EMULSION POLYMERIZATION OF ISOPRENE

BY

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ABSTRACT

The emulsion polymerization of isoprene has been produced by using as initiating agents various compounds which are known to dissociate to a certain extent in solution into free radicals.

The rate of thermal decomposition of some of the diazothio ethers employed as initiating agents have been measured by observing the rate of evolution of nitrogen from a solution of the compounds in butylphthalate.

ACKNOWLEDGEMENT

I wish to acknowledge the guidance and interest of Dr. R.H. Clark, who has supervised the work done on the polymerization of isoprene at this university.

Acknowledgement is also made of the help of Dr. J.S. Tapp, Assistant Director of Research, Poylmer Corporation of Canada, and the financial support of the Polymer Corporation through grants from the National Research Council which made possible the continuation of this work during the summers of 1948 and 1949.

Arthur Lee Johnson.

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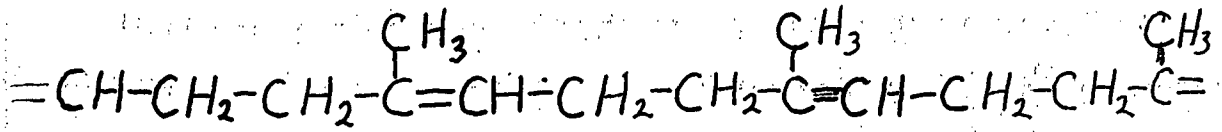
EMULSION POLYMERIZATION OF ISOPRENE

HISTORY

As early as 1835 attempts were made to deduce the structure of natural rubber by pyrogenetic decomposition. However, it was not until 1862, that Greville Williams isolated a hydrocarbon having a boiling point of 37-38° C from the low boiling fraction of the distillate of natural rubber. This hydrocarbon he named isoprene, but it was twenty years later before Tilden proposed the present structural formula for isoprene. Wallach showed that the higher boiling fractions of the distillate from natural rubber were either dimers, trimers, or other related homologues of isoprene. It was also soon observed that isoprene on prolonged standing again formed rubberlike products. It appeared, therefore, that isoprene and rubber were genetically related. It was, of course, a long step from the first observations to the actual preparation of synthetic rubber from isoprene.

From 1885 on research in the field of rubber increased, and in 1906, Harries, as a result of extensive research greatly extended the knowledge of the chemistry of rubber by means of ozone degradation of natural rubber. He found that decomposition of the ozonides with hot water gave an almost quantitative yield of derivatives of the unit group C_5H_8,

that is, levulinic aldehyde, levulinic acid, and levulinic aldehyde peroxide. The presence of these compounds on degradation show that the rubber molecule contains a recurring double bond after each fourth carbon and could be represented by the following structure



Along with the study of the structure of the rubber molecule, and the determination of isoprene as the building unit, were many attempts to synthesize artificial rubber from isoprene. Although a great many attempts were made, it cannot be said that any of these attempts were very successful, and in 1910 due to the high price of natural rubber, research was started to investigate the possibility of polymerizing butadiene. This work resulted in the production of the Buna rubbers, which had properties that made them a fairly suitable substitute for natural rubber.

During World War I, German chemists had little success with their synthetic rubbers. During World War II, supplies of natural rubber were almost completely lost to the Allied rubber industries, and it was imperative to develop immediately a suitable synthetic rubber. Most of the research was directed towards the goal of perfecting and putting into large scale production, GR-S (emulsion polymerized butadiene-styrene) with the result that a satisfactory substitute

for natural rubber for most purposes was obtained. The work on isoprene during this time was negligible.

THEORY

It was shown in 1932 by Fischer & Harkins[3] that the absorbed film between a hydrocarbon oil and a sodium oleate solution at o.1 M concentration is monomolecular, with the polar groups oriented toward the water, and the hydrocarbon group toward the oil. This orientation is accompanied by a decrease in free energy and therefore is the more stable condition. However, it was found that at room temperature potassium laurate gives a clear solution in water up to 33% and potassium myristate up to 26%. These high values might be taken to indicate that solid soap may reduce its free energy by going into solution in some other form than that of single molecules. In general, it has been found that most of the soap dissolved is present as aggregates, each of which contain a large number of molecules. These aggregates are designated as soap micelles. The general structure of these soap micelles consists of three double layers of soap molecules with the polar groups toward the water, and the oil groups towards each other, with a layer of water between each double layer of soap molecules[6]. This water layer is an integral part of the soap micelle rather than a solvent, and is usually referred to as "bound water", in contrast to the term free water (water as a solvent). Besides being an emulsifier, soap is also a solubilizer. It has been fairly conclusively shown that when monomer is added to soap

solution, that it is solubilized between the hydrocarbon ends of the oriented soap molecules.

The soap micelle is the prominent initial locus for polymerization[7]. However, it is not a locus throughout the polymerization since the polymer particle formed adsorbs a monolayer of soap molecules. This causes a rapid disappearance of the soap from the micelles, and hence the micelles themselves seem to completely disappear from a five percent. solution at a conversion of about twelve percent. At low yields the polymer has been shown to contain more monomer than polymer and thus after twelve percent. yield the main locus of reaction is the polymer-monomer particle. The monomer droplets which persist after the soap micelles have disappeared are not thought to act primarily as loci of reaction, but rather as reservoirs of monomer from which monomer molecules diffuse into all of the other loci.

