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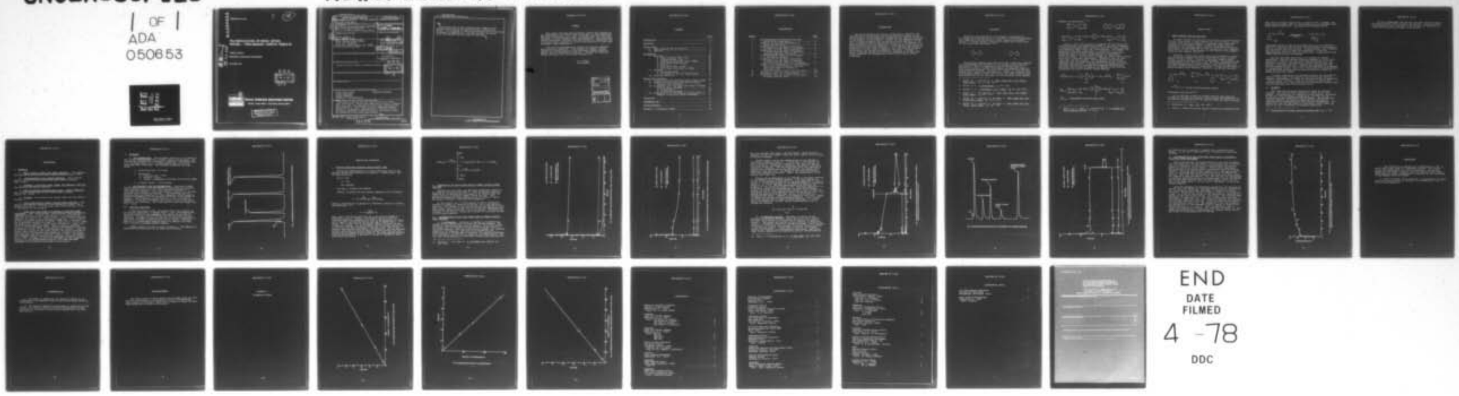

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POLYMERIZATION OF SPIRO ORTHO ESTERS – PRELIMINARY KINETIC RESULTS

HUBERT J. BOOTH

RESEARCH & TECHNOLOGY DEPARTMENT

24 AUGUST 1977

NAVAL SURFACE WEAPONS CENTER

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EXPANDING MONOMERS

20. ABSTRACT (Continue on reverse side if necessary and identify by block number)

Preliminary kinetic data has been obtained on a model spiro ortho ester. Spiro ortho esters are a class of monomers which have near zero shrinkage or even slight expansion when they polymerize. The concept of having expanding monomer systems is an important consideration in improving potting materials, adhesives, structural resins, and casting resins for industrial and military applications.

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The kinetic data to date indicates that competing side reactions occur during the polymerization of spiro ortho esters. The influence of these side reactions must be minimized by changes in temperature or catalyst in order to realize fully the potential of this class of materials.

SUMMARY

This report describes the preliminary kinetic data obtained on the polymerization of a model spiro ortho ester at room temperature. The spiro ortho esters are a class of monomers which have near zero shrinkage or slight expansion when they polymerize. The preliminary kinetic information indicates that modifications in temperature and/or catalyst may be required to utilize these materials to their best advantage in Navy applications.

This work was performed with funding from Internal Research, Work Package No. WR01AA741. This project is, however, closely related to a bigger program in non-shrinking polymers funded by NAVAIR, Task No. WR02-206-001/A320-0000. The work was conducted during the period July 1976 through January 1977.

J. R. DIXON
By direction

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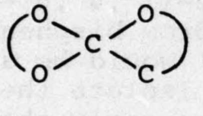
ILLUSTRATIONS

INTRODUCTION

The use of polymers for potting, encapsulating, adhesive, and composite matrix applications has often presented a problem to the user because of the shrinkage that accompanies the chemical conversion of the monomers to the polymers. To date, all the commercial monomers used to prepare polymers, such as epoxies and polyurethanes, for the above and similar applications shrink during cure. For example, in a potting application, this reduction in volume can be severe enough to damage delicate electrical components. In an adhesive application the adhesive, on curing, tends to shrink or pull away from the surfaces being bonded, and the bond is weakened. Therefore, a monomer or series of monomer systems that have zero shrinkage or in some cases slight expansion upon polymerization would offer several obvious advantages.

