mm. glass tubes in the cold. It was then transferred to the constant temperature bath for polymerization.

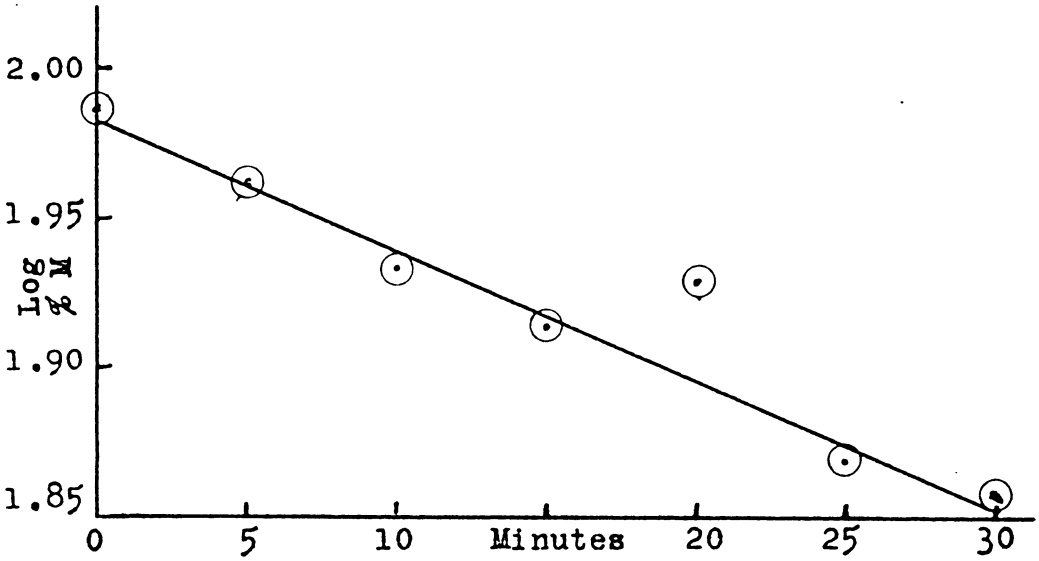
b. The reactants formed a tough plastic after about 45 minutes.



Glycoldimethacrylate

0.01477 m.f. benzylhyponitrite

K = 0.5983



POLYMERIZATION: (41) Glycoldimethacrylate with 0.01477 mol fraction of benzylhyponitrite at 60°C.

19.821 g. monomer 0.3634 g. catalyst

Time minutes	Sample weight grams	Ml.Br	Ml.TS	Titre	% M	Log % M	Aliquot ml.
0	0.2887	15.00	10.47	4.53	97.1	1.987	1
5	0.2412	15.00	11.43	3.57	91.7	1.962	1
10	0.1596	15.00	12.79	2.21	85.6	1.933	1
15	0.1276	15.00	6.57	8.43	81.8	1.913	5
20	0.1523	15.00	4.55	10.45	84.8	1.928	5
25	0.1824	15.00	4.12	10.88	73.9	1.869	5
30	0.1432	15.00	6.65	8.35	72.2	1.858	5
35	Jel insoluble in pyridine.						
240	Hard, clear polymer, contains bubbles.						

Remarks:

a. The reactants were mixed and sealed in 6mm. glass tubes for polymerization.

b. Polymerization was stopped for sampling by putting the reaction tube in an ice bath.

POLYMERIZATION: (42) Benzenediazoniumfluoroborate

An attempt was made to evaluate the catalytic activity of benzenediazoniumfluoroborate as a polymerization catalyst for the five monomers chosen; however, it was found to be insoluble in all of them from 0° to 60°C.

No further experiments were conducted with diazonium fluoroborates.

POLYMERIZATION: (43) Redox system

Monomer - benzoylperoxide - bisulfite addition product

An attempt was made to dissolve 0.0049 mol fraction of each of the bisulfite salts in each of the five monomers; however, they would not dissolve, even at 60°C.

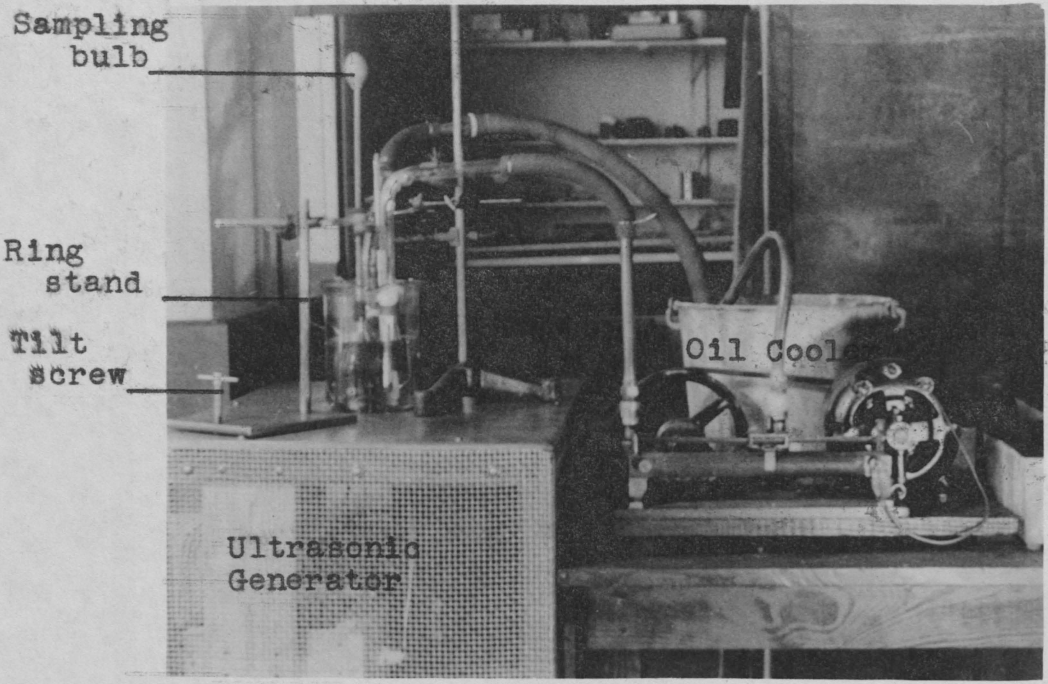
These salts were abandoned.

POLYMERIZATION: (44) Co-polymerization of 0.4926 mol fraction of allylbutyrate with 0.4926 mol fraction of citraconic anhydride catalyzed by 0.01477 mol fraction of benzoylperoxide at 60°C.

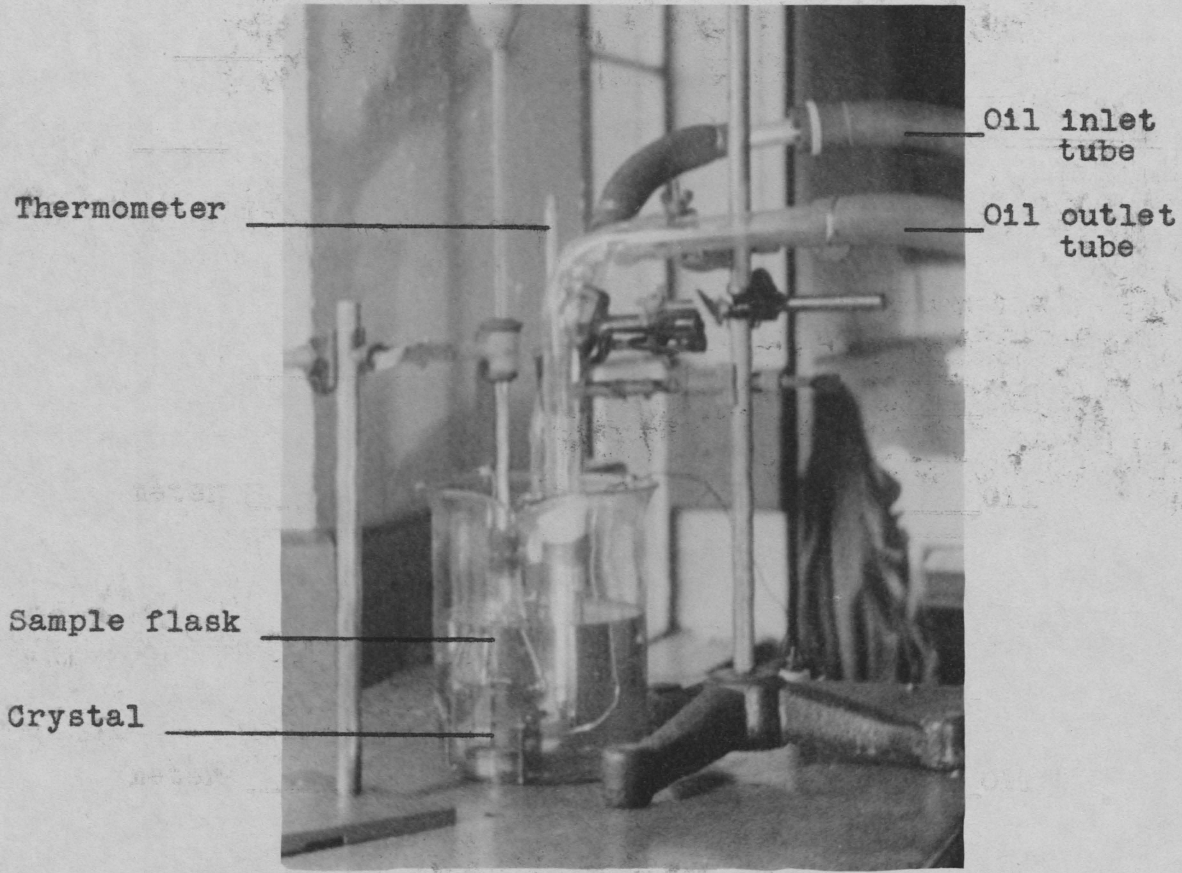
The monomers were freshly distilled at 1.5 cm. Hg pressure, mixed and the peroxide added. The solution was placed in the bath at 60°C. for one week. No change in the unsaturation of the mixture occurred.

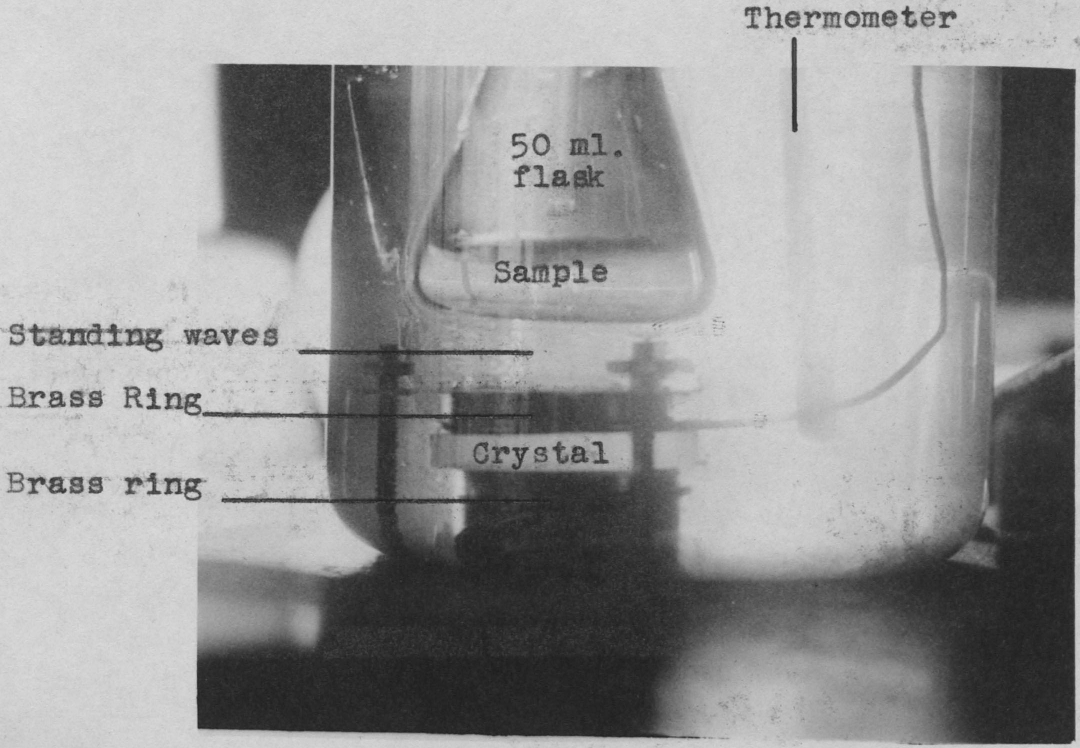
This experiment was repeated, being very careful to use clean apparatus and keeping a nitrogen atmosphere over the reactants; however, no polymerization occurred.

It was felt that polymerization would have occurred, if possible, under these conditions. The reaction was abandoned.

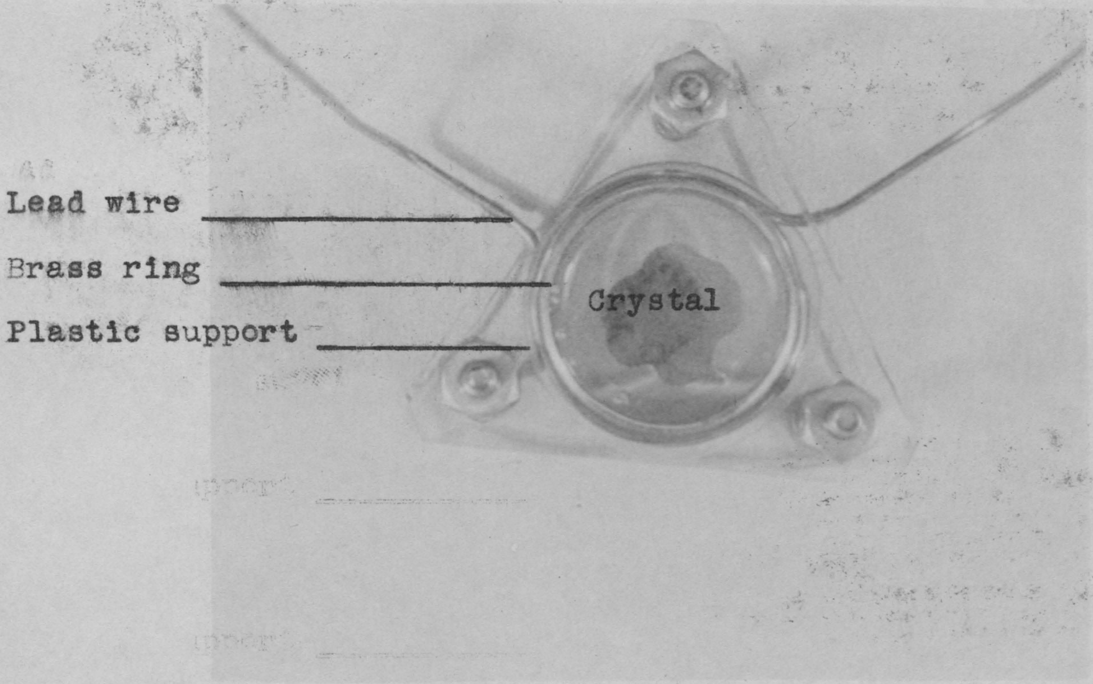


ULTRASONIC REACTOR APPARATUS





REACTOR AND PIEZOELECTRIC CRYSTAL IN BATH



PIEZOELECTRIC CRYSTAL

ULTRASONIC POLYMERIZATION

The piezo-electric generator circuit used in these experiments was developed by the Physics Department and is described in the Appendix. It had a frequency of 500 kc and an effective power output of about 50 watts.