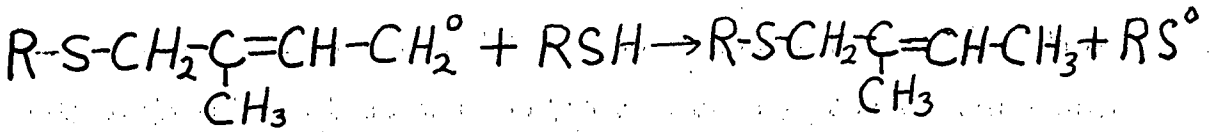
In a free radical type of reaction the molecules grow very rapidly--in the order of a fraction of a second. In order, therefore, to exert any control over the size of the molecules it must be a process of balancing chain initiations and chain termination. Many of the mercaptans which are effective as chain initiators are also effective in controlling molecular weight through chain transfer, e.g.

chain initiation

$$R\text{-}SH + O_2 \rightarrow RS^{\circ} + HO_2^{\circ}$$

$$R\text{-}S^{\circ} + CH_2{=}\underset{\displaystyle CH_3}{\overset{\displaystyle |}{C}}{-}CH{=}CH_2 \rightarrow R\text{-}S\text{-}CH_2\text{-}\underset{\displaystyle CH_3}{\overset{\displaystyle |}{C}}{=}CH\text{-}CH_2^{\circ}$$

and chain termination

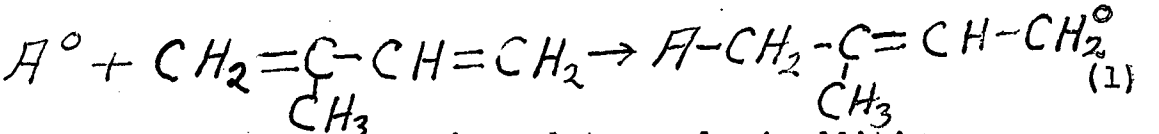


Analysis of various polymers indicates the presence of one sulphur atom per molecule[14]. Also in polymers made by using thioglycolic acid and ethyl thioglycolate as modifiers, it is found that the ratio of sulphur atoms to carboxyl or carbethoxyl groups is nearly 1:1[15]. The extent of modification obtained will depend on the rate of formation of mercaptyl radicals by the oxidizing agent, the rate of reaction of the free mercaptyl radicals with the monomer molecules, and the rate of reaction of the growing polymer chain with mercaptans. Diffusion rate of the mercaptan is important. As Harkins has shown, the reaction takes place either in the aqueous solution or in polymer-monomer particle formed by diffusion from the original emulsion monomer droplet.

The main function of the mercaptan, aside from its initiating action, is to control the size of the polymer chain. However, it is plain that even under the most favorable conditions a wide variation in molecular weight will be obtained. The major factor responsible for the wide molecular weight distribution is the variation in the concentration of the modifier throughout the reaction. At a conversion of 70% there is approximately a tenfold change in mercaptan concentration.[9] Thus the molecular weight

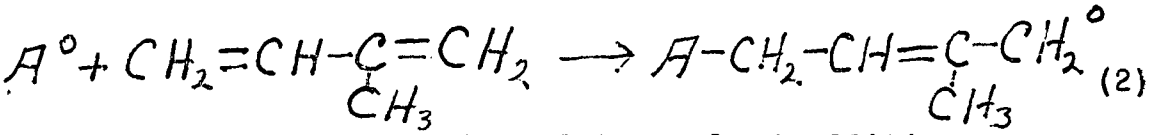
distribution will change with conversion due to the change in modifier concentration during the course of the reaction. The reaction time will also affect the amount of modification especially with mercaptans which have a slow rate of diffusion. Reaction temperature would also be expected to change the properties of the polymer due to the change of rate of reaction, of the rate of diffusion, and the total solubility of the mercaptan as well as the other factors.

For a diolefin such as isoprene each step in the propagation may take place in one of several different ways. For the addition of a free radical it would be possible to have the following initial steps



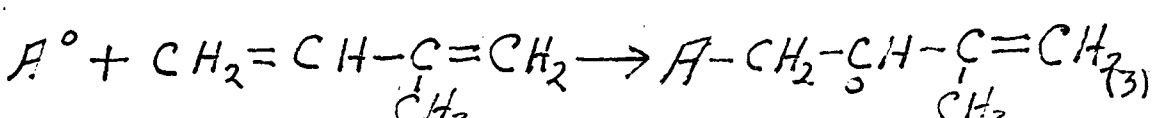
(1)

cis and trans 1, 4 addition



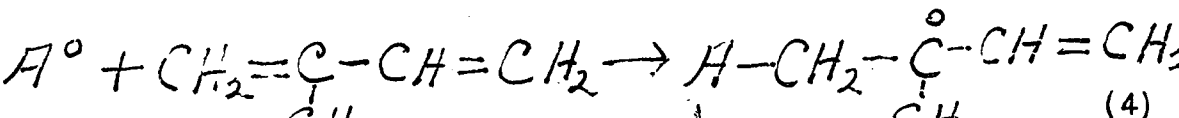
(2)

cis and trans 1, 4 addition



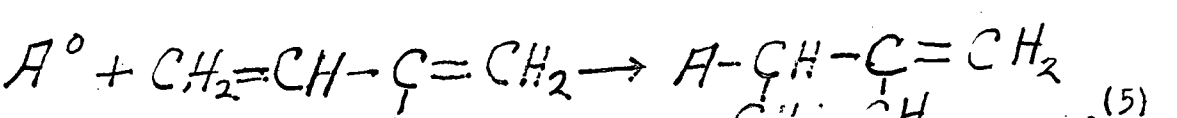
(3)