BACKGROUND

Research being conducted at the University of Maryland by Dr. Bailey and co-workers has been successful in synthesizing monomers that indeed have zero shrinkage or slight expansion on polymerization.[1-6] Monomer systems investigated include spiro ortho esters (I) and spiro ortho carbonates (II).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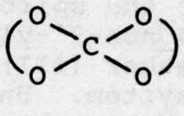
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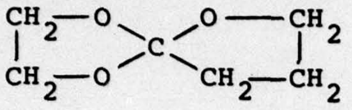
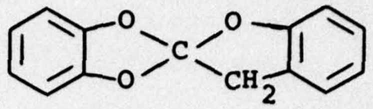
Naval Surface Weapons Center/White Oak has a continuing interest in the development and evaluation of new polymer systems for Navy applications. Thus, in cooperation with Dr. Bailey, this lab initiated a program of polymer development and assessment based on these expanding monomers. The spiro ortho esters (I) were the first monomer system chosen for investigation. Bailey and co-workers have synthesized a number of spiro ortho esters, and these materials have been polymerized without shrinkage to yield polyester ether polymers.

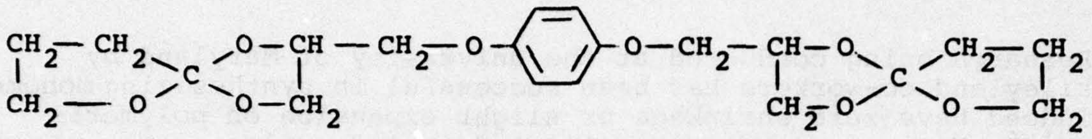
---

1. Bailey, W. J., and Sun, R. L., Amer. Chem. Soc., Div. Polym. Chem. Prepr., 13 (1), 400, 1972.
2. Bailey, W. J., J. Elastoplast., 5, 142, 1973.
3. Bailey, W. J., J. Macrolmol. Sci. - Chem., A9 (5), 849, 1975.
4. Bailey, W. J., and Katsuki, H., Amer. Chem. Soc., Div. Polym. Chem. Prepr., 14, 1679, 1973.
5. Bailey, W. J., Katsuki, H., and Endo, T., Amer. Chem. Soc. Div. Polym. Chem. Prepr., 14, 1976, 1973.
6. Bailey, W. J., Katsuki, H., and Endo, T., Amer. Chem. Soc. Div. Polym. Chem. Prepr., 15, 445, 1974.

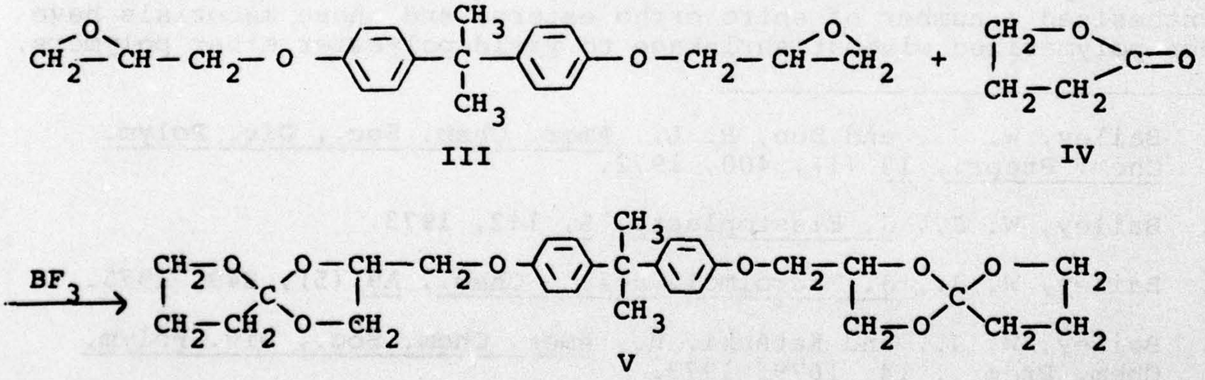
Examples are shown below.[1 3,7]







However, from a more practical standpoint of availibility of starting materials and properties desired, we were more interested in developing polymers from a series of spiro ortho esters prepared from commercial epoxy resins and γ-butyrolactone. For example, the synthesis of the spiro ortho ester V, 2,2-bis{p-(1',4',6'-trioxaspiro[4.4]non-2'-ylmethoxy)phenyl}propane, from bisphenol A diglycidyl ether (III) and γ-butyrolactone (IV) would be an attractive system. Unfortunately, attempts to isolate the pure spiro ortho ester V have been unsuccessful. Therefore, only the crude ortho ester has been studied. The preliminary investigations indicated that the preparation and polymerization of V involved competing side reactions. Infrared data on the polymerization of a pure spiro ortho ester confirmed that competing reactions were occurring, and the need of studying the details of the reaction, particulary the kinetic details, became apparent.