The apparatus used is pictured in the accompanying photographs. The sample flask was suspended over the oscillating crystal in the oil bath by the sample tube. This tube was clamped to a tilting ring stand. The oil bath serves two purposes: it helps to remove heat generated by the sound waves and it transmits the sound waves to the sample flask very efficiently. The best energy transmission can be realized by raising or lowering the sample flask slowly until maximum agitation of the sample is observed. At this point the distance is an exact multiple of the wave length and the sound waves reenforce each other. These standing waves can be seen in the oil bath between the crystal and the flask. An ordinary mercury thermometer cannot be used in the sample flask because the sound waves heat the mercury raising the temperature readings 30° to 40°C.

The heat generated by the unit was found to be about 800 cal./min. or 48,000 cal./hr. This requires the use of about two pounds of ice per hour to maintain a constant temperature. This is roughly the same amount of heat which would by given off by a 60 watt electric light. If we assume that

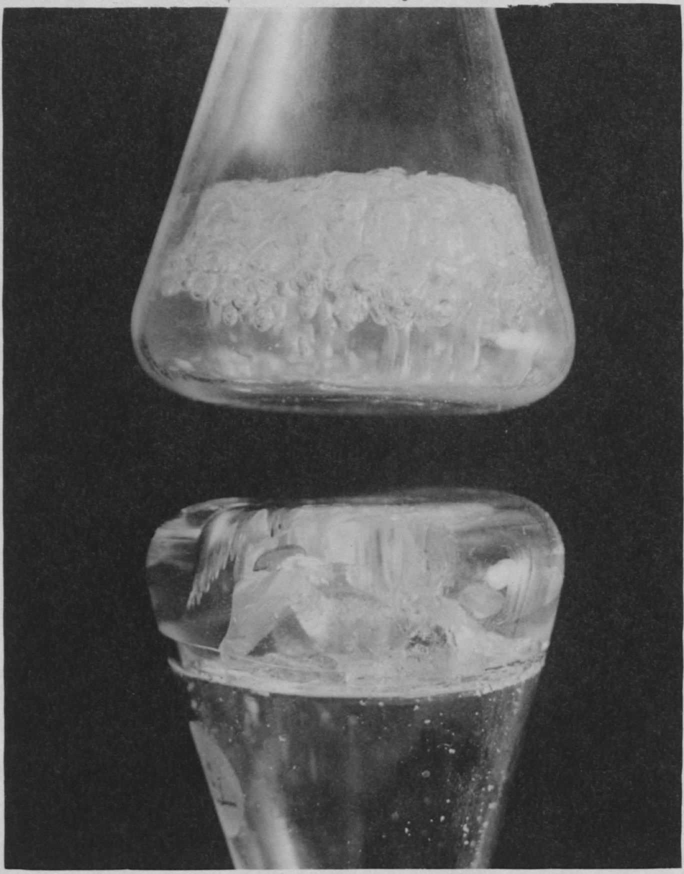
$\frac{1}{4}$ of this energy is dissipated in the sample flask, a 50 ml. pyrex erlenmeyer, then it can be calculated that the sample will be about 6°C. warmer than the oil bath, due to the thermal resistance of the glass flask. This was verified by experiment. A thermometer was placed in the oil bath, not in the path of the ultrasonic waves, and its readings used to estimate the temperature in the sample flask.

Experiment #1

Freshly distilled isobutylmethacrylate was subjected to ultrasonic energy @ 12°C. for three hours. The monomer was agitated so violently that a mist could be seen in the flask at times. No physical change of the monomer was noticed. Samples analyzed every hour showed no change in unsaturation.

Experiment #2

Isobutylmethacrylate and 0.015 mol fraction of benzoyl peroxide were subjected to ultrasonic energy @ 25°C. for three hours. No change in physical properties was noticed. Samples analyzed every hour showed no change in unsaturation or peroxide content. It is known that solid benzoyl peroxide is decomposed by thermal shock and that dissolved peroxide is fairly stable. It was hoped that the dissolved peroxide would not be stable toward ultrasonic agitation, and that polymerization could be induced thereby. This situation, however, was not realized.



Isobutylmethacrylate

Diethyleneglycol bis(allylcarbonate)

Experiment #3

Diethyleneglycol bis(allylcarbonate) was subjected to ultrasonic energy @ 25°C. for three hours with no physical changes and no change in unsaturation found. All attempts to induce polymerization by ultrasonic energy were negative.

Experiment #4

Polyisobutylmethacrylate, prepared by polymerizing freshly distilled monomer with 0.015 mol fraction of benzoylperoxide at 60°C. for 22 hours, was subjected to ultrasonic energy @ 18°C. for four hours. No visible effects or physical changes were noted.

Experiment #5

Polydiethyleneglycol bis(allylcarbonate), polymerized as the methacrylate, and subjected to the same ultrasonic treatment was fractured in several spots, but no depolymerization effects were noted.

The photograph which is enlarged shows these two polymers in 50 ml. erlenmeyer flasks after ultrasonic treatment. The original polymethacrylate sample was a hard, water white solid with a foamy upper strata. This strata was formed by poor heat transfer and rapid polymerization. The monomer became so hot that it began to boil and rapid polymerization entrapped the vapor, forming a hard spongy mass. This occurred before ultrasonic treatment and was in no way affected thereby.

The polyallyl ester was a very heavy jel which was water white in color and contained no bubbles or cracks before ultrasonic treatment. A clear solid plastic was formed in this case because polymerization occurred at a much slower rate and the heat was dissipated as it developed. Many cracks were formed in the polymer by the ultrasonic treatment. They started forming at the bottom of the beaker and gradually worked their way to the surface. No change in viscosity of the jel and no partially liquefied areas were formed.

Experiment #6

A 0.0840 g. sample of polyisobutylmethacrylate, prepared by polymerization of freshly distilled monomer @ 60°C. for 20 hours with 0.015 mol fraction of benzoylperoxide was made up to 45 ml. volume with pyridine @ 25°C. The density of the pyridine was found to be 0.982 @ 25°C. A 5 ml. sample of the pyridine solution was taken for analysis.

ULTRASONIC GENERATOR

Time hours	Oil Bath Temp. C°	Meter 1 M.A.	Meter 2 M.A.	Remarks
1:40	19	30	175	Droplets being thrown from surface of liquid. Started up.
2:40	17	32	200	Bubbles formed in polymer solution by cavitation.
3:40	18	31	190	Same.
4:40	20	32	200	Same. Shut down.

Experiment #7 - Wt. polyisobutylmethacrylate 0.0926 g. pyridine 45 ml. Procedure same as #6.

10:30	22	30	175	Started run.
11:30	20	30	175	Bubbles due to cavitation.
12:30	21	30	175	Same.
1:30	28	30	175	Shut down.

The viscosity was determined with an Ostwald viscosimeter which gave readings of 79.7 seconds for distilled water @ 25°C. and 80.9 seconds for pyridine @ 25°C. The density was determined @ 25°C. using a Westphal balance. Unsaturation analyses were run using a 5 ml. aliquot of the sample solution according to the general analytical method. (See analytical section.)

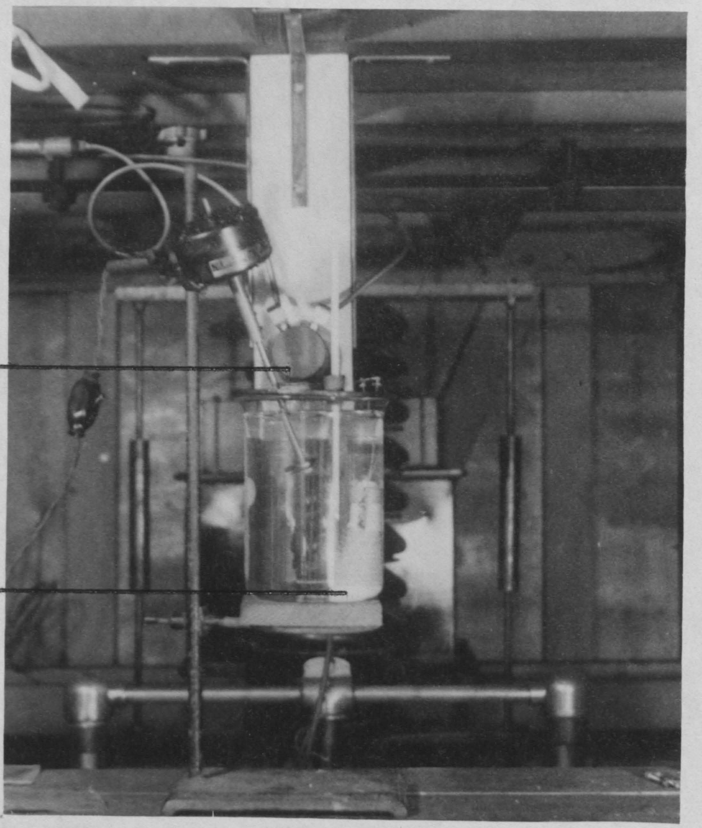
Experiment # 6 - contd.

$$\% M = \frac{\text{Titre}}{\text{S. wt.}} \times 3.1992$$

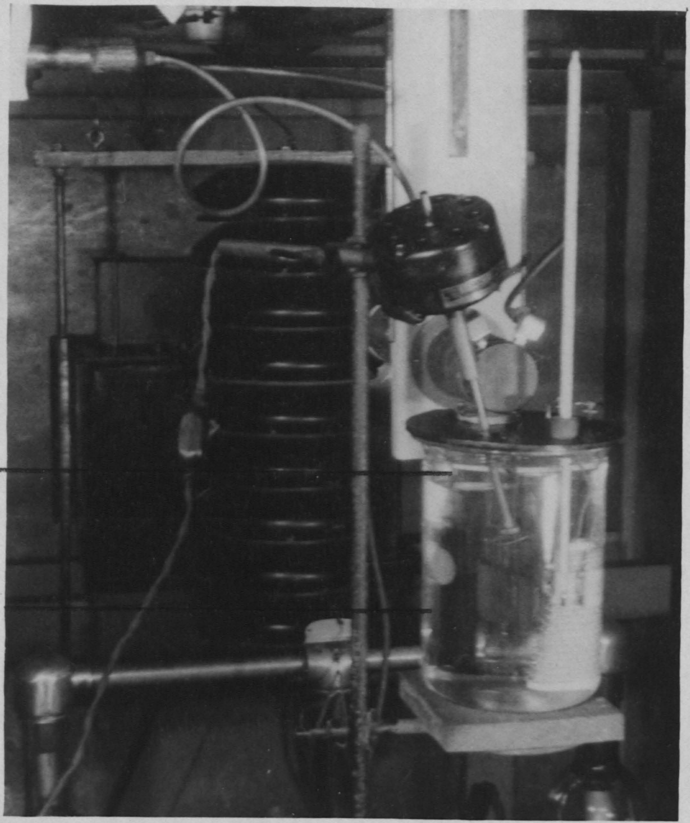
VISCOSITY @ 25° C.			UNSATURATION			
Density	Time Sec.	Viscosity Centipoise	Ml.Br	Ml.TS	Titre	% M
0.982	86.69	1.195	10.00	8.83	1.17	44.6
0.982	83.2	1.149	10.00	8.84	1.16	44.2
0.982	83.1	1.147	10.00	8.82	1.18	45.0
0.982	83.1	1.147	10.00	8.83	1.17	44.6

Experiment #7 - contd.

Density	Time Sec.	Viscosity Centipoise	Ml.Br	Ml.TS	Titre	% M
0.982	86.89	1.198	10.00	8.99	1.01	34.9
0.982	83.48	1.152	10.00	8.96	1.04	35.9
0.982	83.17	1.147	10.00	8.97	1.03	35.6
0.982	83.18	1.147	10.00	8.98	1.02	35.2



X-RAY TREATMENT APPARATUS



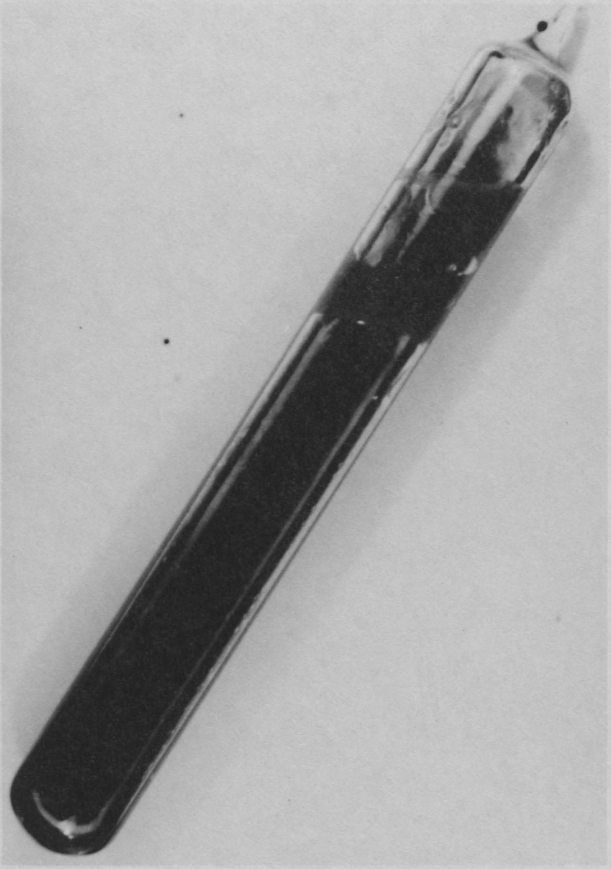
X-RAY POLYMERIZATION OF ISOBUTYLMETHACRYLATE

Experiment #1

About 20 ml. of freshly distilled isobutylmethacrylate was placed in a 50 ml. beaker and tightly covered with cellophane. This beaker was set into a constant temperature bath, held at 60°C. ± 1°C. and the unit placed just below the x-ray tube. (See photographs). The sample was irradiated for three, one-half hour intervals and samples were taken after each interval. Analyses of unsaturation and of refractive index revealed no evidence of polymerization.

Experiment #2

A 20 ml. sample of freshly distilled isobutylmethacrylate was put into a 50 ml. beaker and sealed with a cellophane cover in a nitrogen atmosphere. The sample was irradiated for 1 1/2 hours @ 60°C. Analyses of unsaturation and of refractive index revealed no evidence of polymerization.