1, 2 addition



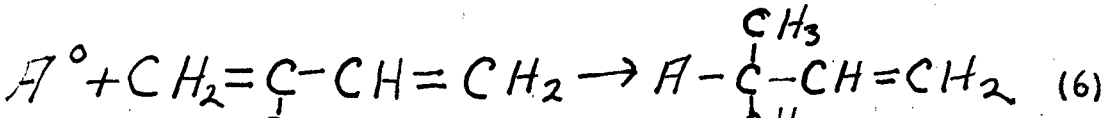
(4)

1, 2 addition



(5)

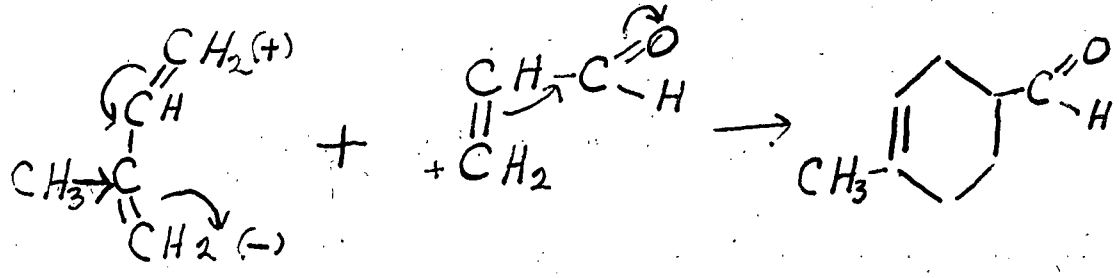
3, 4 addition



(6)

3, 4 addition

However, the tendency of the methyl group to cause a drift of electrons away from itself is well known . We should expect, therefore, a centre of electron density as indicated in the following equation. That this is the case has also been shown by the Diels Alder reaction with acrylic aldehyde on isoprene and other similar reactions [8] .



Since the free radical is looking for a centre of electron density we should expect that by analogy we could largely eliminate equations 2, 3, 5, and 6. Also it has been shown that in the case of butadiene the amount of 1, 2 addition is negligible [12]. By analogy again we should expect, therefore, the elimination of equation 4. It has been frequently stated in the literature that isoprene is believed to add largely 1 - 4, and the above theory is advanced as an explanation of the tendency of isoprene to add 1 - 4.

EXPERIMENTAL WORK

PART I

The effect of oxygen from the air on the rate of polymerization has been reported by various workers from time to time. We have previously reported,[13] that in the polymerization of isoprene using H_2O_2 as an oxidizing agent, that both yield and the intrinsic viscosity varied with the time of exposure of the soap-ferrous sulphate-mercaptan mixture to the air. Both the yield and viscosity curves were found to pass through a maximum. This effect could be explained by--(a) the formation of soap peroxides by the action of oxygen on the unsaturated parts in the soap molecules; (b) the oxidation of part of the mercaptan to the disulphide and hence less modification would be obtained; (c) the absorption of oxygen into the soap gel thus increasing the total amount of oxidizing agent. In order to determine if soap peroxides were formed, the method of E.J. Better and A. Davidsohn was used. However, although a small quantity of peroxides were found present initially, there was no detectable increase in the soap peroxide value upon exposure to air for forty eight hours at 25° C. Confirmation of this data has previously been published by F.D. Gunstone and T.P. Hilditch[5] who found no increase in peroxide value upon exposure of methyl oleate to air at 25° C. for periods less than one hundred hours. I.M. Kolthoff and I.K. Miller[10] have shown that there is a measureable rate of oxidation of

mercaptan in soap solution to the disulphide. Therefore, it is concluded that the observed initial increase in yield is due to a combination of (b) and (c), whereas, the eventual decrease of yield is due to the oxidation of a large portion of the mercaptan to the disulphide and thus the amount of chain initiation is slight. In order to test the validity of these conclusions it seemed necessary to test the effect of the disulphides on polymerization, and compare the effect of the disulphides with the corresponding mercaptans. The compounds synthesised in this class were n didodecyl disulphide, phenyl mercaptan and diphenyl disulphide.

Dodecyl Disulphide

Preparation of dodecyl disulphide by the method of Fore and Bost:[4]

Ten grams of dodecyl mercaptan was dissolved in boiling ethyl alcohol and sufficient alcoholic lead acetate was added slowly to ensure complete precipitation of the yellow lead derivative. The precipitate was digested one hour and filtered hot. The residue was washed with cold water, and then with successive portions of hot acetone and boiling ether until no more soluble material could be extracted. Fifteen grams of the lead salt were suspended in 500 mls. of hot glacial acetic acid, and a slight excess of iodine in the same solvent was added drop by drop. The solution was diluted with water and cooled, then filtered and washed with cold water. The residue was shaken with three 150 ml.

portions of 20% K I to convert the PbI_2 to the soluble complex $KPbI_3$. This latter part of the procedure does not work well since the residue is extremely resistant to wetting by water. However, the product can be crystallized well from glacial acetic acid and since the PbI_2 is relatively insoluble it can be filtered off. The second recrystallization gives long white needles of the disulphide with a very sharp melting point of 34.5° C. This melting point is constant upon further recrystallization.