III

IV

V

$\xrightarrow{BF_3}$ CROSSLINKED POLYESTER ETHER RESIN

---

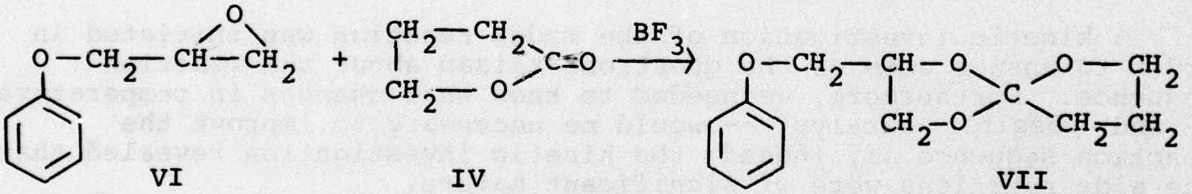
7. Bailey, W. J., Iwama, H., and Tsushima, R., J. Polymer Sci. Poly. Symposia Edition, in Press.

KINETIC STUDY

I. MODEL COMPOUND AND ITS REACTIONS

In order to study the kinetics of the formation and polymerization of spiro ortho esters, a model compound had to be selected. Because the spiro ortho ester of bisphenol A diglycidyl ether (hereafter referred to as SOE-DGEBA) yields a crosslinked polymer when it polymerizes, this reaction makes a kinetic investigation difficult. Furthermore, the SOE-DGEBA has not been isolated as a pure compound, again making a kinetic investigation of the formation and polymerization of this material difficult.

Therefore, a model spiro ortho ester whose preparation yields a pure isolatable compound and whose polymerization gives a soluble polymer had to be chosen. Moreover, this model compound should closely simulate the reactivity of the SOE-DGEBA. The formation and polymerization of the spiro ortho ester VII, 2-phenoxymethyl-1,4,6-trioxaspiro[4.4]nonane of phenyl glycidyl ether (VI) was selected; the ideal reaction sequence is given below. The spiro ortho ester of phenyl glycidyl ether (hereafter referred to as SOE-PGE) has been synthesized and purified.[8,9]



VI IV VII

$\xrightarrow{BF_3}$ SOLUBLE POLYESTER ETHER POLYMER

Let us look more closely at several possible side reactions involved in the reaction sequence. First, during the preparation of the SOE-PGE, polymerization of the SOE-PGE itself may occur since the

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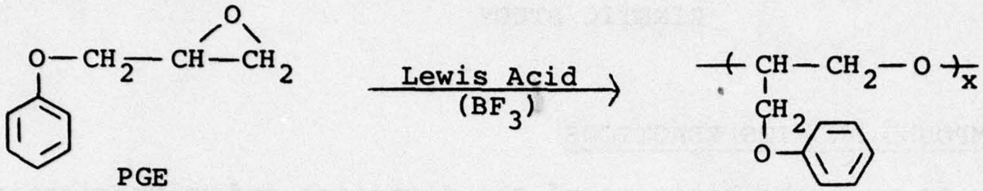
8. Bodenbenner, K., Ann., 623, 183, 1959.

9. Iwama, H., Master of Science Thesis, University of Maryland, 1975.

same type of catalyst (Lewis Acid) is used for both. Secondly, the phenyl glycidyl ether (PGE) may homopolymerize in the presence of the Lewis Acid as shown below. Furthermore, the mechanism of the



PGE

homopolymerization of PGE and the polymerization of the SOE-PGE is such (i.e., cationic) that reaction may occur between all monomers or growing polymers derived from them. γ-Butyrolactone (γ-BL), however, does not react in any of these side reactions. It does not homopolymerize under the reaction conditions[10]; γ-butyrolactone only reacts with PGE to form the SOE-PGE.

The side reactions could result in a polymer of unknown composition. The ideal polymer should be composed of a one to one molar ratio of PGE to γ-BL (as occurs from polymerization of the SOE-PGE); in reality, the polymer may contain more PGE than γ-BL because of the side reactions. Infrared data indicated that the reaction between PGE and γ-BL to form the SOE-PGE might be reversible to a significant extent. Thus, even if pure SOE-PGE were polymerized, enough PGE might be formed by the reverse reaction to affect the makeup of the final polymer.

A kinetic investigation of the model reaction was initiated in order to answer some of the questions raised about the reaction sequence. Furthermore, we needed to know what changes in temperature -- and possibly catalyst -- would be necessary to improve the reaction sequence if, indeed, the kinetic investigation revealed that the side reactions were of significant nature.

II. APPROACH

There were several routes available to study the reaction sequence. One route involves studying the makeup of the final polymer. By determining the composition of the polymer, the amounts of PGE and γ-BL in the polymer would be known, and then the side reactions and their importance could be deduced. The second route involves examining the reactions themselves by following the appearance and/or disappearance of the reactants and products. The second route was the one chosen for this kinetic study; later, we hope to be able to determine the polymers' composition.

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[10] Encyclopedia of Polymer Science and Technology, 11, p. 103.