DISCUSSION OF EXPERIMENTAL RESULTS

It was necessary to find a suitable means of analysis for unsaturation in the polymer mixtures before the rate studies could be started. The analytical procedure recommended by Bartlett and Altschul was investigated and (3) found to be inadequate. It was abbreviated so much in the journal that some of the necessary information was not present. The analysis was perfected in our laboratory until we were able to analyze allylbutyrate correctly. However, it did not give consistent results with any of the other four monomers.

The monomer-polymer mixture was made soluble in their method by hydrolyzing it with a caustic soda solution at 100°C. We found that this hydrolysis step caused further polymerization of all the monomers except allylbutyrate. The accompanying photograph shows the monomer-caustic soda solution sealed in a test tube. A band of polymerized material, which formed during the hydrolytic treatment is seen at about one third the length of the tube.

The procedure finally settled upon is described fully in the analytical section. The polyester samples were precipitated in a very finely divided state from a pyridine solution by dropwise addition to aqueous bromide-bromate reagent. The bromine released upon acidification added quantitatively to the finely dispersed sample and the excess

bromine was determined by conventional iodometric analysis.

A general view of the constant temperature bath and analytical apparatus is shown in the accompanying photograph. The bath is seen to the right and the pipet stand, titrating flasks, volumetric flasks and burettes to the left of it on the bench top. Left to right on the shelf below the bench are the analytical solutions, the pans with which the titration flasks were covered to keep them in the dark during bromine addition and the solvent bottles for cleaning equipment.

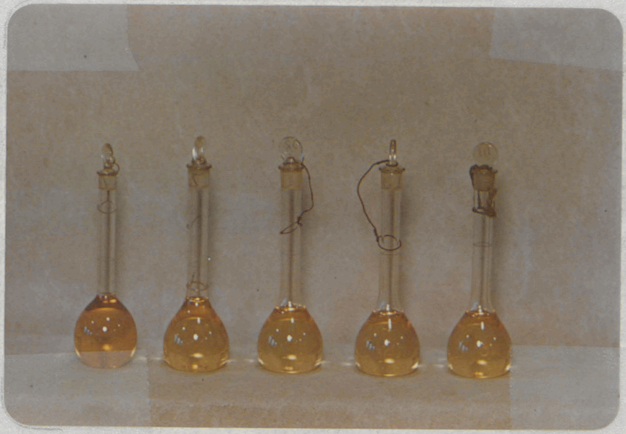
The sources of the impurities which caused induction periods and altered the rate of polymerization had to be found and eliminated before accurate rate studies could be made. The constant temperature bath was made light tight to prevent polymerization due to actinic radiation. The polymerizations were all carried out at 60°C. to prevent changes in the rate due to temperature. These factors, however, had no effect upon the induction periods.

All the reactants were prepared and used in as pure a state as possible. It was found that the various monomers polymerized best if used immediately after they were distilled. Isobutylmethacrylate had to be distilled at temperatures below 65°C. if induction periods were to be minimized. At temperatures a little above 65°C. the distillate took on a light yellow hue and analyzed low for unsaturation. The ditertiarybutyldiperphthalate was found to be impure and had to be reprecipitated before it gave satisfactory results. (See polymerization experiments # 25 and #25-a.)

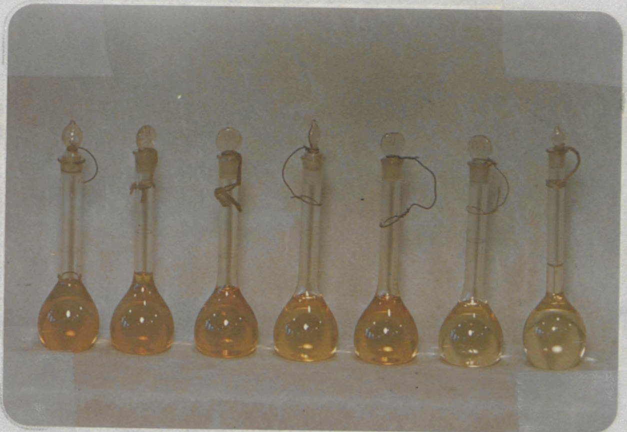
Induction periods still occurred even though the reactants were pure and the apparatus appeared to be clean. It was found that material leached from the cork or rubber stopper of the reaction tube by monomer caused induction periods. This was remedied by covering the stoppers with tin foil. Induction periods were also diminished if the reaction tube and the monomer receiver were heated to a red heat and allowed to cool slowly just prior to adding the monomer to them. Evidently the adsorbed surface layer of dirt or solvent molecules was enough to increase the induction period.

Air and water vapor were found to have only a minor effect on the induction period. If they were allowed to be in contact with the monomer during the polymerization reaction a top layer of about one sixteenth of an inch would remain soft and would not polymerize completely. If the reactor was kept stoppered, momentary opening for sampling did not allow enough air to enter to cause the soft upper layer to form. Air would probably completely inhibit the polymerization of a thin surface layer of monomer, such as might occur in a paint film.

When the reaction occurred so fast that it was necessary to take a sample every fifteen minutes or less, the reactants were divided and sealed in several glass tubes, (see polymerization experiments #36, 40 and 41). They were then allowed to polymerize together and each could be withdrawn for analysis without disturbing the reaction occurring in the other



Allylbutyrate



Isobutylmethacrylate

tubes. This procedure avoided contamination of the reactants during sampling.

By following these few expedients it was possible to reduce the induction periods to a negligible value.

After a suitable method of analysis had been evolved, the equipment had been assembled and the factors governing polymerization rate and induction periods had been discovered, it was possible to go ahead and carry out the polymerization rate studies. These are found in the experimental section. Each polymerization has been written up and graphed separately.

It was possible to eliminate almost completely the induction period in all but the tetrachlorohydroquinone reactions. In these reactions the induction period appeared to be proportional to the amount of tetrachlorohydroquinone and it could not be eliminated by further purification of the quinone. The pyridine-polymer solution of this material showed a gradation in color from brown to light orange or yellow, depending upon the time of the polymerization reaction. It was found that the induction periods corresponded to the time required for the pyridine-polymer solutions to change color and that no further color change occurred after the polymerization reaction finally started. Hence, we had a visual indication of the length of the induction period. The two color photographs on the opposite page show this effect for allylbutyrate and isobutylmethacrylate.

The origin of the color was not ascertained. When benzoylperoxide and tetrachlorohydroquinone were allowed to react in acetic acid solution, samples of the material, which were made up in 25 ml. of pyridine for unsaturation analysis, were found to be colorless. This indicated that monomer was necessary for the color formation step. The colored substance was probably a reaction product of the peroxide and quinone which formed only in the presence of monomer.

ORDER OF POLYMERIZATION REACTIONS

0,1 = zero or first order reaction

1 = first order reaction

m.f. = mol fraction

Catalyst combination	Allylbutyrate	Diethyleneglycol-bis(allylcarbonate)	Triallylcitrate	Isobutylmethacrylate	Glycoldimethacrylate
0.0147 m.f. benzoylperoxide	1	1	0,1	1	1
Same	1	1		1	
0.0291 m.f. benzoylperoxide				1	
0.0147 m.f. benzoylperoxide 0.0049 m.f. tetrachlorohydroquinone	0,1	0,1	1	1	1
Same			1		
0.0146 m.f. benzoylperoxide 0.0097 m.f. tetrachlorohydroquinone				0,1	
0.0147 m.f. benzoylperoxide 0.0049 m.f. hydrazobenzene	0,1	0,1	0,1	0,1	0,1
Same				1	
0.0147 m.f. 1-hydroxycyclohexyl-hydroperoxide-1		1	1	0,1	0,1
0.0147 m.f. ditertiarybutyl-diperphthalate		0,1		0,1	1
Same				1	
0.0147 m.f. diazoaminobenzene	1	1	1	0,1	1
0.0147 m.f. benzoylperoxide 0.0049 m.f. diazoaminobenzene	1	0,1	0,1	1	1
0.0147 m.f. benzylhyponitrite	1	0,1	0,1	1	1

THE ORDER OF THE RATE REACTIONS AND ITS SIGNIFICANCE

The order of the polymerization reactions was determined from the graphed rate data. If the % M vs. time graph was a straight line, then the reaction was zero order. If the Log % M vs. time graph was a straight line, then the reaction was first order.

We looked over the graphs in the experimental section, assuming that the data was accurate within ± 1%, and found the reactions to be of the order indicated in the accompanying table. It is seen that 27 out of 45 different reactions are definitely first order reactions. The order of the other 18 reactions could be either zero or first because the analytical data was not accurate enough for discrimination.

It is seen that no one monomer or catalyst gave all first order or all zero order reactions. The orders seem to be fairly randomly distributed. Polymerization experiments #15 and #15-a explain the reason for most of this anomalous rate data. Experiment #15, carried out for 2 hours, could be interpreted as either a zero or a first order reaction. When it was repeated, #15-a, for 5 hours it was seen to be a definite first order reaction. The experiments in which the time or percentage ranges were too short are the ones in which the graphs could not be positively interpreted. It is felt, therefore, that all these reactions were first order.

A first order reaction is one in which the rate of the reaction is directly proportional to the concentration of the reacting substance. Our systems consisted of several components, either monomer and catalyst; or monomer, catalyst and promoter. There was a possibility for second order and third order reactions. Since our reactions appeared to be first order we must assume that the reaction occurring with the slowest rate was a first order reaction and determined the rate of the entire system.

It appeared that the decomposition reaction of the catalyst or catalyst system was the rate determining step. This was indicated in several ways. The reaction rates always appeared to be first order. This meant that the rates of all other reactions were so much greater than the slow first order rate that they did not interfere with it. Secondly, each catalyst-monomer system had its own characteristic reaction rate and the rates of different systems with the same monomer varied greatly. This indicated that the maximum polymerization rate of the monomer had not been reached. Other investigators proved (4) that the catalyst controlled the first order reaction rate of allylacitate. The catalyst was, therefore, the predominant rate determining factor.

Table III, page 182, Reaction Rate Ratio, indicates that the number of unsaturated groups in the monomer has an effect on the reaction rate. In both the allyl and the acrylic groups the difunctional monomers polymerized 1.5 to 2 times as fast as the monofunctional monomers. This seems to indicate that the concentration of unsaturated groups in the monomer has a direct relation to the reaction rate. On the other hand, the reaction rate of triallylcitrate was no greater than that of allylbutyrate. This might lead us to believe that the number of functional groups in a molecule had no effect on the reaction rate. We do not know the reason for the conflicting data.

The anomaly may be due to steric hindrance. The larger trifunctional monomers may not orient themselves properly or fast enough to react with maximum speed. It may be that the greater polarity of the compound aids these steric effects. The effect may be purely chemical. The free radicals might attack the hydroxyl group in preference to the allylic groups. The elucidation of these phenomena would be a good thesis problem.

The free radical polymerization catalysts are not catalysts in the strict sense of the term. They are a necessary reactant. No polymerization occurred when the pure monomers were heated at 60°C. for a week, yet a trace of a free radical yielding material caused polymerization of isobutylmethacrylate within two hours. The free radical material cannot be recovered from the polymer after it has reacted because it becomes chemically bonded to the polymer chain molecule.

Table I

FIRST ORDER REACTION RATE CONSTANTS

K = Rate/hr.

m.f.= mol fraction

Catalyst combination	Allylbutyrate	Diethyleneglycol-bis(allylcarbonate)	Code
Thermal	0	0	AA
0.0147 m.f. benzoylperoxide	0.0053	0.0098	A
Same	0.0056	0.0097	B
0.0291 m.f. benzoylperoxide			C
0.0147 m.f. benzoylperoxide 0.0049 m.f. tetrachlorohydroquinone	0.0052	0.0159	D
Same			E
0.0146 m.f. benzoylperoxide 0.0097 m.f. tetrachlorohydroquinone			F
0.0147 m.f. benzoylperoxide 0.0049 m.f. hydrazobenzene	0.0028	0.0153	G
Same			H
0.0147 m.f. 1-hydroxycyclohexyl-hydroperoxide-1	--	0.0019	I
0.0147 m.f. ditertiarybutyl-diperphthalate	--	0.0016	J
Same			K
0.0147 m.f. diazoaminobenzene	0.0113	0.0208	L
0.0147 m.f. benzoylperoxide 0.0049 m.f. diazoaminobenzene	0.0125	0.0219	M
0.0147 m.f. benzylhyponitrite	0.0196	0.0387	N

Code	Triallylcitrate	Isobutylmethacrylate	Glycoldimethacrylate
AA	0	0	0
A	0.0056	0.0932	0.1575
B		0.1254	
C		0.2582	
D	0.0035	0.2215	0.2930
E	0.0038		
F		0.1444	
G	0.0055	0.1411	0.2946
H		0.1426	
I	0.0010	0.0218	0.0287
J	--	0.0198	0.0364
K		0.0250	
L	0.0117	0.0279	0.0412
M	0.0131	0.2512	0.3606
N	0.0239	0.4495	0.5983

Table II

REACTION RATE RATIO

$$\text{Ratio} = \frac{\text{Rate(catalyst combination)}}{\text{Rate 0.0147 m.f. benzoylperoxide}}$$

m.f. = mol fraction

Catalyst combination	Allylbutyrate	Diethyleneglycol-bis(allylcarbonate)	Code
0.0147 m.f. benzoylperoxide	0.946	1	A
Same	1	0.970	B
0.0291 m.f. benzoylperoxide			C
0.0147 m.f. benzoylperoxide 0.0049 m.f. tetrachlorohydroquinone	0.922	1.624	D
Same			E
0.0146 m.f. benzoylperoxide 0.0097 m.f. tetrachlorohydroquinone			F
0.0147 m.f. benzoylperoxide 0.0049 m.f. hydrazobenzene	0.500	1.561	G
Same			H
0.0147 m.f. 1-hydroxycyclohexyl-hydroperoxide-1		0.194	I
0.0147 m.f. ditertiarybutyl-diperphthalate		0.1632	J
Same			K
0.0147 m.f. diazoaminobenzene	2.02	2.122	L
0.0147 m.f. benzoylperoxide 0.0049 m.f. diazoaminobenzene	2.23	2.24	M
0.0147 m.f. benzylhyponitrite	3.50	3.95	N

Code	Triallylcitrate	Isobutylmethacrylate	Glycoldimethacrylate
A	1	0.743	1
B		1	
C		2.058	
D	0.625	1.764	1.861
E	0.678		
F		1.150	
G	0.983	1.124	1.872
H		1.136	
I	0.1787	0.1738	0.1822
J		0.1578	0.235
K		0.199	
L	2.09	0.222	0.261
M	2.34	2.00	2.224
N	4.27	3.58	3.80

COMPARISON OF REACTION RATES

The first order reaction rates of the polymerization reactions are given in Table I. The fastest reaction occurred with glycoldimethacrylate and benzylhyponitrite. A hard plastic was formed within 45 minutes. On the other hand the rate of thermal polymerization was so slow as to be undetectable. The dashed spaces in the allylbutyrate column indicate that polymerization occurred at a detectable rate, but so slowly that the rate could not be calculated.