Phenyl Mercaptan

Fifty grams of phenyl mercaptan were prepared by reducing eighty five grams of benzene sulphonyl chloride with two hundred grams of tin and five hundred mls. of hydrochloric acid. The mercaptan was steam distilled, extracted with ether, and after driving off the ether was distilled at atmospheric pressure at 166-170° C.

Diphenyl disulphide

Diphenyl disulphide was prepared by evaporating five grams of phenyl mercaptan with a few mls. of dilute ammonia and upon cooling crystals of diphenyl disulphide were obtained, and after recrystallization had a melting point of 61 ± 1° C.

RESULTS:

Each model was prepared by dissolving 4.5 grams of R.R.C. soap and 0.1 grams of ferrous sulphate in two hundred mls. of hot water. The oxidizing agent, modifier, and one hundred grams of isoprene were added after the soap solution had been cooled to 30° C. Polymerization was accomplished by end over end rotation of the bottles at a rate of eighteen revolutions per minute in a constant temperature bath at 45° C. In all cases listed below the time of polymerization was twenty-four hours.

TABLE I

Modifier	Oxidizing Agent	% Yield
.2 g. $C_{12}H_{25}SH$	6 mls. of 3% H_2O_2	70
" "	" " "	72
" "	" " "	73
.2 g. $C_{12}H_{25}S\text{-}SC_{12}H_{25}$	" " "	10
" "	" " "	10
" "	" " "	9
.2 g. C_6H_5SH	" " "	negligible
" "	" " "	"
" "	" " "	"
.2 g. $C_6H_5S\text{-}SC_6H_5$	" " "	"
" "	" " "	"
" "	" " "	"

It seems probable that phenyl mercaptan is a poor initiating agent for polymerization since it is too easily oxidized to the disulphide as is the case with the lower aliphatic members. The fact that n-didodecyl disulphide is unreactive bears out our previous conclusions

PART II

Since the mechanism of polymerization is believed to proceed through free radical formation, it was decided to try various diazo thio ethers as initiating agents which, according to T.B. Reynolds , decompose by thermal decomposition according to the following equation:

$$R-N=N-S-R' \xrightarrow{\Delta} R + N_2 + R'S$$

Originally the mercaptans used in coupling, namely, thio β naphthol and para methyl phenyl mercaptan were prepared as indicated below. However, all final tests were made with mercaptans obtained from Eastman Kodak Co.

Thio β Naphthol

Sodium naphthalene sulphonate was prepared by the method of Fieser[2], and the sodium salt was converted to the corresponding sulphonyl chloride by heating the dry sodium s. salt with phosphorous pentachloride at 150° C. The product was recrystallized from chloroform. The sulphonyl chloride thus obtained was reduced with tin and hydrochloric acid. The thio β naphthol was steam distilled and recrystallized from alcohol. Melting point 82 ± 1° C.

P-Thio Cresol

Sodium p-toluene sulphonate was prepared by the method of Fieser,[1] converted to the acid chloride as above, and then reduced to the corresponding mercaptan. The mercaptan

was recrystallized from alcohol. Melting Point 42 ± 1° C.

Diazo Thio Ethers

A typical preparation of a diazo thio ether consisted of dissolving 0.1 moles of an amine in one hundred mls. of 3.0 N acid. The temperature of the acid solution of the amine was kept at 0° C. throughout the dropwise addition of an aqueous solution of sodium nitrite. The addition of sodium nitrite was continued until a permanent reaction of nitrous acid with starch iodide paper was obtained. The diazotized solution was then filtered with decolorizing carbon through a chilled Buchner into a chilled flask. Coupling was accomplished by slowly adding the diazotized solution with constant stirring to an alkaline ice solution of the mercaptan consisting of slightly more than 0.1 moles of mercaptan in a solution of four hundred mls. of 2.0 N sodium hydroxide and twenty grams of sodium carbonate. The resulting yellow solid was filtered off and dried under vacuum. This procedure worked well for most of the diazo thio ethers attempted, however, oils were obtained when using phenyl mercaptan, and hence was unsatisfactory for this particular mercaptan.

The rate of decomposition of some of the diazo ethers was measured by observing the rate of evolution of nitrogen from a solution of the ether in one hundred mls. of butyl phthalate. The rates of decomposition of the diazo ethers is greatly influenced by temperature, a twenty degree decrease in temperature increases the induction period and

the half life period by approximately a factor of seven for p-methyl benzene diazo thio β naphthol. The temperature for decomposition was chosen at 65° C. since it provides a convenient rate of reaction for most of the ethers. After the induction period is over the decomposition closely parallels a first order reaction. Results for the decomposition of various diazo ethers appear in Tables II, III, and IV. (Pages 17, 18, & 19)

TABLE II

Decomposition of p-methyl benzene diazo thio-β-naphthol at 65° C.