The gas chromatograph (GC) was the instrument chosen to monitor the concentrations of the reactants and products. One of the major disadvantages of the GC was that it did not have the capability to follow the concentration changes of the polymer.

EXPERIMENTAL

I. MATERIALS

A. PHENYL GLYCIDYL ETHER (PGE, SHELL CHEMICALS). This material was purified by distillation under reduced pressure, $bp_{20} = 140^{\circ}C$.

B. γ-BUTYROLACTONE (γ-BL, ALDRICH CHEMICAL). This starting material was purified by distillation under reduced pressure, $bp_{30} = 110^{\circ}C$.

C. BISPHENOL A DIGLYCIDYL ETHER (DGEBA, DOW CHEMICAL'S DER 332). This material was used as received.

D. BORON TRIFLUORIDE ETHERATE [$BF_3O(C_2H_5)_2$, ALDRICH CHEMICAL]. The catalyst was purified by distillation under nitrogen, $bp_{760} = 125 - 126^{\circ}C$.

E. SOLVENTS. All solvents were reagent grade and were used as received.

F. SPIRO ORTHO ESTER OF PHENYL GLYCIDYL ETHER (SOE-PGE). This material was prepared according to the procedure of Iwama.[9] The melting point was 74 - 77°C; the wide range in melting point is due to the mixture of stereoisomers.

G. CRUDE SPIRO ORTHO ESTER OF BISPHENOL A DIGLYCIDYL ETHER (SOE-DGEBA). Into a three-necked, round-bottomed flask equipped with a magnetic stirrer, nitrogen inlet and outlet, and condensor was added 44g (0.512 moles) of γ-butyrolactone. The γ-butyrolactone was cooled to 5°C under a slow nitrogen purge, and then 1.8 ml (2 mole %) of boron trifloride etherate was added. DGEBA (87g, 0.256 moles) in 90g of methylene chloride was added over a period of 1.5 hours. After the addition was completed, stirring was continued for 1 hour; then 2.5 ml of triethylamine was added. After 15 minutes, methylene chloride (50 ml) was added, and the solution was washed with six 50-ml portions of water (or until the washings were neutral). After the organic layer was dried over sodium sulfate, the solvent and some of the unreacted γ-butyrolactone were removed on a rotavac with first a water aspirator and then in vacuo for 2 hours at 60°C. The product was a slightly yellow, viscous liquid which had a workable viscosity at 60 - 70°C. Attempts to purify the SOE-DGEBA were not successful. According to gas chromatography analysis, the crude SOE-DGEBA contained 1.9% by weight of unreacted γ-butyrolactone.

II. EQUIPMENT

A. GAS CHROMATOGRAPH. The instrument used was a F & M model 720 dual column chromatograph with a thermal conductivity detector. The recorder was equipped with a mechanical integrator. The columns were 6 ft. stainless steel, ¼" O.D. columns packed with 10% SE-30 on chromosorb W-HP, 60/80 mesh. The equipment parameters are given below.

1. Helium Flow Rate - 60 cc/min
2. Temperature
   a. Injection Port - 250°C
   b. Detector - 300°C
   c. Column - programmed at 30°C/min from 120°C to 290°C
3. Filament Current - 150 milliamps

B. CALIBRATION OF THE GAS CHROMATOGRAPH. Solutions of known concentration of PGE, γ-BL, and SOE-PGE in chloroform were prepared. Also, standard solutions of all three components combined in chloroform were prepared. After known amounts (usually 8 μℓ) of these solutions were injected and analyzed, it was determined that the standard solutions containing all three components could be used for calibration purposes since no reactions took place in the absence of catalyst. The calibration curves (Figure 8, 9, 10) are given in Appendix A. Each point represents the average of the results from a minimum of ten injections. The coefficients of variation ranged from 2.12 - 4.12%.

III. REACTION CONDITIONS

In this preliminary study, the temperature of the reaction was not strictly controlled; it ranged from 21 - 23°C (room temperature). The concentrations of the components were determined from one GC injection. The fast initial reaction rate did not permit multiple injections. Attempts to stop the reaction by adding triethylamine to neutralize the boron trifluoride gave erratic results. Reactions were run in a serum-capped reaction bottle and samples were taken with a syringe to minimize moisture effects.

A sample trace of a GC run is given in Figure 1. The temperature program was activated when the air peak started eluding.