It is seen that more polymerizations were carried out with isobutylmethacrylate than any other monomer. This was because it usually formed a solid polymer within six to eight hours which was soluble in pyridine; hence it was possible to carry the polymerization reactions beyond the jel stage. This was impossible with the polyfunctional monomers because they form jels which are insoluble. Isobutylmethacrylate was used more often for this reason.

Table II depicts the reaction rate ratios for each monomer, based upon the rate with 0.0147 m.f. of benzoylperoxide. For instance, the second value of allylbutyrate with 0.0147 m.f. of benzoylperoxide was felt to be the correct one; hence it has a ratio of one. The first value based upon the second has a value of 0.946. The ratio of the rates of allylbutyrate with diazoaminobenzene to the second rate with benzoylperoxide was 2.02. The table was developed in this manner for each monomer.

Comparing the values for benzoylperoxide catalysis it is seen that the reaction rates are reproducible within 3 to 6%. This was also born out by triallylcitrate polymerized with benzoylperoxide and tetrachlorohydroquinone and by isobutylmethacrylate polymerized with benzoylperoxide and hydrazobenzene.

It can be shown that the reaction rate is directly proportional to peroxide concentration. Isobutylmethacrylate had a rate of 1 with 0.0147 m.f. of benzoylperoxide and a rate of 2.058 with twice as much peroxide, 0.0291 m.f. A similar analogy was found when isobutylmethacrylate was polymerized with ditertiarybutyldiperphthalate. The same amount of catalyst was used for each reaction, however, the run using catalyst which had a peroxide content of 79% had a rate of 0.158 whereas the run whose catalyst had a peroxide content of 99% had a rate of 0.199. If we compare these figures:

$$\frac{0.158}{0.199} = \frac{79}{99}$$

it will be found that the ratio holds within the 3 to 6% range of error indicated previously.

No common proportionality factor was found to hold when considering the effect of the promoter. Isobutylmethacrylate polymerized at an increased rate when 0.0049 m.f. of tetrachlorohydroquinone was added to the system; however, when the concentration of quinone was increased to 0.0097 m.f. the rate was decreased somewhat.

A glance down the table will reveal that the different catalysts cause the reaction rates of each monomer to be changed about the same amount. For instance the reaction rates with benzylhyponitrite are roughly 3.5 to 4 times as great as with benzoylperoxide. With 1-hydroxycyclohexylhydroperoxide-1 they are only about 0.18 to 0.19 as great. There is one notable exception with diazoaminobenzene, in which the rate of acrylate polymerization was decreased, whereas the rate of allylpolymerization was increased.

We can draw a few general conclusions governing relative catalytic activity:

1. Benzoylperoxide caused the greatest polymerization rates of the three peroxides tested. It was roughly about 5 times as effective as the other two catalysts.
2. Tetrachlorohydroquinone acts as a promoter for benzoylperoxide with the acrylic monomers, but has a variable effect with the allyl monomers.
3. Hydrazobenzene promotes benzoylperoxide in the same manner and to about the same degree that tetrachlorohydroquinone does.
4. Diazoaminobenzene is a good catalyst for allyl monomers, although it is inferior to benzoylperoxide for acrylic monomers.
5. The benzoylperoxide-diazoaminobenzene couple is an active

Table III

REACTION RATE RATIO

$$\text{Ratio} = \frac{\text{Rate any monomer}}{\text{Rate isobutylmethacrylate}}$$

(with catalyst in common)

Catalyst combination	Allylbutyrate	Diethyleneglycol-bis(allylcarbonate)	Code
0.0147 m.f. benzoylperoxide	0.0422	0.0782	A
Same	0.0447	0.0757	B
0.0291 m.f. benzoylperoxide			C
0.0147 m.f. benzoylperoxide 0.0049 m.f. tetrachlorohydroquinone	0.0233	0.0718	D
Same			E
0.0146 m.f. benzoylperoxide 0.0097 m.f. tetrachlorohydroquinone			F
0.0147 m.f. benzoylperoxide 0.0049 m.f. hydrazobenzene	0.0198	0.1082	G
Same			H
0.0147 m.f. 1-hydroxycyclohexyl-hydroperoxide-1		0.0873	I
0.0147 m.f. ditertiarybutyl-diperphthalate		0.0808	J
Same			K
0.0147 m.f. diazoaminobenzene	0.405	0.746	L
0.0147 m.f. benzoylperoxide 0.0049 m.f. diazoaminobenzene	0.0498	0.0872	M
0.0147 m.f. benzylhyponitrite	0.0437	0.0863	N

Code	Triallylcitrate	Isobutylmethacrylate	Glycoldimethacrylate
A	0.0447	0.743	1.256
B		1	
C		I	
D.	0.0158	1	1.323
E	0.0172		
F		1	
G	0.0389	1	2.090
H		1	
I	0.0458	1	1.318
J		1	1.840
K		1	
L	0.419	1	1.476
M	0.0522	1	1.436
N	0.0532	1	1.332

catalyst for acrylic monomers, but shows little improvement over diazoaminobenzene alone for allyl monomers.

6. Benzylhyponitrite was the most active polymerization catalyst studied, for both types of monomers.

This work indicates that diazoamino compounds should be further investigated as polymerization catalysts for allyl monomers. Substitution of the benzene rings of diazoaminobenzene with positive groups such as alkyl, halogen and amino which would tend to make the diazonium linkage less stable would probably yield more active catalytic agents. These new compounds could also be used with benzoylperoxide to make new and more active catalytic couples for acrylic monomer polymerization.

Benzylhyponitrite was shown to be the most active polymerization catalyst. Other compounds of this type should be investigated, in order to find substances with good catalytic activity which are more stable at room temperature and easier to handle.

Table III, page 182, compares the reaction rates of the various monomers with the rate of isobutylmethacrylate when using the same catalyst. For instance, with 0.0147 m.f. of diazoaminobenzene, allylbutyrate polymerizes only 0.405 as fast as isobutylmethacrylate, while glycoldimethacrylate polymerizes 1.476 as fast.

We see from the table that the reactivities of the monomers bear a general relationship with one another. Glycoldimethacrylate usually polymerizes about 1.5 times as fast as isobutylmethacrylate, whereas allylbutyrate polymerizes about 0.045 as fast, diethyleneglycol bis(allylcarbonate) about 0.08 as fast and triallylcitrate about 0.043 as fast.

With both allyl and acrylic monomers the difunctional compound polymerizes from 1.5 to 2 times as fast as the monofunctional compound. The allyl group of monomers shows a decreasing activity of the trifunctional monomer compared with the difunctional monomer. Evidently the trend of the higher polyfunctional allyl monomers, such as allyl starch, not to polymerize readily with free radical catalysts starts with trifunctional monomers. It appears that difunctional monomers polymerize most readily and that mono and trifunctional monomers polymerize at about the same rate.

CHAIN TRANSFER

Table IV compares the solidification time of the various monomer-catalyst systems. Allylbutyrate was not included because we were not able to polymerize it to a solid. It is seen that glycoldimethacrylate polymerized to a jel faster than any other monomer and that the acrylates polymerized much faster than the allyl compounds. In general these values are proportional to the reaction rates and the same conclusions concerning the reactions may be drawn from both tables I and IV.

Table IV

SOLIDIFICATION TIME, hours

Jel stage, no flow @ 60°C.

Catalyst combination	Diethyleneglycol-bis(allylcarbonate)	Triallylcitrate	Isobutylmethacrylate	Glycoldimethacrylate
Thermal	∝	∝	∝	∝
0.0147 m.f. benzoylperoxide	24	32	4	2
Same	26		2.5	
0.0291 m.f. benzoylperoxide			1.25	
0.0147 m.f. benzoylperoxide 0.0049 m.f. tetrachlorohydroquinone	30	80	4	3.5
Same		80		
0.0146 m.f. benzoylperoxide 0.0097 m.f. tetrachlorohydroquinone			6	
0.0147 m.f. benzoylperoxide 0.0049 m.f. hydrazobenzene	20	32	2	1.25
Same			1.75	
0.0147 m.f. 1-hydroxycyclohexyl-hydroperoxide-1	120	216	14	10
0.0147 m.f. ditertiarybutyl-diperphthalate	104		26	8
Same			12	
0.0147 m.f. diazoaminobenzene	16	22	19	11
0.0147 m.f. benzoylperoxide 0.0049 m.f. diazoaminobenzene	10	14	1.5	0.83
0.0147 m.f. benzylhyponitrite	7	10	0.75	0.50

Table V
% MONOMER AT THE

SOLIDIFICATION POINT

Catalyst combination	Diethyleneglycol-bis(allylcarbonate)	Triallylcitrate	Isobutylmethacrylate	Glycoldimethacrylate
0.0147 m.f. benzoylperoxide	70.9	78.5	73.3	71.5
Same	70.8		72.1	
0.0291 m.f. benzoylperoxide			71.2	
0.0147 m.f. benzoylperoxide 0.0049 m.f. tetrachlorohydroquinone	63.4	71.0	48.7	48.3
Same		72.0		
0.0146 m.f. benzoylperoxide 0.0097 m.f. tetrachlorohydroquinone			46.9	
0.0147 m.f. benzoylperoxide 0.0049 m.f. hydrazobenzene	70.8	77.4	69.5	66.0
Same			69.0	
0.0147 m.f. 1-hydroxycyclohexyl-hydroperoxide-1	70.2	82.6	71.9	71.5
0.0147 m.f. ditertiarybutyl-diperphthalate	70.5		69.3	71.1
Same			71.3	
0.0147 m.f. diazoaminobenzene	64.1	73.1	57.2	61.1
0.0147 m.f. benzoylperoxide 0.0049 m.f. diazoaminobenzene	73.8	80.0	67.8	71.5
0.0147 m.f. benzylhyponitrite	68.6	77.3	71.2	72.2

There are a couple of discrepancies, however, which should be pointed out. In the catalyst system benzoylperoxide-tetrachlorohydroquinone the reaction rates were greater than with benzoylperoxide alone, yet the solidification times were greater. The same relationship was also found for all monomers with diazoaminobenzene catalyst.

Table V compares the unsaturation of the various monomers at the solidification point. Diethyleneglycol bis-(allylcarbonate) generally solidifies at about 70%, triallylcitrate at about 77 to 80%, isobutylmethacrylate at about 68 to 71% and glycoldimethacrylate at about 71 to 72%. There are several exceptions in which the percentage is much lower than usual. These are the reactions with benzoylperoxide-tetrachlorohydroquinone catalyst and with diazoaminobenzene catalyst.

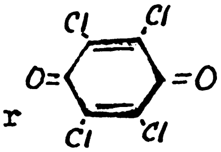
It is seen that the two catalysts diazoaminobenzene and benzoylperoxide-tetrachlorohydroquinone cause longer solidification times and lower unsaturation at the solidification point, yet they have reaction rates which are generally equal to or greater than the corresponding rates with benzoylperoxide alone. This phenomena can be ascribed to a chain transfer reaction.

Chain transfer is the process whereby a growing polymer chain reacts with a constituent of the reaction mixture, terminating the chain growth and forming a new free radical which acts as the nucleus upon which another polymer chain may grow.

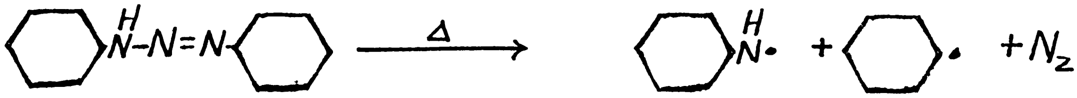
$$(M)_x^{\bullet} + CCl_4 \longrightarrow (M)_xCl + CCl_3\bullet$$

$$CCl_3\bullet + M \longrightarrow CCl_3M\bullet \xrightarrow{M} CCl_3(M)_x\bullet$$

In these equations carbontetrachloride is the chain transfer agent which forms a trichloromethyl radical when it reacts. The chain transfer reaction (47) causes shorter polymer chains to form. This means the polymer will have a lower average molecular weight and that a longer time will be required before the solidification point is reached. It was also stated that a chain transfer agent does not change the rate of polymerization appreciably. Therefore, we would expect the polymer formed by chain transfer to have a lower degree of unsaturation at the jel point. It is seen that our two catalysts yield data indicative of chain transfer.

Chloranil  has been shown to be an effective chain transfer agent(10). A chlorine atom is split out similar to the carbontetrachloride reaction to cause chain transfer. Since tetrachlorohydroquinone is the reduced form of chloranil we might expect it to be the chain transfer agent in our experiments. Perhaps the tetrachlorohydroquinone was oxidized to chloranil by benzoylperoxide during the induction period and the chloranil was actually the chain transfer agent during polymerization. This second hypothesis is probably correct because the chlorine would be much more stable in the benzene structure than in the quinone structure.

The explaination is not as simple with diazoaminobenzene. This material decomposes to form two different free radicals:



Since the phenyl group does not usually cause much chain transfer, we would expect that the hydrogen atom attached to the nitrogen was probably the atom which caused chain transfer. When the catalyst couple diazoaminobenzene-benzoylperoxide was used no appreciable chain transfer occurred. This indicated that the part of the diazoaminobenzene which caused chain transfer was destroyed by reaction with benzoylperoxide. This substantiates our thought that the amino hydrogen atom was the one causing chain transfer.

PROPERTIES OF PLASTIC SAMPLES

The properties of the final solid polymers varied in many ways. Some were harder than others, some appeared to have a crystalline structure, some were full of bubbles, some were colored and many had other unique properties. These properties will be reviewed and contrasted here.

The monofunctional isobutylmethacrylate formed a thermoplastic glass. It fractured yielding smooth rounded surfaces when cold and softened when heated to a viscous putty like solid.

The difunctional monomers, diethyleneglycol bis (allylcarbonate) and glycoldimethacrylate formed infusible thermosetting plastics. The soft jel of the allyl monomers yielded a crystalline pattern when cut. On further polymerization it formed a brittle glass which did not fracture smoothly. The glycoldimethacrylate shrunk appreciably on polymerization. The strains set up by this shrinkage caused cracks to form in many of the samples before they were removed from the constant temperature bath. The final product was a hard, brittle, partially cracked plastic.

Triallylcitrate, a trifunctional monomer, formed a soft crystalline jel similar to that of diethyleneglycol bis (allylcarbonate). Further polymerization yielded a hard glass like plastic with few cracks. It had about the same look and feel as the isobutylmethacrylate plastic, except that it was an infusible, thermosetting material.