Sample #1		Sample #2	
Time in Secs.	Mls. of N_2	Time in Secs.	Mls. of N_2
0	0.0	0	0.0
1560	1.0	1620	1.0
1920	2.0	2000	2.0
2200	3.0	2295	3.0
2400	4.0	2530	4.0
2575	5.0	2715	5.0
2730	6.0	2900	6.0
2900	7.0	3070	7.0
3055	8.0	3220	8.0
3210	9.0	3360	9.0
3337	10.0	3500	10.0
3875	15.0	4100	15.0
4585	20.0	4760	20.0
5310	25.0	5485	25.0
6100	30.0	6340	30.0
7020	35.0	7250	35.0
8100	40.0	8355	40.0
9325	45.0	9660	45.0
11020	50.0		
Total	71.5	Total	70.0

Neglecting the induction period the time for half decomposition for p-methyl benzene diazo thio-β-naphthol in one hundred mls. of butyl phthalate is 82±1 minute at 65° C.

TABLE III

Decomposition of p-methyl benzene diazo thio p toluene at 65° C.

Sample #1		Sample #2	
Time in Secs.	Mls. of N_2	Time in Secs.	Mls. of N_2
0	0.0	0	0.0
970	1.0	962	1.0
1228	3.0	1216	3.0
1415	5.0	1397	5.0
1602	7.0	1570	7.0
1770	9.0	1762	9.0
1952	11.0	2000	13.0
2286	15.0	2240	16.0
2520	18.0	2590	20.0
3086	24.0	3052	25.0
3527	28.0	3595	30.0
4345	34.0	4278	35.0
5020	38.0	5095	40.0
Total	58.2	Total	60.0

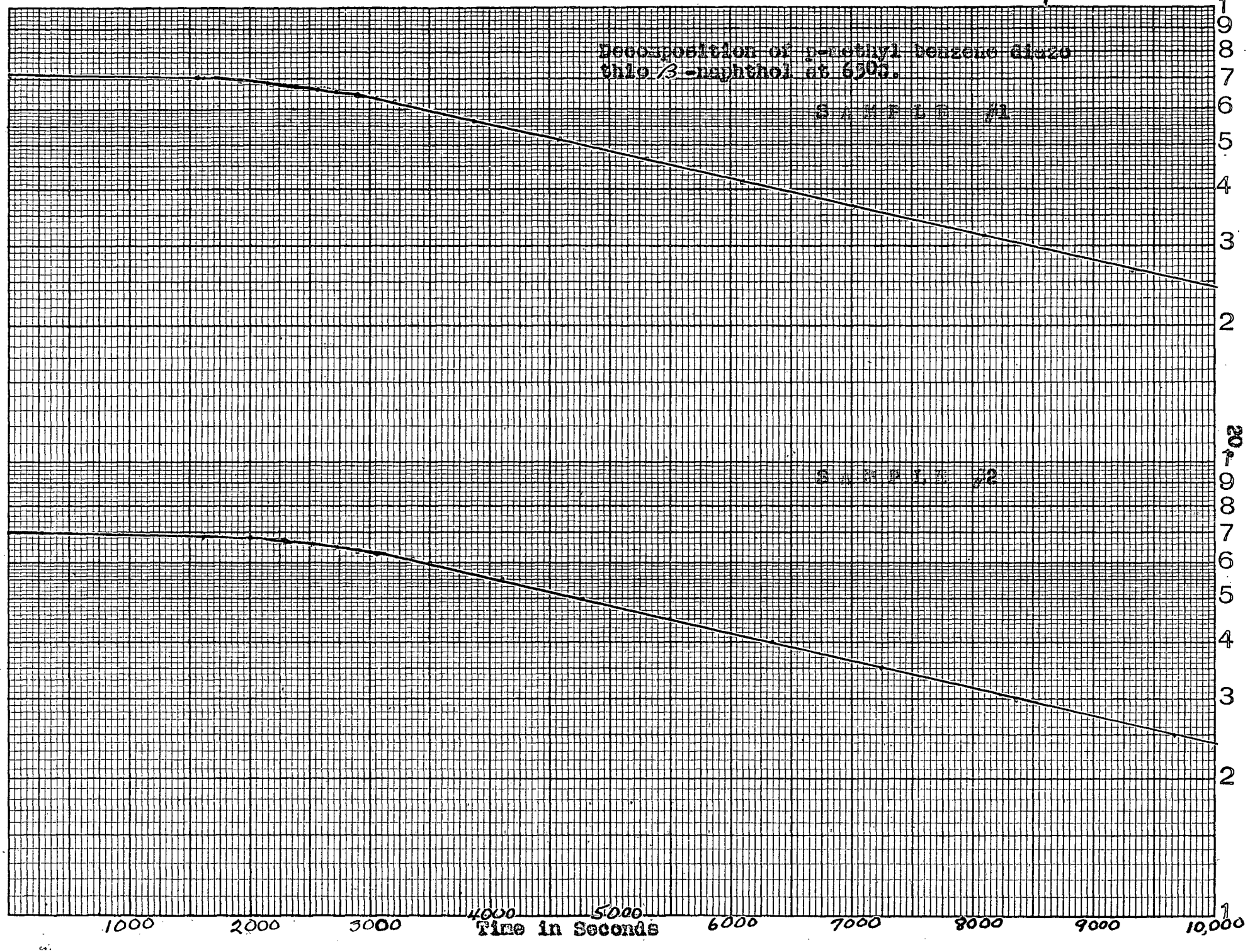
Neglecting the initial induction period, the time for half decomposition of p-methyl benzene diazo thio p-toluene is 42 ± 1 minutes in one hundred mls. of butyl phthalate at 65° C.