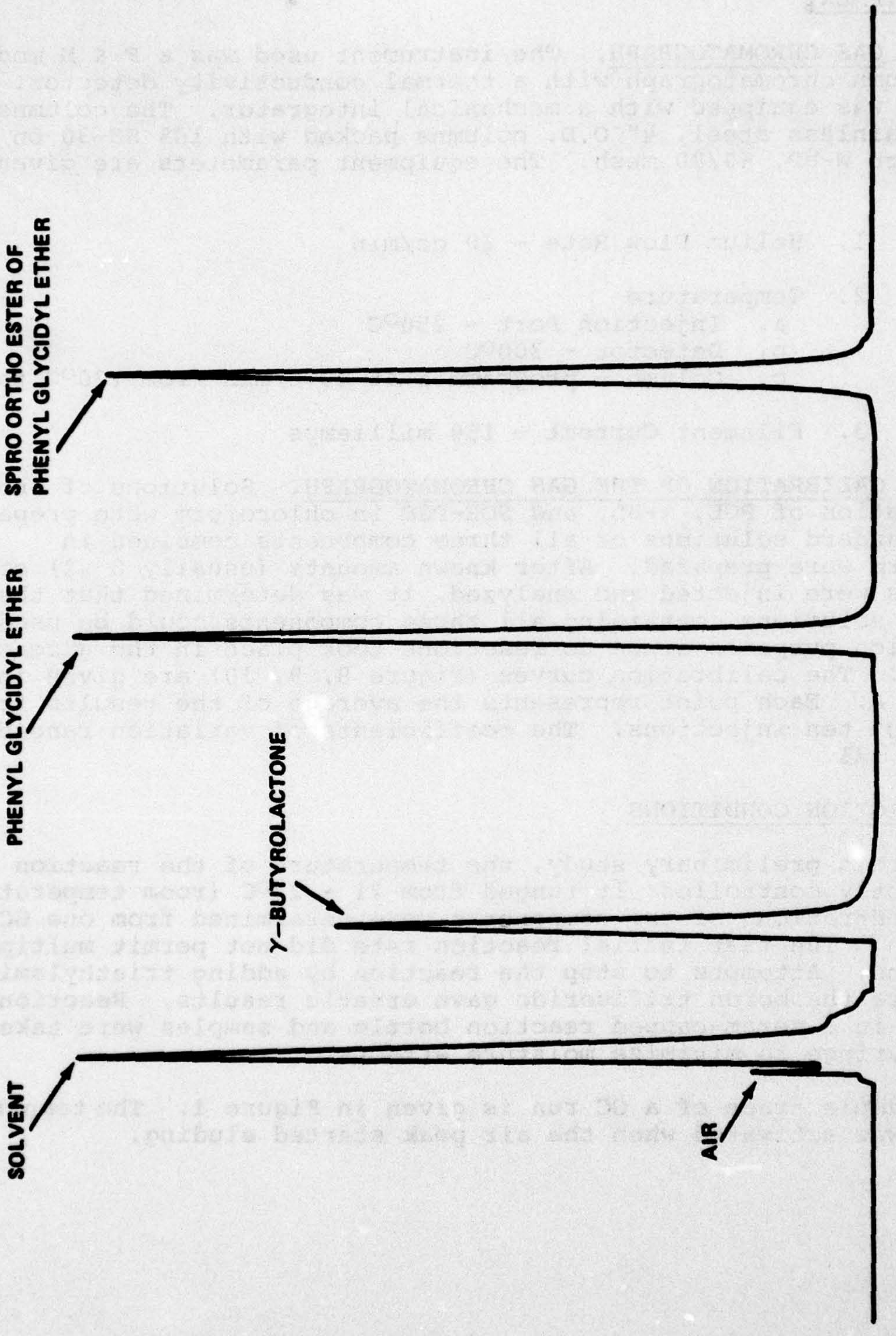


FIG. 1 GAS CHROMATOGRAM OF MATERIALS MONITORED DURING KINETIC EXPERIMENTS

RESULTS AND DISCUSSION

I. POSSIBLE REACTIONS OCCURRING DURING KINETIC STUDY

During the polymerization of a spiro ortho ester such as the SOE-PGE, several side reactions are possible. Schematically, they are described below.