Table VI

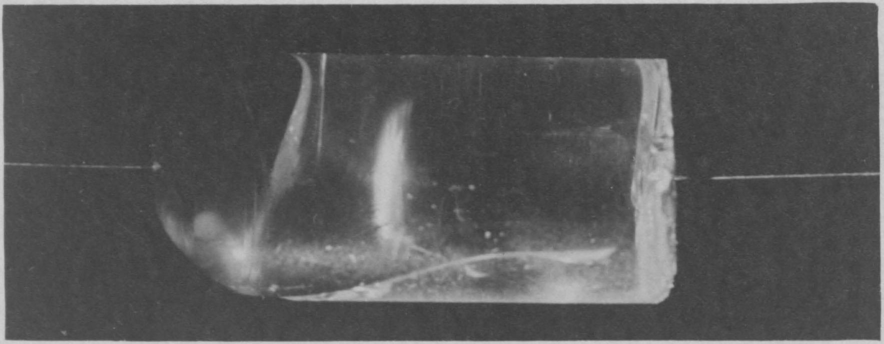
COLOR OF SOLID PLASTICS

C= colorless
P= pink
Y= yellow
O= orange
B= brown   M= maroon

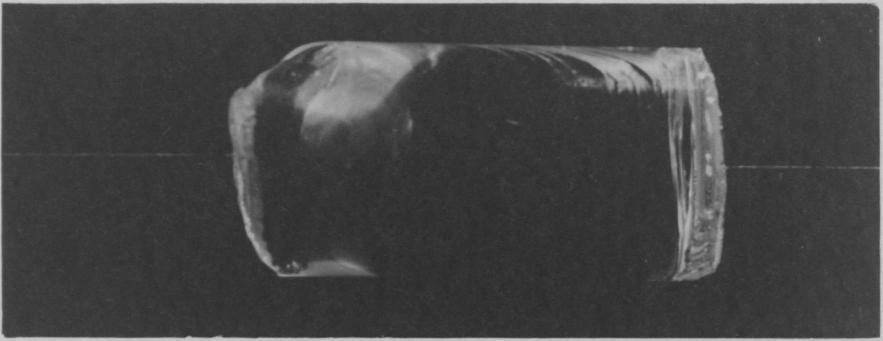
Catalyst Combination	Diethyleneglycol bis(allylcarbonate)	Triallylcitrate	Isobutylmethacrylate	Glycoldimethacrylate
0.01477 m.f. benzoyl peroxide	C	C	C	C
Same	C		C	
0.0291 m.f. benzolyperoxide			C	
0.0147 m.f. benzoylperoxide 0.0049 m.f. tetrachlorohydroquinone	Y	P	Y	Y
Same		Y		
0.0146 m.f. benzoylperoxide 0.0097 m.f. tetrachlorohydroquinone			Y	
0.0147 m.f. benzoylperoxide 0.0049 m.f. hydrazobenzene	YO	YO	YO	YO
Same			YO	
0.0147 m.f. 1-hydroxycyclohexyl-hydroperoxide-1	C	C	C	C
0.0147 m.f. ditertiarybutyl-diperphthalate	C		C	C
Same			C	
0.0147 m.f. diazoaminobenzene	O	O	O	O
0.0147 m.f. benzoylperoxide 0.0049 m.f. diazoaminobenzene	OB	OB	M	OB
0.0147 m.f. benzylhyponitrite	C	C	C	C

The monomers were all clear and colorless liquids. Any color which developed in the plastics was due to the catalyst and not the monomer. The accompanying table, # VI, indicates the colors that were formed. The peroxides and benzylhyponitrite yielded colorless polymers. Tetrachlorohydroquinone caused a faint pink to yellow coloration. Hydrazobenzene caused a yellowish-orange polymer to form and diazoaminobenzene formed orange to deep red colored plastics. It is seen that the colors are characteristic of the catalyst system and not common to the monomer.

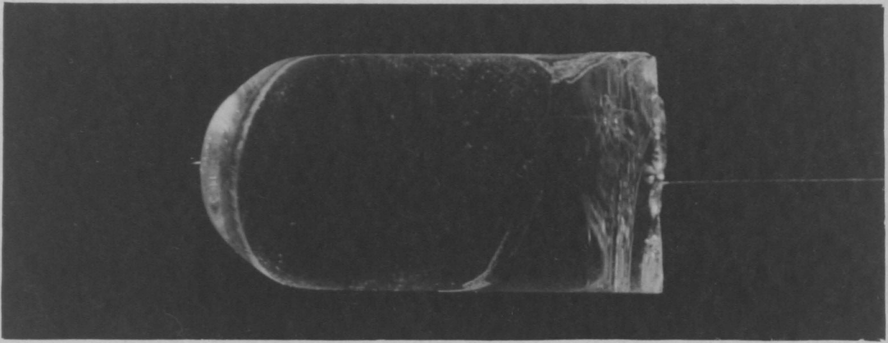
Bubble formation in the polymers was generally characteristic of the polymerization catalyst used. The peroxides usually yielded clear plastics with few bubbles. In some instances a few large bubbles were found at localized spots within the polymer. These were usually caused by gas bubbles trapped in the viscous syrup during sampling. Tetrachlorohydroquinone and hydrazobenzene did not induce bubble formation. Diazoaminobenzene and benzylhyponitrite did cause bubble formation. It was felt that this was due to the nitrogen which was liberated when the azo linkage was broken. The bubbles formed by these agents were usually well dispersed and scattered through the polymer. The bubbles created such force in the isobutylmethacrylate-benzylhyponitrite system that the polymer was expanded against and could hardly be separated from the glass walls of the reaction tube.



Triallylcitrate
0.0147 m.f. diazoaminobenzene



Triallylcitrate
0.0147 m.f. benzoylperoxide
0.0049 m.f. tetrachlorohydroquinone

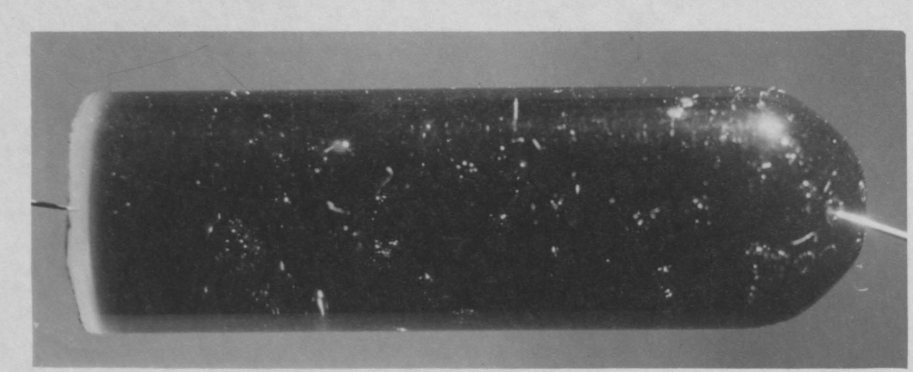


Triallylcitrate
0.0147 m.f. benzoylperoxide

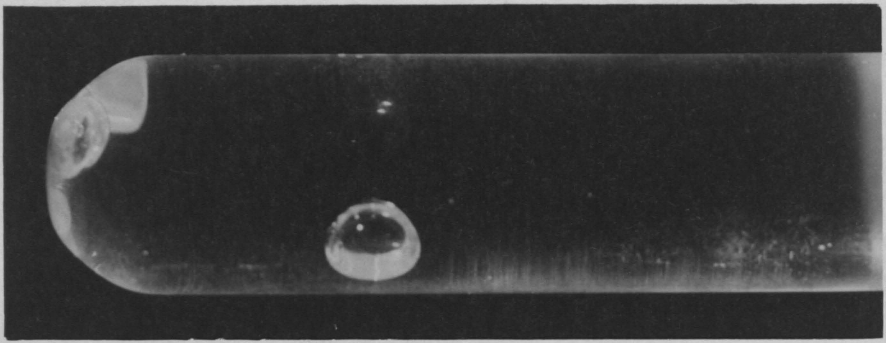
Photographs of some of the polymer samples have been included to demonstrate the physical appearance of the plastics formed by the different monomer-catalyst systems.

The triallylcitrate polymers pictured here are clear and bubbleless. A few crystalline fractures are visible at the square end which were formed in cutting the plastic. Light surface fractures are seen on the lower two photographs which were formed when the plastic shrank and broke away from the walls of the reactor.

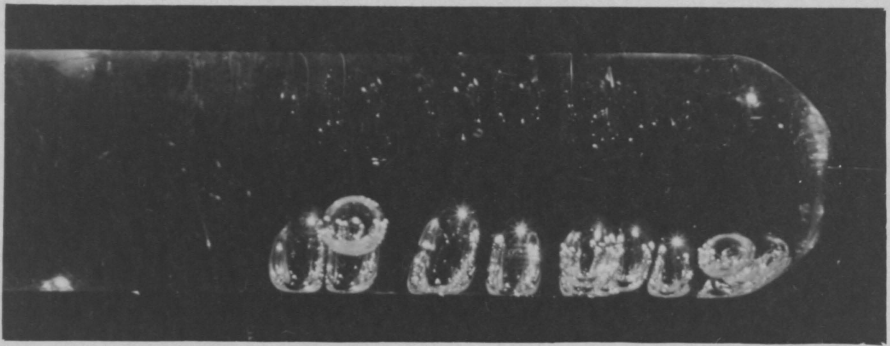
A longitudinal internal crack is seen in the upper photograph which was due to shrinkage during polymerization.



Isobutylmethacfylate
0.0147 m.f. benzoylperoxide
0.0049 m.f. diazoaminobenzene



Isobutylmethacrylate
0.0147 m.f. ditertiarybutyldiperphthalate



Isobutylmethacrylate
0.0147 m.f. 1-hydroxycyclohexylhydroperoxide-1

1. The maroon color of this isobutylmethacrylate sample was characteristic of the diazoaminobenzene catalyst used. The bright specks scattered through the polymer are due to light reflected from bubbles inside the polymer. These bubbles were obscured from the camera by the deep color of the sample. The light layer at the square end was caused by contact with air or water vapor.

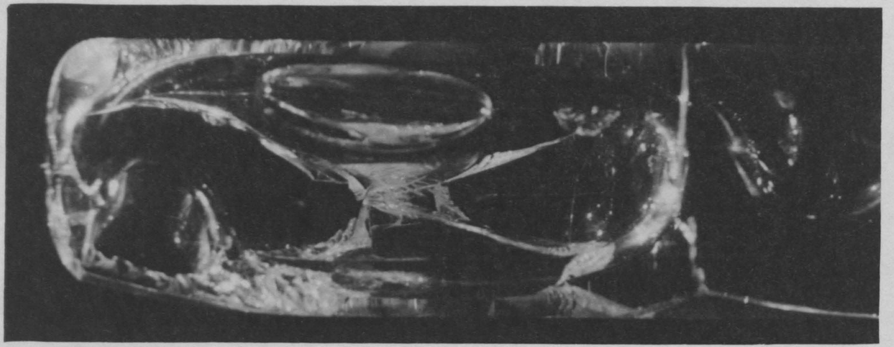
2. Clear, colorless plastic. The bubbles were introduced by sampling.

3. Clear, colorless plastic. The bubbles were probably introduced by sampling.

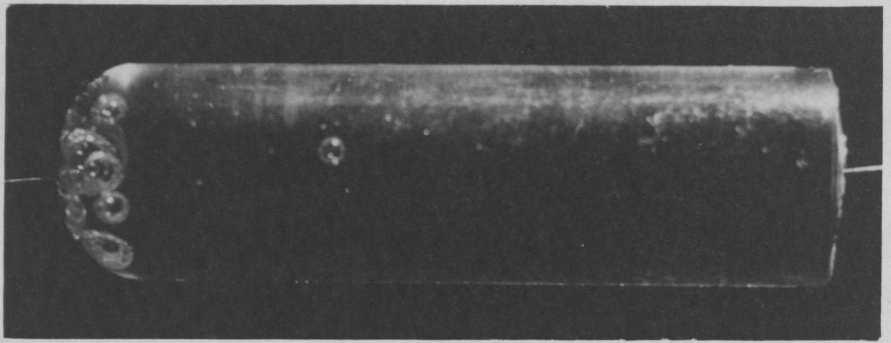
1. Clear, colorless plastic. The large bubbles are characteristic of benzylhyponitrite catalyst. The cracks which appear in the middle and toward the left side are in the glass reaction tube which could not be broken from the plastic.

2. Orange colored plastic. The bubbles are thought to be due to trapped nitrogen released when the catalyst decomposed.

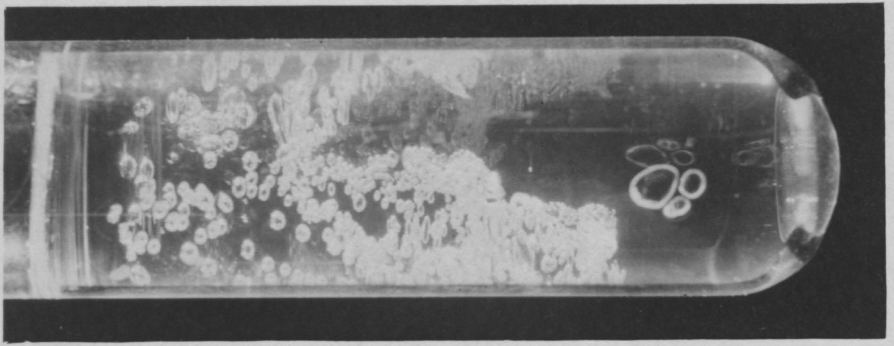
3. A high polymerization temperature allowed the reaction to occur so fast that the exothermic reaction caused the monomer to partially vaporize and many bubbles became trapped in the polymer.



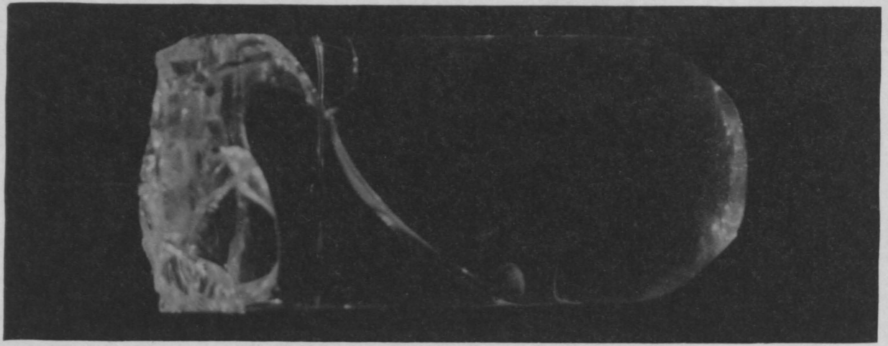
Isobutylmethacrylate
0.0147 m.f. benzylhyponitrite



Isobutylmethacrylate
0.0147. m.f. diazoaminobenzene

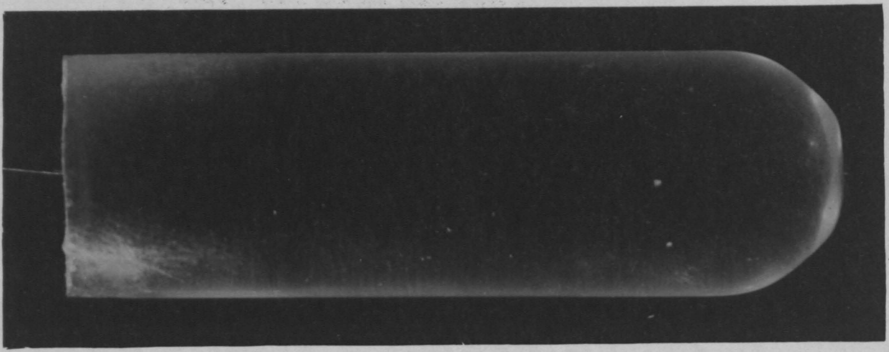


Isobutylmethacrylate
0.0147 m.f. benzoylperoxide @ 90°C.