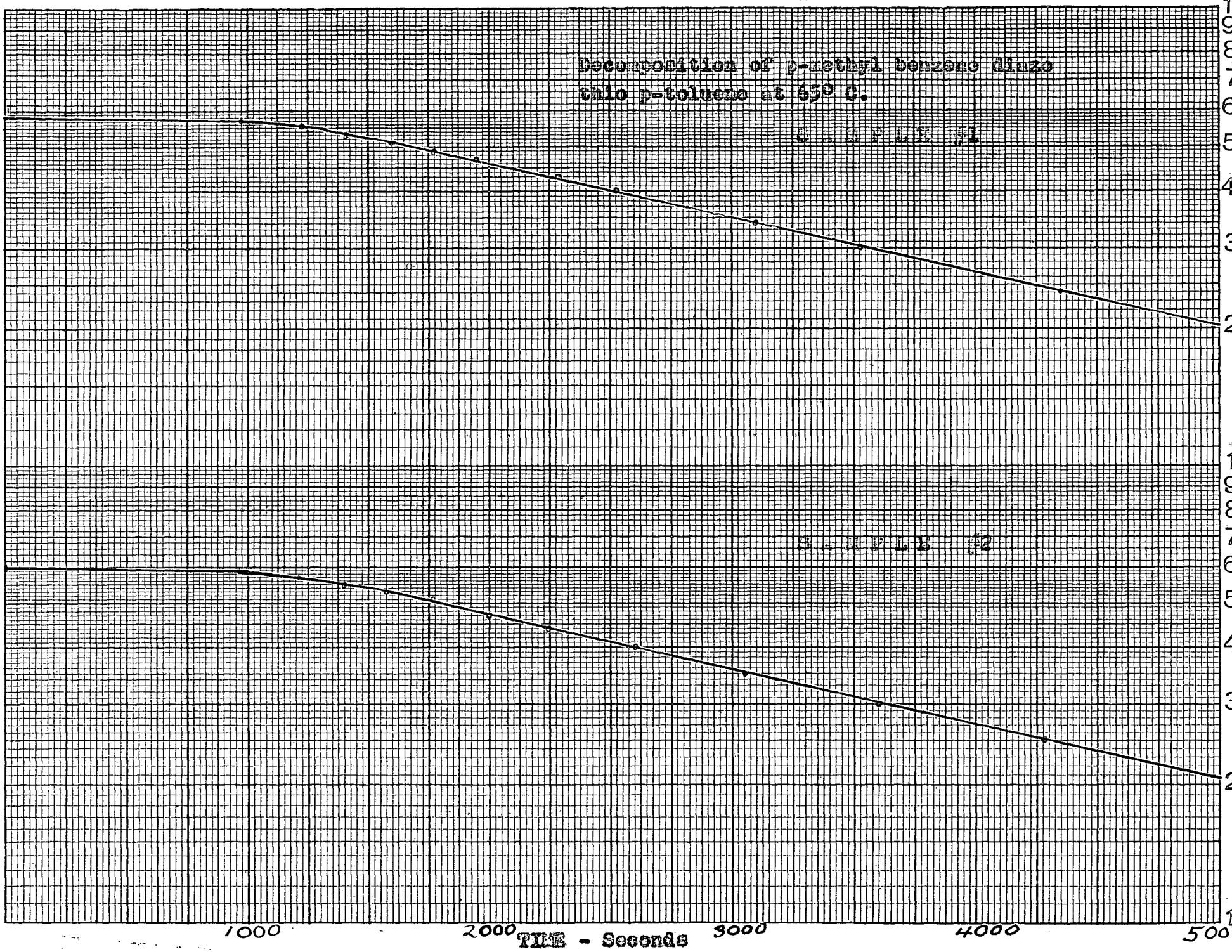
TABLE IV

Decomposition of p-bromo benzene diazo thio p-toluene at 65°C

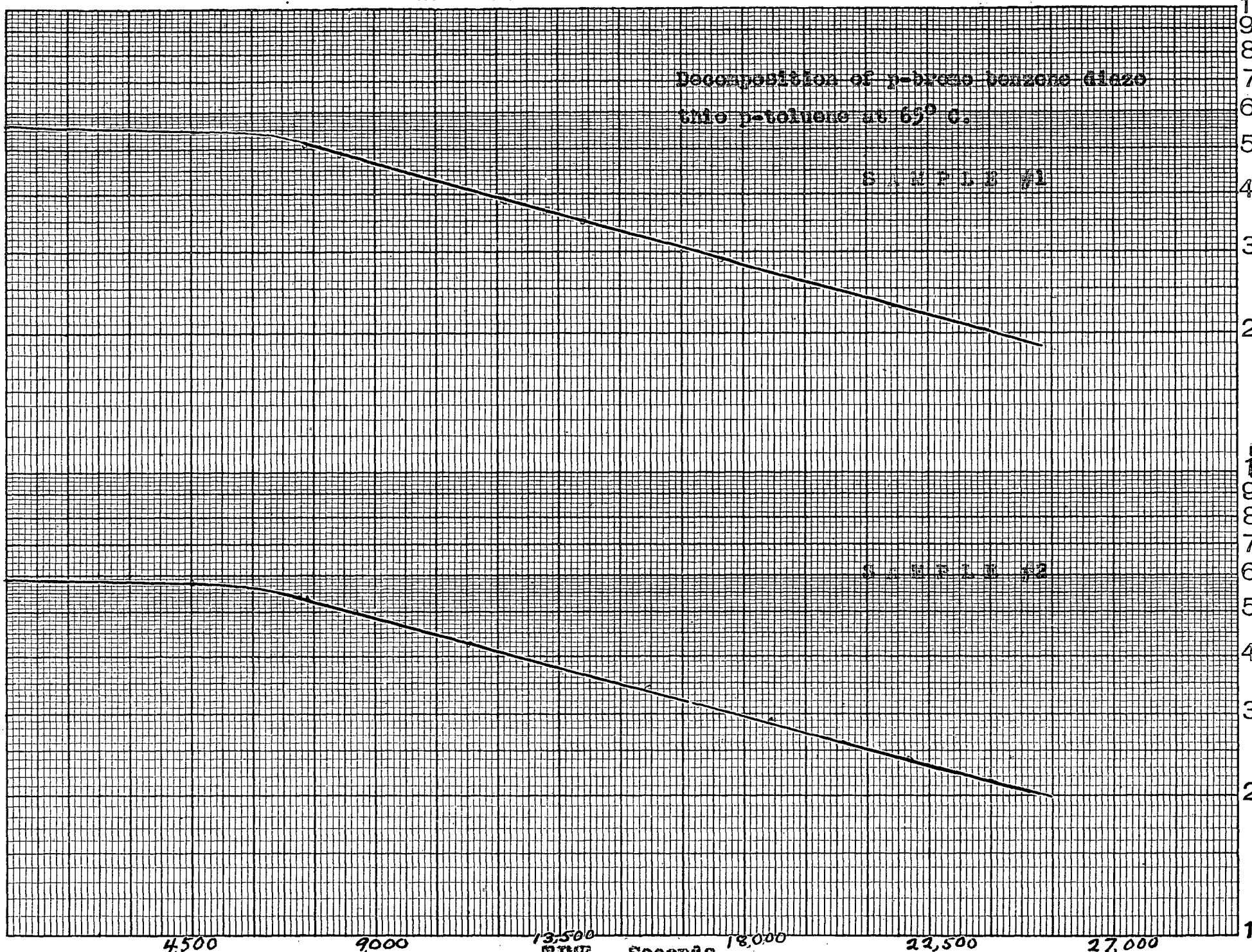
Sample #1		Sample #2	
Time in Secs.	Mls. of N_2	Time in Secs.	Mls. of N_2
45 0	0.0	0	0.0
4590	1.0	4520	1.0
7320	5.0	7400	6.0
8140	7.0	8510	9.0
9650	11.0	9675	12.0
12150	17.0	11355	16.0
13200	19.0	13200	20.0
14120	21.0	15700	25.0
17520	27.0	18680	30.0
21600	33.0	22040	35.0
Total	56.1	Total	58.9

Neglecting the initial induction period the time for half decomposition of p-bromo benzene diazo thio p-toluene in one hundred mls. of butyl phthalate at 65° C. is 212±3 minutes.





LOGARITHMIC CYCLES. MADE IN CANADA. E.I.L.



Measurements on the rates of decomposition of the diazo thio ethers were discontinued since the rates of decomposition were found to be influenced by surface area. Both the induction period and the time for half decomposition were found to be less when the decomposition was carried out in a vessel in which the surface area had been greatly increased by packing with glass. However, since the rates of decomposition previously recorded were measured under similar conditions they do afford a relative comparison of the stabilities of the ethers. A relative comparison of the stability of these ethers should also be obtained from the rates of polymerization obtained by using these ethers as initiating agents. This comparison should at least be valid for any one series, and may be valid from one series to another. Following are typical tables of the results obtained using diazo thio ethers as initiating agents. The amount of the particular diazo thio ether used in a model was based on a weight equivalent to one gram of p-methyl benzene diazo thio β-naphthol.

Preparation of Model

Each model was prepared by dissolving 4.5 grams of R.R.C. soap in two hundred mls. of water by heating. After cooling the soap solution to 25° C., one hundred grams of isoprene containing the dissolved diazo ether was added. Polymerization was accomplished by end over end rotation of the bottles at a rate of eighteen revolutions per minute

at a temperature of 45° C.