Let A = PGE

B = γ-BL

AB = SOE-PGE

and $(AB)_x$ = polymer from SOE-PGE

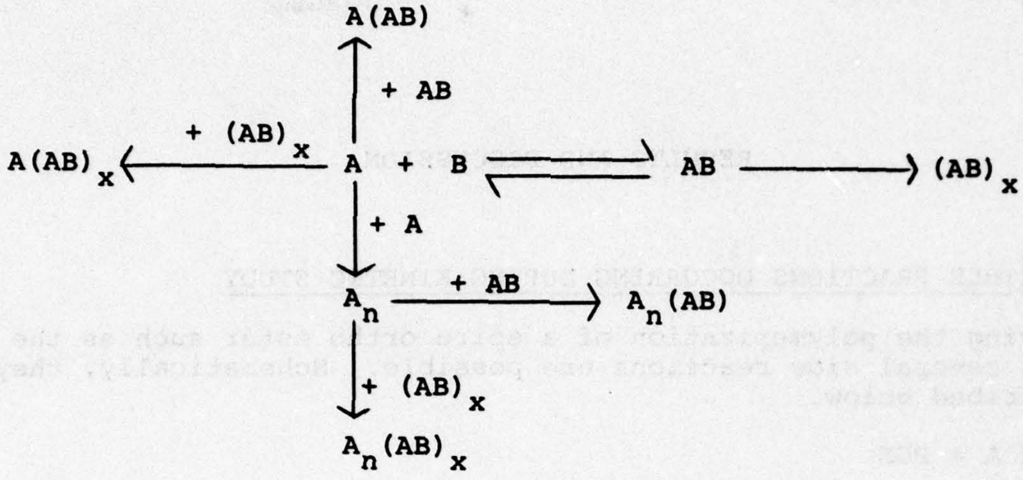
Ideally, we would like the reaction sequence to be as follows:

$$A + B \xrightarrow{BF_3} AB \xrightarrow{BF_3} (AB)_x$$

However, the formation of AB may be a reversible reaction of significant magnitude, i.e.

$$A + B \overset{BF_3}{\rightleftharpoons} AB$$

Thus, even if one starts with pure AB, A and B may be formed in significant amounts. Normally, the reverse reaction would not seriously affect the polymerization since as AB polymerizes to $(AB)_x$ and is removed from the equilibrium, more AB is formed from A and B. But, in this case, A can rapidly react with itself to form oligomers or polymer. A, the oligomers, and the polymer formed from it can react with AB or oligomers or polymer of AB. Some of the possible reactions are shown below. The results of the side reactions are that some portion of B will remain unreacted and that the real polymer may be composed of more A than B. The ideal polymer obtained from the polymerization of AB would of course be composed of equal molar parts of A and B.



II. FORMATION OF THE SPIRO ORTHO ESTER OF PHENYL GLYCIDYL ETHER (SOE-PGE)

Previous work had shown that PGE forms homopolymer rapidly in the presence of boron trifluoride.[11] Thus, we did not expect the formation of the SOE-PGE and its polymer to be feasible from the direct reaction of equimolar amounts of PGE and γ-BL. (The SOE-PGE is prepared by slowly adding PGE to an excess of γ-BL.[9]) The results in Figure 2 confirmed this assumption.

In this kinetic run, 2.5 mole percent of boron trifluoride etherate was added to a solution of PGE and γ-BL in chloroform at time zero. The changes in the concentration of the PGE and γ-BL are rapid; within about two minutes most of the PGE has homopolymerized. Some PGE has reacted with γ-BL to form the SOE-PGE. Therefore, the remainder of the kinetic studies were confined to using pure SOE-PGE as the starting material.

III. POLYMERIZATION OF THE SPIRO ORTHO ESTER OF PHENYL GLYCIDYL ETHER (SOE-PGE)

A. IN CHLOROFORM. A solution of SOE-PGE in chloroform was catalyzed with 5 mole percent of boron trifluoride etherate. The changes in concentration are given in Figure 3. This data pointed out clearly that the formation of SOE-PGE from PGE and γ-BL is a reversible reaction. After the rapid initial changes, the concentrations level off somewhat. The data also revealed that the polymerization of the SOE-PGE is slow under the reaction conditions, i.e., slow after the fast initial change in its concentration. The fact that the concentration of the PGE is always lower than that of

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[11] Krejear, E., and Lunak, S., J. of Polym. Sci., Part C, 16, 643, 1967.