Glycoldimethacrylate
0.0147 m.f. benzoylperoxide

Glycoldimethacrylate
0.0147 m.f. diazoaminobenzene

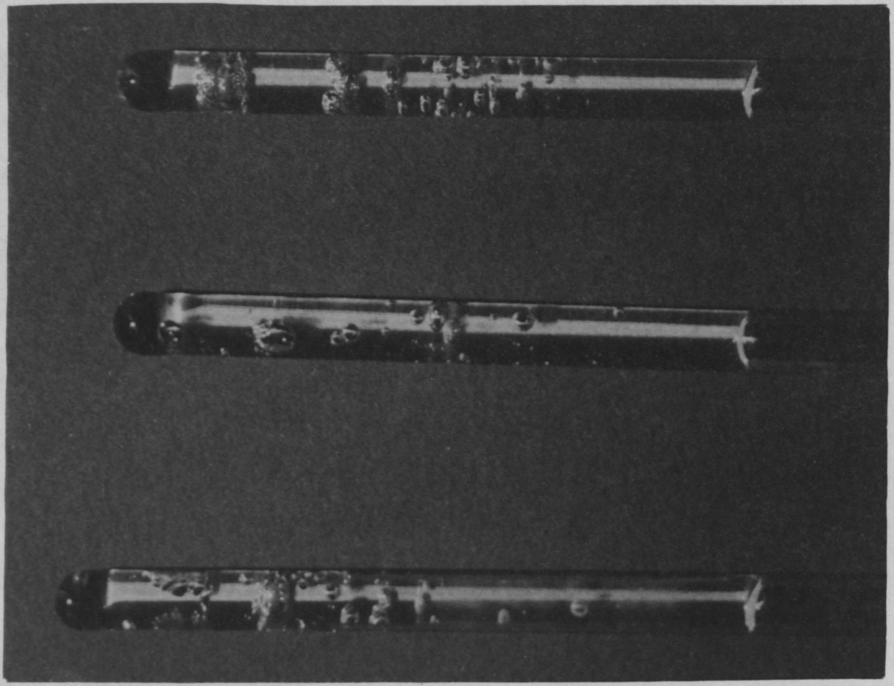


Isobutylmethacrylate
0.0291 m.f. benzoylperoxide

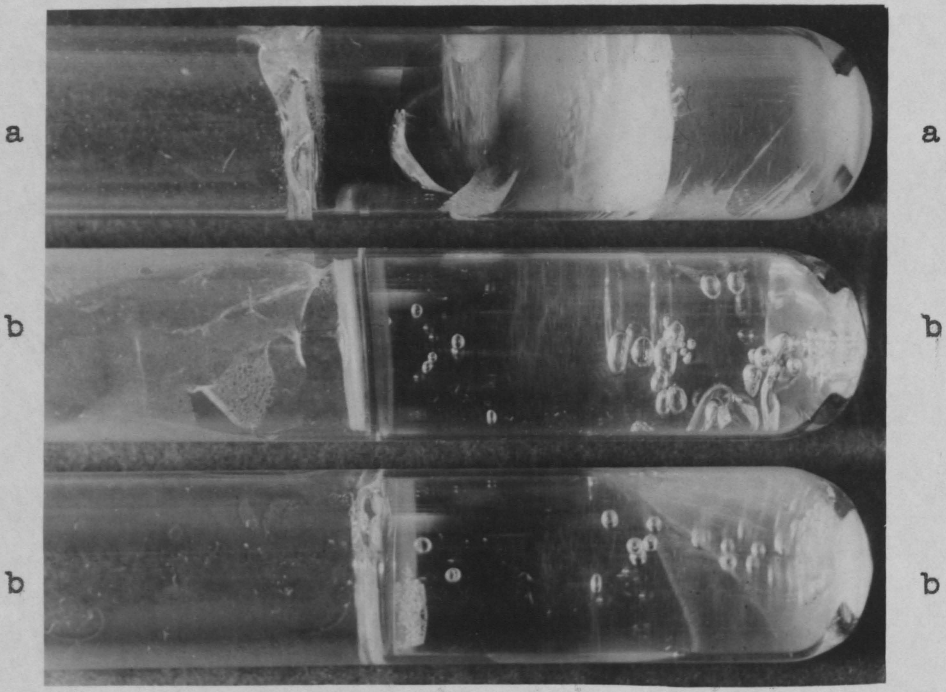
1. The hard brittle character of the glycoldimethacrylate polymer is demonstrated by the many cracks in the square end of the plastic.

2. The orange color of the plastic obscures some of the bubbles formed by decomposition of the diazoaminobenzene.

3. A large amount of benzoylperoxide caused the polymer to be cloudy and not clear. Light is reflected evenly from the surface of the polymer which appeared to be etched instead of smooth and glassy.



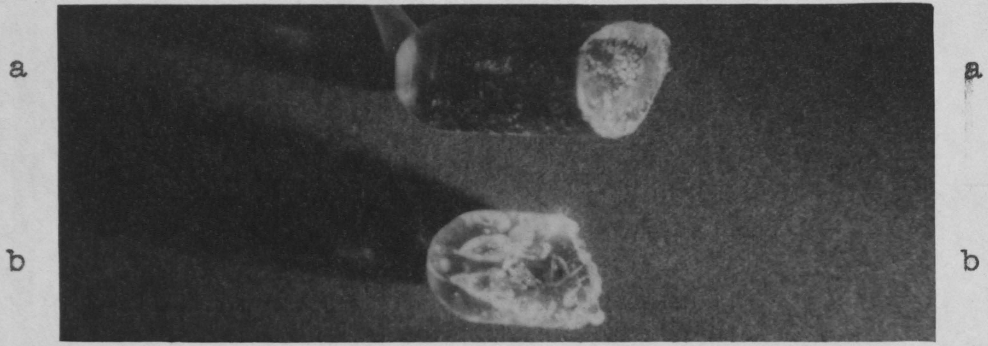
Glycoldimethacrylate
0.0147 m.f. benzylhyponitrite



Glycoldimethacrylate
a. 0.0147 m.f. hydroxycyclohexylhydroperoxide
Isobutylmethacrylate
b. 0.0147 m.f. hydroxycyclohexylhydroperoxide

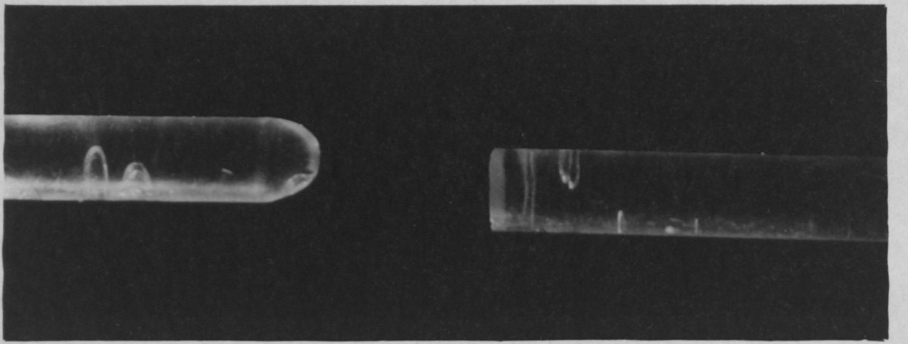
1. The bubbles were due to nitrogen gas which was released when the hyponitrite catalyst decomposed. The polymer is still sealed in the 6 mm. tubes inwhich it was polymerized.

2. The bright layer in the polymer in the upper tube was due to a large internal crack. All these samples are in the test tubes inwhich they were polymerized. It can be seen from the reflections that they have all shrunk away from the surface of the reaction tubes.



Diethyleneglycol bis(allylcarbonate)
a. 0.0147 m.f. benzoylperoxide
0.0049 m.f. hydrazobenzene
b. 0.0147 m.f. diazoaminobenzene

Diethyleneglycol bis(allylcarbonate)
a. 0.0147 m.f. benzoylperoxide
0.0049 m.f. tetrachlorohydroquinone
b. Triallylcitrate
0.0147 m.f. benzoylperoxide, 0.0049 m.f. hydrazobenzene



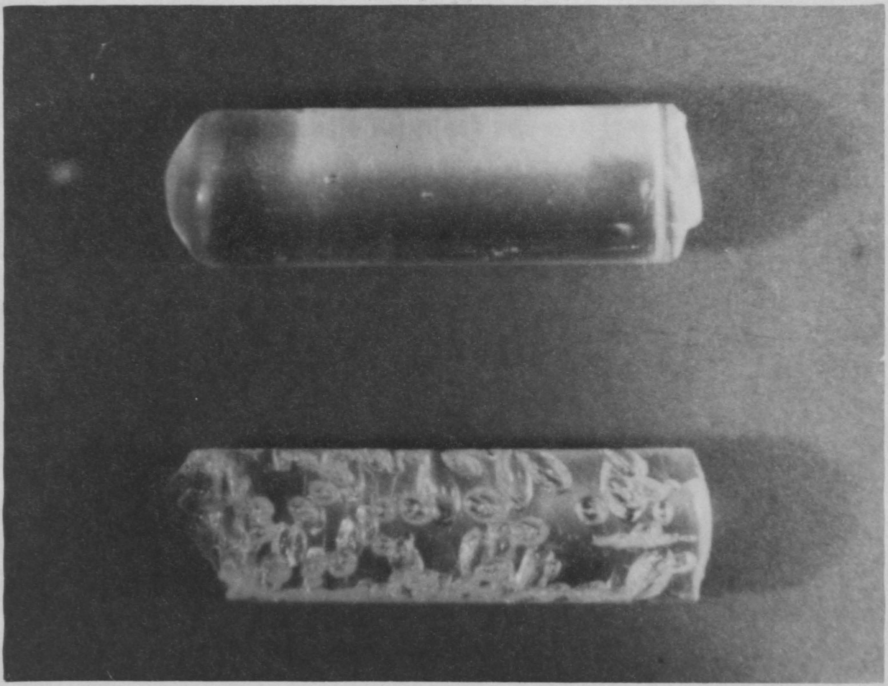
Isobutylmethacrylate
0.0147 m.f. benzoylperoxide

1. a. The clear, light tan colored polymer contains no bubbles.
    b. The diazoaminobenzene product contains several bubbles which were characteristic of this catalyst. It had a tan color.

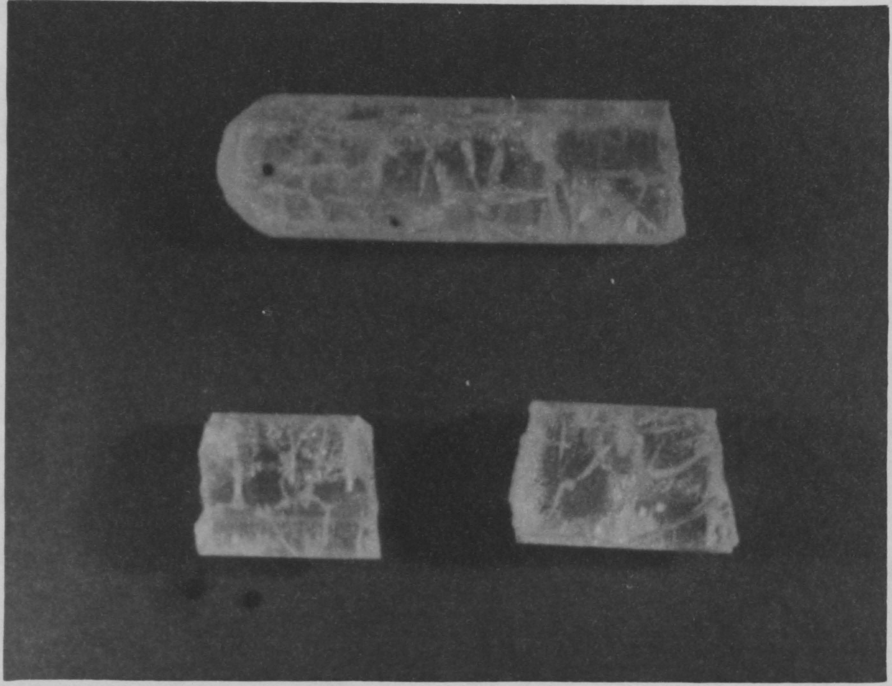
2. a. The clear plastic had a light yellow color and contained no bubbles.
    b. The polymer had a light tan color. It was a clear, hard material, the internal crack on the left hand side which formed during the polymerization reflects the light strongly.

3. This is an enlarged photograph of the polymer which formed in the 6 mm. glass tubes. It has the same properties as the plastic formed in the regular 6 inch test tubes.

Isobutylmethacrylate
0.0147 m.f. benzoylperoxide



Triallylcitrate
0.0147 m.f. benzylhyponitrite



Diethyleneglycol bis(allylcarbonate)
0.0147 m.f. benzoylperoxide

1. The upper sample is characteristic or the clear, bubbleless polymer from benzoylperoxide catalysis.

   The lower plastic is characteristic of the benzylhyponitrite catalyst, clearly showing the many bubbles entrapped in the polymer.

2. The crystalline nature of the diethyleneglycol bis allylcarbonate is shown very clearly by these pieces of polymer which were purposely cracked to reveal it.

ULTRASONIC CATALYSIS

The effects of ultrasonic energy on different forms of matter have only begun to be evaluated within the last five to ten years. Ultrasonic energy is very high frequency sound waves. The energy of these waves is largely dissipated as mechanical work and heat. The vibrations which are induced in matter are very strong and cause a shearing effect. For instance, bacterial cells are broken apart by ultrasonic energy; mercury can be homogenized in water; hydrogen peroxide is formed in aerated water and some chemical reactions are catalyzed by ultrasonic energy.

Polymers and jels have been degraded by subjecting them to ultrasonic energy 53 (31) 52, the degradation being more effective in dilute solutions. The change of viscosity of the solution and polymer precipitation have been used to evaluate the degree of degradation. Upon this basis it has been concluded that the degradation was due to the breaking of polymer chains by disruption of the carbon-carbon bonds.

We felt that ultrasonic energy might initiate polymerization of the acrylates and allylesters because it has some chemical catalytic effects and it has been shown to attack high polymers. Three experiments were conducted to evaluate this hypothesis.

Isobutylmethacrylate and diethyleneglycol bis(allylcarbonate) were not polymerized when treated with ultrasonic energy as determined by analysis for unsaturation. A solution of benzoylperoxide in isobutylmethacrylate did not polymerize either. These experiments demonstrated that ultrasonic energy does not cause polymerization to occur.

Depolymerization of polyallylesters and polymethacrylates was next attempted to see whether we could duplicate results already reported in the literature and thus check the effectiveness of our experimental procedures.

Two experiments, one with polyisobutylmethacrylate and the other with polydiethyleneglycol bis(allylcarbonate) demonstrated that ultrasonic energy having a frequency of 550 k.c. has no apparent effect on the degree of polymerization of the solid polymers. This is in accord with the literature.