TABLE V

Initiating Agent	Time of Polymerization	Yield %	Gel %
1.00 g. p-CH_3-C_6H_4-N=N-S-$C_{10}H_7$	9 hours	70 68 68	0 0 0
1.23 g. p-Br-C_6H_4-N=N-S-$C_{10}H_7$	24 hours	22 21 18	0 0
1.08 g. p-NO_2-C_6H_4-N=N-S-$C_{10}H_7$	24 hours	< 5 < 5 < 5	0 0 0
1.08 g. o-NO_2-C_6H_4-N=N-S-$C_{10}H_7$	24 hours	< 5 < 5 < 5	0 0 0
.87 g. p-CH_3-C_6H_4-N=N-S-C_6H_4-CH_3	9 hours	88 91 90	0 0 0
1.08 g. p-Br-C_6H_4-N=N-S-C_6H_4-CH_3	24 hours	36 36 38	0 0 0
.20 g. CH_3-C_6H_4SH and 6 mls. of 3% H_2O_2	24 hours	0 0 0	
.20 g. -$C_{10}H_7$SH and 6 mls. of 3% H_2O_2	24 hours	0 0 0	

In order to determine if a valid comparison from one series to another of the diazo ethers could be made, the rate of polymerization with p thio cresol and β Naphthyl mercaptan was tested. Both gave negative results as was the case with the phenyl mercaptan previously mentioned, and the reason for lack of iniation is probably the same.

TECHNIQUES

Product Yields

The yields calculated in this thesis were based on the total solids content, and a correction was made for the soap content and any other solids present. Twenty to thirty grams were sampled into a weighing bottle and weighed rapidly to milligram accuracy. After the sample was dried in a drying oven (60° C.) itwas reweighed, and from this the total yield can be calculated.

Preparation of the Anti Oxidant

In order to prepare a suitable colloidal suspension of P.B.N.A. (phenyl naphthylamine) the following formula was added directly to a Waring Blendor:

H_2O	100 mls.
R.R.C. Soap	3.0 g.
P.B.N.A.	20.0 g.

Five minutes whipping in the blendor is sufficient to form a suitable suspension. If the yield is low it is necessary to strip the latex of excess isoprene, otherwise coagulation of the P.B.N.A. results when it comes in contact with the latex, and a fine precipitate of P.B.N.A. throughout the crumb is not obtained.

Precipitation of the Latex

Precipitation was achieved by adding brine-acid solution of the following formula:

H_2O	6,000 mls.
NaCl	367 g.
H_2SO_4	10.5 mls.

Sufficient brine-acid solution is added to the latex (containing sufficient P.B.N.A. to total 1.25% of the dried polymer) until the latex coagulates and a solution of pH 4 - 4.5 results. For very low yields it is necessary to precipitate the sample with isopropyl alcohol which breaks the emulsion by dissolving the soap. Any precipitate obtained in this way is polymer only.

Determination of Gel Content

Kolthoff and Medalia[11] in October, 1945, summarized the theory and method of determination of the gel content of a polymer. The Harris cage was used here for the determination of all gel contents. A sample of from o.1 to 0.2 grams of the polymer was cut into small pieces in order to facilitate solution, and then the sample was placed in the cage. The cage was suspended in a beaker containing one hundred mls. of toluene in such a manner that it was completely immersed without touchigg any surface. This was now placed in a desiccator containing toluene in the bowl, and was left for a period of at least forty-four hours away from the actinic light. The sol part of the rubber will disperse throughout the toluene during this time, while the swollen gel will remain inside the cage.

On completion of the standing time, the cage was removed carefully from the beaker and suspended in air for a few minutes to evaporate off the majority of the solvent. The cage was finally dried in an oven at 60° C. The percentage gel content was calculated as follows:

Let X be the weight of the empty cage

Let Y be the weight of the cage plus the sample

Let Z be the weight of the cage plus the dried gel

$$\text{Percent sol} = \frac{Y - Z}{Y - X} \times 100 + 1$$

Percent gel = 100 - percent sol

The one percent was added to the sol to take into account the amount of sol trapped in the swollen gel. This correction is fairly accurate for small amounts of gel, but a higher correction factor is needed for high gel content polymers.

CONCLUSIONS

If the mechanism of polymerization does proceed through the formation of free radicals and terminate through chain transfer, then it should be possible to synthesize a product that would dissociate or decompose in solution to provide a suitable concentration of free radicals. Such products were obtained in the preparation of p-methyl benzene diazo thio -naphthol and p-methyl benzene diazo thio p-toluene. It has been previously shown in this paper that a good rate of polymerization could be obtained simply be adding one of the above compounds to emulsified isoprene. Thus by the following dissociation of the compounds

$$R-N=N-S-R' \xrightarrow[\Delta]{SOLVENT} R + N_2 + R'S$$

two free radicals are obtained, and since there are no other compounds present, it is conclusively shown that initiation does proceed through a free radical mechanism as proposed earlier in the theory part of this paper. It has also been shown that the presence of groups such as Br, $N\overset{=O}{\rightarrow O}$, in the amine part of the molecule greatly reduces the effectiveness of the diazo thio ether. The ethers formed by coupling with thio β naphthol are more stable than those formed by coupling with p-thio cresol. The greater stability of the former could be attributed to the greater resonance possible in the naphthalene nucleus as compared

to the benzene nucleus. In addition the introduction of a nitro group in the para or ortho position of the amine part contributes strongly to other resonance possibilities. Similarly the haolgens in the ortho or para positions of the amine part contribute to other resonance possibilities. However, in the latter case the inductive and resonance effects are opposed and the overall contribution to resonance would be expected to be much less. In the case of the methyl group in the ortho or para position of the amine part there are no new possible resonance structures of energy contents which are similar. Therefore, theoretical considerations would lead us to the conclusion that the p-methyl derivative would dissociate more readily than the p-bromo and the latter in turn more readily than the 0-, or p-nitro derivatives.

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