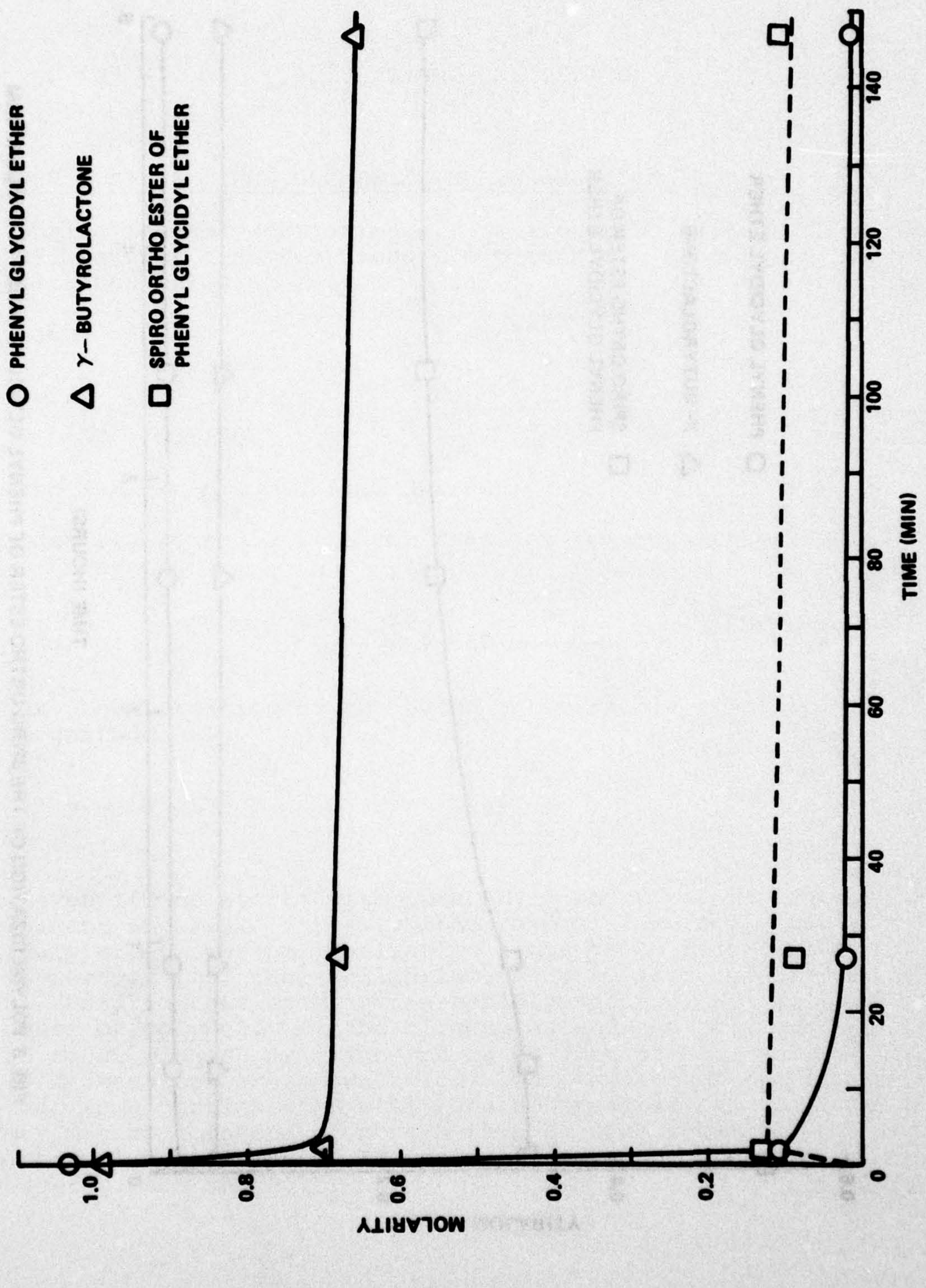


FIG. 2 FORMATION OF THE SPIRO ORTHO ESTER OF PHENYL GLYCIDYL ETHER

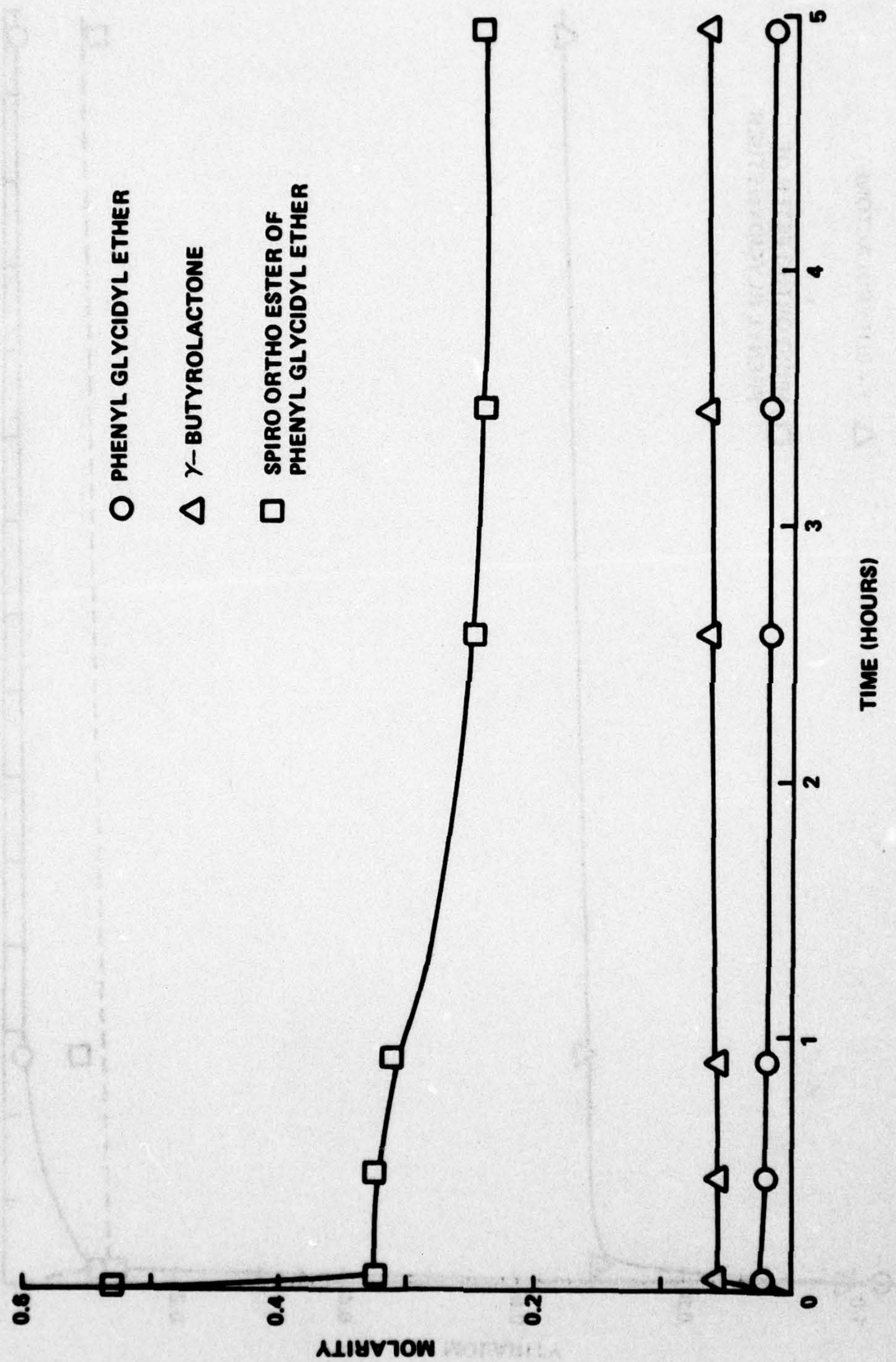
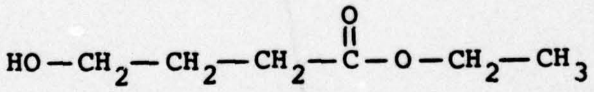


FIG. 3 POLYMERIZATION OF THE SPIRO ORTHO ESTER OF PHENYL GLYCIDYL ETHER IN CHOLORFORM

the γ-BL indicates that some of the PGE formed - which should be equimolar to the γ-BL formed - reacts by one or several of the routes previously discussed.

Another kinetic run of the polymerization of the SOE-PGE in chloroform is shown in Figure 4. In this case, 5 mole percent of boron trifluoride etherate was injected at time zero and again at time 19.98 hours. We wanted to investigate the effect of multiple injections of catalyst. The data shows that after each addition of catalyst the concentrations of the SOE-PGE and γ-BL undergo rapid change and then level out. The shapes of the curves are similar after each injection of catalyst. Again, the concentration of PGE remains lower than γ-BL.

Running the polymerization of the SOE-PGE in chloroform resulted in the formation of an unknown compound. A GC trace showing the elution of the unknown in relation to the known materials is given in Figure 5. A mass spectrograph of the unknown assigned it a molecular weight of 131 - 132. The mass spectrograph also indicated the presence of γ-BL, molecular weight of 