It is known (54) that ultrasonic energy decreases the apparent molecular weight of the polymer in a dilute solution. This decrease in molecular weight has been determined by viscosity and polymer precipitation measurements. No unsaturation analyses have been applied. We decided, therefore, to carry out the degradation and determine both the viscosity and the degree of unsaturation of the polymer solution.

In experiments #6 and #7 the viscosity decreased rapidly during the first hour of each run and then leveled off during the remaining time. This behavior has been observed before (31) and appears to be characteristic of the ultrasonic polymer degradation process. It was postulated that there was a critical size above which ultrasonic degradation occurs and that degradation ceases when the molecules have been reduced below this size.

The total decrease in viscosity of each sample was about five percent, whereas the increase in unsaturation appeared to be two percent or less and fell within the range of experimental error. Experiments #6 and #7 indicate that unsaturation was not formed in ultrasonic polymer degradation.

Staudinger[57](32) found the molecular weight of high polymers to be a function of the specific viscosity:

$$\frac{N_c}{N_o} - 1 = N_{sp}. \qquad M.W. = N_{sp} \times K$$

N_c - viscosity of polymer solution

N_o - viscosity of solvent

N_{sp} - specific viscosity

M.W. - molecular weight of polymer

K - constant for particular solvent-polymer combination

Applied to our experimental data:

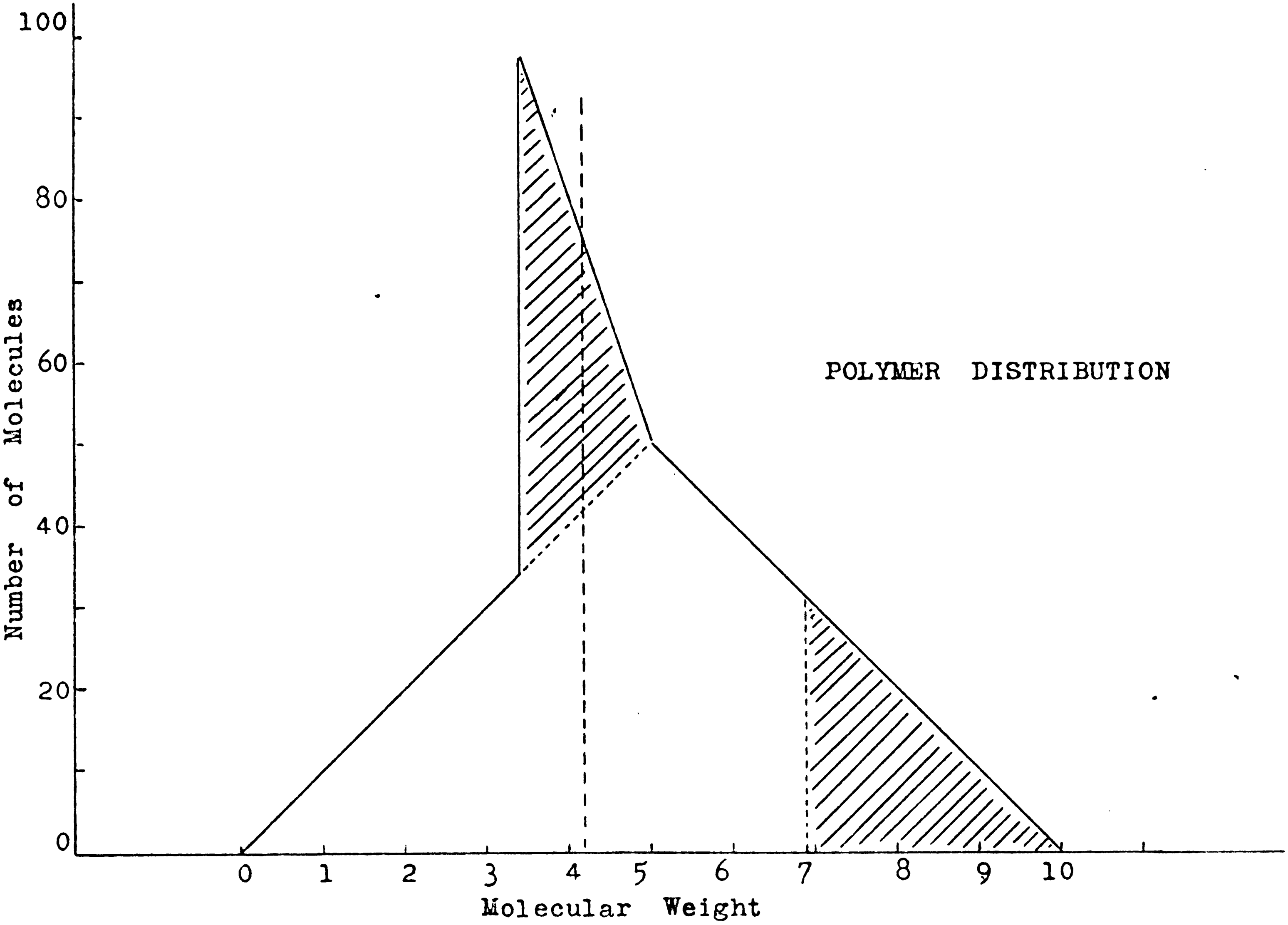
Before treatment

$$\frac{1.195}{0.900} - 1 = 0.330$$

After treatment

$$\frac{1.147}{0.900} - 1 = 0.275$$

$$\Delta N_{sp} = 0.055$$


POLYMER DISTRIBUTION
Number of Molecules
100
80
60
40
20
0
0
1
2
3
4
5
6
7
8
9
10
Molecular Weight

The percentage change of specific viscosity is:

$$\frac{0.055}{0.330} \times 100 = 16.66\%$$

This indicates that the average molecular weight of the polymer was reduced 16.66 percent.

To elucidate this figure let us assume a very simplified polymer distribution, as being triangular in shape. (See graph.) If we reduce the average molecular weight 5, by 16.66% we have a molecular weight of about 4.2. If this is accomplished by splitting the highest mol. wt. molecules into two equal parts, then all the molecules having molecular weights above 7 will have to be split. This means that about 18% of the polymer present must be split to reduce the molecular weight 16.6%. Each carbon bond broken during treatment could furnish two active centers which would add halogen, free radicals or other groups. If these groups were preserved we should expect an 18% increase in unsaturation expressed as monomer. Since our analytical methods are accurate enough to indicate clearly a change as great as this, it must be assumed that no unsaturation was developed or that it was destroyed immediately.

Review

Let us review some of the facts of ultrasonic polymer degradation:

1. Degradation occurs only in fairly dilute solutions. Jels and solids are not appreciably affected.
2. Degradation reduces the molecular weight of the polymer,

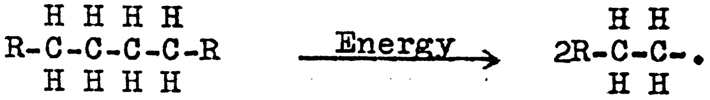
as determined by viscosity and fractional precipitation analyses.

3. The degradation products have approximately the same properties as the original polymer. For instance, no carbonaceous deposits, color changes or unsaturation changes are noticed. Only the molecular weight changes.
4. A critical degradation size for the polymers is recognized.
5. The viscosity increases slightly immediately after ultrasonic treatment due to formation of weak bonds by Van der Waal's forces. (Thixotropy.)
6. Increasing the air pressure over the polymer solution subjected to ultrasonic energy increased the rate of degradation.
7. The greatest rate of decrease in viscosity occurs at the beginning of the treatment.
8. The treated polymer solution has a narrower mol. wt. distribution than the original solution.
9. An optimum ultrasonic intensity of 10 watts/cm.^{2} was found. More power did not increase the polymerization rate appreciably, whereas less power decreased it markedly.

Interpretation:

I do not believe the true nature of ultrasonic degradation of polymer solutions is known. Our findings do not fit the general interpretation evolved by Mark and his coworkers. The phenomena occurring during treatment are certainly much more complex than he has lead us to believe.

It has been postulated that the viscosity decrease is due to breaking of carbon bonds. The breaking of a carbon-carbon bond might result in the formation of a pair of unsatisfied valences.

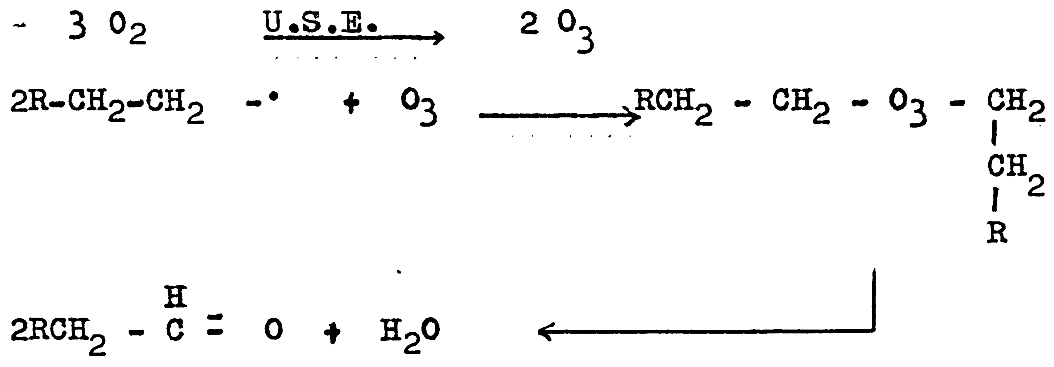


$$R-\overset{H}{\underset{H}{C}}-\overset{H}{\underset{H}{C}}-\overset{H}{\underset{H}{C}}-\overset{H}{\underset{H}{C}}-R \xrightarrow{\text{Energy}} 2R-\overset{H}{\underset{H}{C}}-\overset{H}{\underset{H}{C}}-.$$

If the radicals were formed, they must have been destroyed; otherwise analysis for unsaturation would have revealed them.

A clue might be found in the fact that increased air pressure increases the rate of degradation.

Pressure can cause a reaction to proceed at a faster rate in only two ways – by increasing the concentration of a gaseous reactant, or by allowing higher reaction temperatures to be employed. Since no temperature advantage was taken it must be assumed that the air plays a role in polymer degradation. Ozone may be the actor, as demonstrated by the following sequence of equations:



$$3\ O_2 \xrightarrow{U.S.E.} 2\ O_3$$

$$2R-CH_2-CH_2-\cdot + O_3 \longrightarrow RCH_2-CH_2-O_3-\begin{array}{c}CH_2\\ |\\ CH_2\\ |\\ R\end{array}$$

$$\longrightarrow 2RCH_2-\overset{H}{C}=O + H_2O$$

Ultrasonic energy will cause formation of hydrogen peroxide in water from dissolved oxygen and I feel, therefore, that it is not presuming too much to suppose that ozone would be produced from air dissolved in anhydrous solution. The amount of air involved would be very small and would be difficult to detect. A process of this type would lead to formation of saturated degradation products and would be in accord with our findings.

Further research on the following points would help to elucidate and extend the interpretation of ultrasonic polymer degradation:

1. Analysis of gases given off by cavitation.
2. Analysis of degraded polymer mixtures for aldehyde, ketones and acids.
3. Determination of polymer molecular weight distribution before and after ultrasonic degradation to ascertain the manner in which the higher molecular weight particles were degraded.
4. Determination of rate of polymer degradation in the

absence of air and under pressure of inert atmospheres.

5. A refractometric and dispersion study of polymer degradation to reveal formation of double bonds or polar groups.
6. A spectrophotometric study to reveal the degradation products.

X-RAY POLYMERIZATION OF ISOBUTYLMETHACRYLATE

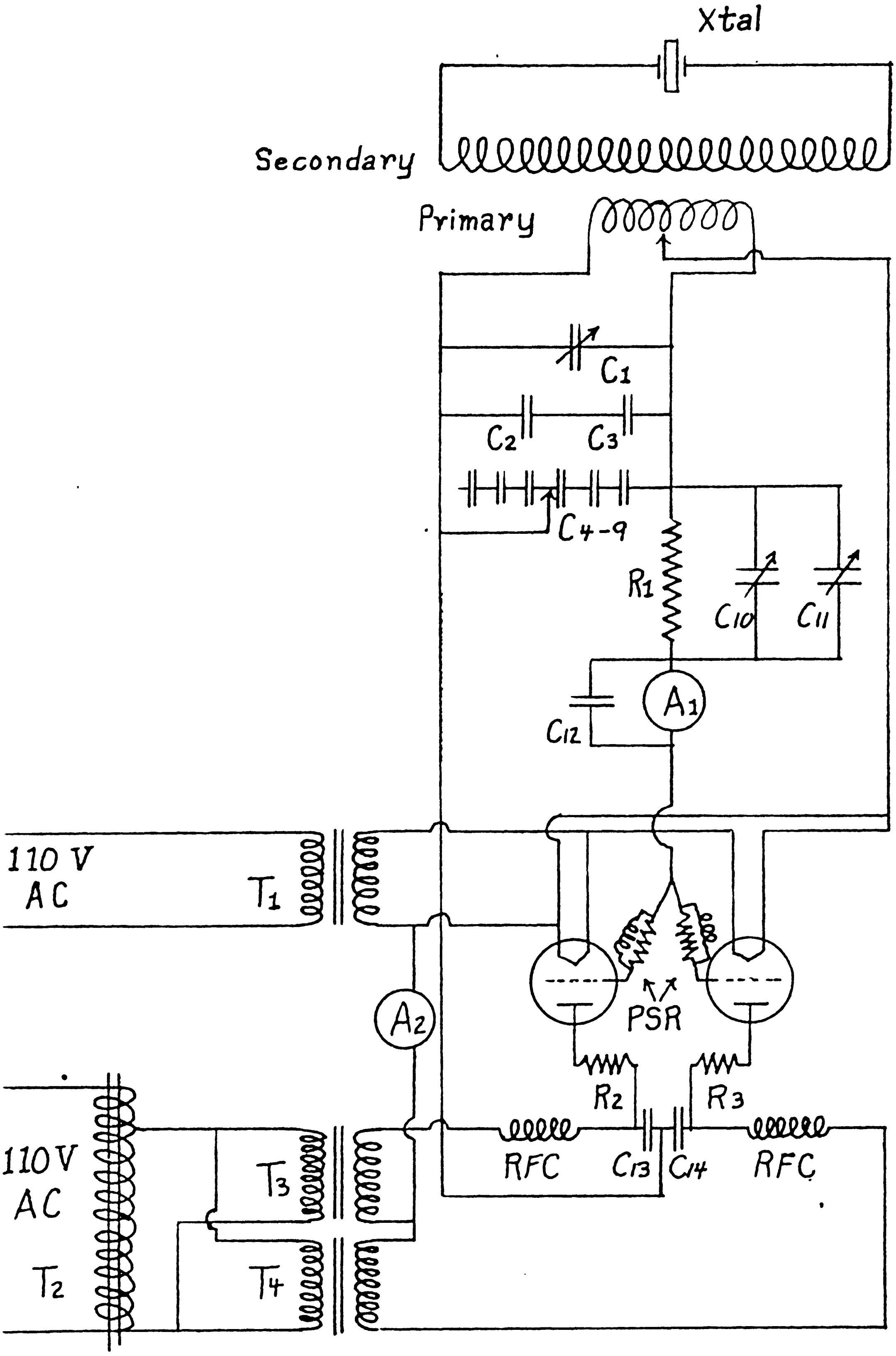
Two unsuccessful attempts were made to polymerize isobutylmethacrylate with x-rays. It was reported (59 that gamma radiation from radium caused acrylic esters to polymerize at room temperature. We felt that x-rays might also be active in this sense. However, the experiments have shown our premises to be wrong.

A special water cooled, high intensity x-ray tube was used which had a beryllium window and a copper target. It was operated at 30,000 volts and 10 milliamperes. The shortest wave length produced under these conditions is 0.41 A^o.

Gamma rays are electromagnetic waves having a wavelength intermediate between those of cosmic rays and x-rays. The wavelengths of the most intense gamma rays vary from about 0.005 A^o to 0.02 A^o. They are even shorter than million volt x-rays, which have a minimum value of about 0.012 A^o. Since the wavelengths we used were about one hundred times longer than those known to be active it is plausible that the catalytic activity could be lost.

If the x-rays had any catalytic power, they would have induced polymerization under these conditions, since 60^oC. is almost the threshold value for rapid thermal polymerization. The high intensity of the x-rays was evidenced by the pyrex beaker which acquired a light brown tint after irradiation.

Ultrasonic Generator



APPENDIX

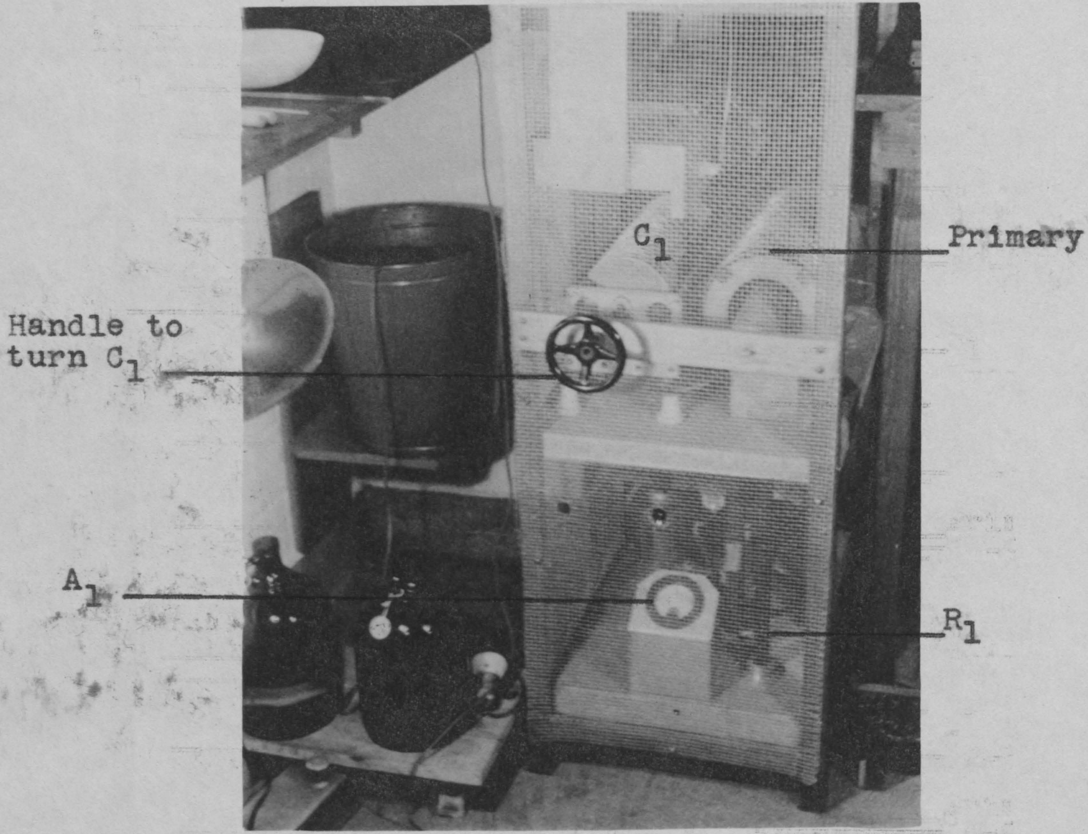
Ultrasonic Generator

The Piezoelectric Ultrasonic Generator used in this work was designed and constructed by Robert E. Kyrlach and Harold Kersten of the Physics Department of the University of Cincinnati. It worked very well and gave no trouble whatsoever. Sound waves were generated having a frequency of 550 kilocycles by means of a circular quartz crystal an inch and a quarter in diameter.

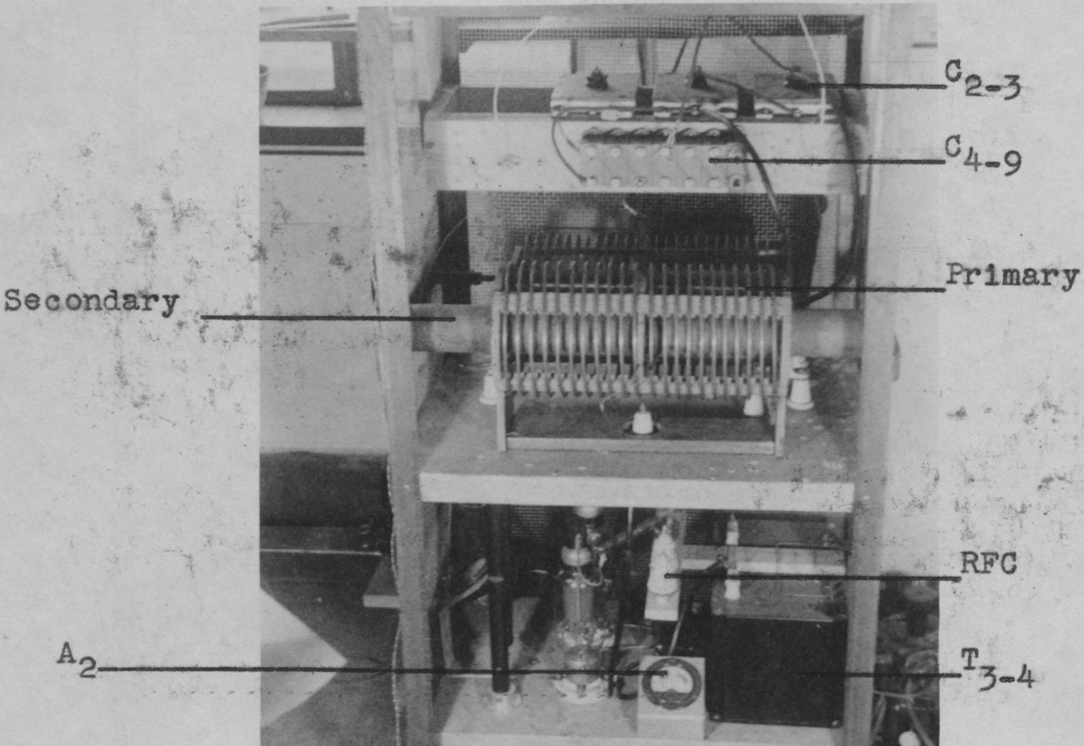
Circuit Constants

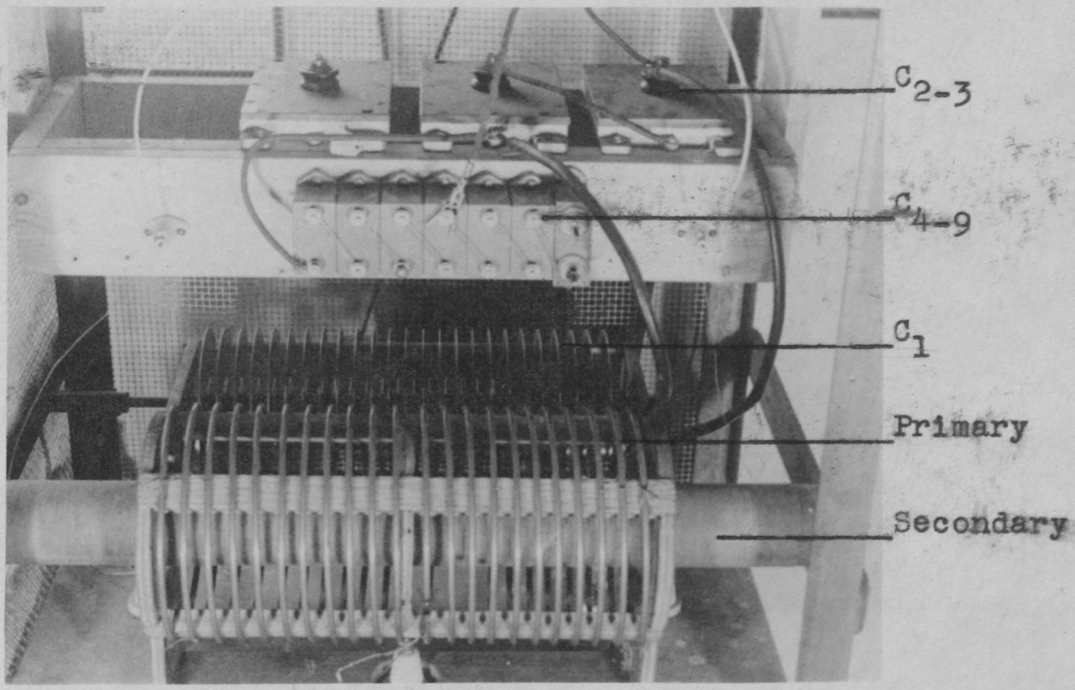
X - Cut Quartz crystal ¼" thick x 1¼" diameter.
Secondary, 400 turns #22 D.C.C. closewound 3½" diameter.
Primary, 22 turns #4 bare wire 6½" diameter 14" long.

C_1	500 $\mu\mu f$	7000 V variable condenser
$C_{2,3}$	0.004 μf condenser	12000 V (10 amp. @ 1000 k.c.)
$C_{4-9,13,14}$	0.004 μf condenser	5000 V (2amp. @ 1000 k.c.)
$C_{10,11}$	100 $\mu\mu f$	1000 V variable condenser
C_{12}	0.01 μf	1000 V condenser
R_1	10.000 ohms, 200 watts	
$R_{2,3}$	5 ohms, 10 watts, wire wound	
RFC	9mh. 2, 4.5 mh, 12 ohms	r.f. chokes in series
T_1	12 V	150 watt



Ultrasonic Generator





Ultrasonic Generator

T_2	Autotransformer 40 to 200 V.
T_3, T_4	3200 V no taps, about 600 watts
$A_{1,2}$	0-100 m.a. D.C.
PSR	Ohmite parasitic suppressor resistors (P-300)
Tubes	HF200 Amperex triodes

The apparatus is operated as follows:

1. Turn on the tube filament heater current (T_1) and allow about a minute for the tubes to heat.
2. Turn on high voltage current (T_2) and turn C_1 until the crystal oscillates.
3. Put load over crystal and adjust its height with the tilt screw in the ring stand until maximum load agitation is observed.
4. Adjust C_2 once more to a minimum A_1 meter values, about 30 milliamperes.

The apparatus is now delivering its maximum power. Under normal operating conditions the grid current (A_1) is about 30 milliamperes and the plate current (A_2) is about 275 milliamperes.

Rate of Heating

A 360 g. porcelain casserole was filled with 700 ml. of transformer oil at 20°C. The crystal vibrator was immersed in the oil. After running the apparatus for 20 minutes the temperature of the oil was 55°C. This temperature rise occurred at a fairly steady rate. The power output was calculated as follows:

Average rate of heating per minute $\frac{35}{20} = 1.75^{\circ}$C./min.

Sp. heat of oil, 0.5 cal/g./C°.

Sp. heat of porcelain, 0.2 cal./g./C°.

Water equivalent of bath = Oil equivalent + casserole equivalent.

$422 = 700 \times 0.5 + 360 \times 0.2$

Assuming about 20% heat loss from other sources, the water equivalent would be 500 ml. Total heat generated = 500 x 1.75 = 875 cal./min. or 14.6 cal./sec. Since 1 calorie is equivalent to 4.2 watts,

14.6 x 4.2 = <u>61.3 watts</u> energy dissipated as heat.

In other words the bath would heat up just as fast if a 60 watt electric bulb was immersed in it. The ice required to dissipate this heat is about 2 lb./hr.

General Notes

The transformer oil used to insulate the crystal and to remove heat from the bath must be kept dry and free from impurities in order to preserve its insulating properties, otherwise, arcing of the electric current would occur and would prevent satisfactory operation of the apparatus. The bath must not be so cold that atmospheric moisture condenses on and contaminates it.

Air bubbles, caused by oil recycling, must be avoided, for they collect under the crystal and cause arcing.

Cavitation drives dissolved air out of the oil. This air also collects under the crystal. A tiny hole in the brass ring under the crystal or some other means must be provided for the trapped air to escape.

Since the crystal generates sound waves in two directions only 30 watts of energy is radiated in each direction. The contents of the flask placed directly over the crystal were found to absorb about 15 watts of energy. It may be concluded that the energy absorbed by the sample is about one fourth of the total output of the apparatus.

SUMMARY

An analytical procedure was developed for determining chemical unsaturation in a monomer-polymer mixture of allyl or acrylic esters.

Polymerization experiments were carried out with five monomers, allylbutyrate, diethyleneglycol bis(allylcarbonate), triallylcitrate, isobutylmethacrylate and glycoldimethacrylate, as follows:

1. Procedures were developed which made it possible to eliminate almost completely the induction period in the polymerization of these monomers and to duplicate the reaction rate data within 3 to 6 percent.
2. The rates of polymerization of these five monomers were determined at 60°C. using fifteen different monomer-catalyst combinations.
3. The polymerization reactions were found to be either first order or indeterminant between zero and first order.
4. The monomers were found to have an activity ratio of about 0.045 : 0.08 : 0.043 : 1 : 1.5 in the order listed in the title, which was generally independent of the catalyst used.
5. The reaction rate was found to be directly proportional to the catalyst concentration.
6. The reaction rate varied with promoter concentration.

7. Of all the catalysts used, benzylhyponitrite and the couple, benzoylperoxide-diazoaminobenzene were found to be the most active.
8. Chain transfer occurred when the benzoylperoxide-tetrachlorohydroquinone couple and diazoaminobenzene were used as catalysts.
9. An induction period was caused by tetrachlorohydroquinone which was directly proportional to the concentration of this substance.
10. The diazo catalysts caused bubbles to form in the polymers which were due to trapped nitrogen gas.
11. The plastics were colorless unless a colored catalytic agent was employed.
12. Ultrasonic and x-ray energy were found to have no catalytic effect on the polymerization reaction.
13. Ultrasonic energy caused a decrease in viscosity of pyridine-polymer solutions, but did not change the chemical unsaturation of these solutions.

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