86. Chloroform contains 0.5 to 0.75% ethyl alcohol as a preservative, and since the difference between 132 and 86 is 46, the molecular weight of ethyl alcohol, we conjectured that in the presence of boron trifluoride the γ-BL or the SOE-PGE was reacting with the ethyl alcohol to give ethyl-4-hydroxybutyrate (VIII). However, a GC analysis of pure VIII[12] failed to confirm the unknown as ethyl-4-hydroxybutyrate. γ-BL in chloroform with catalyst gave no reaction after three days. Of course, PGE in chloroform with catalyst rapidly homopolymerized, and no unknown was detected.



$$HO-CH_2-CH_2-CH_2-\overset{\overset{O}{\|}}{C}-O-CH_2-CH_3$$

VIII

B. <u>IN METHYLENE CHLORIDE</u>. Therefore, a kinetic run was performed in methylene chloride, which contains no ethyl alcohol. The data, which reflects two injections of catalyst, is shown in Figure 6. The results are similar to those obtained in chloroform. However, in methylene chloride no unknown was formed. After the last injection at 3.53 hours (212 minutes), 0.5% ethyl alcohol was added to the reaction mixture. Within about 20 minutes, the unknown compound was detected; its concentration slowly grew. Apparently, ethyl alcohol reacts with the SOE-PGE to give the unknown material,

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[12] Brown, H. C. and Keblys, K. A., J. Org. Chem., 31, 485, 1966.

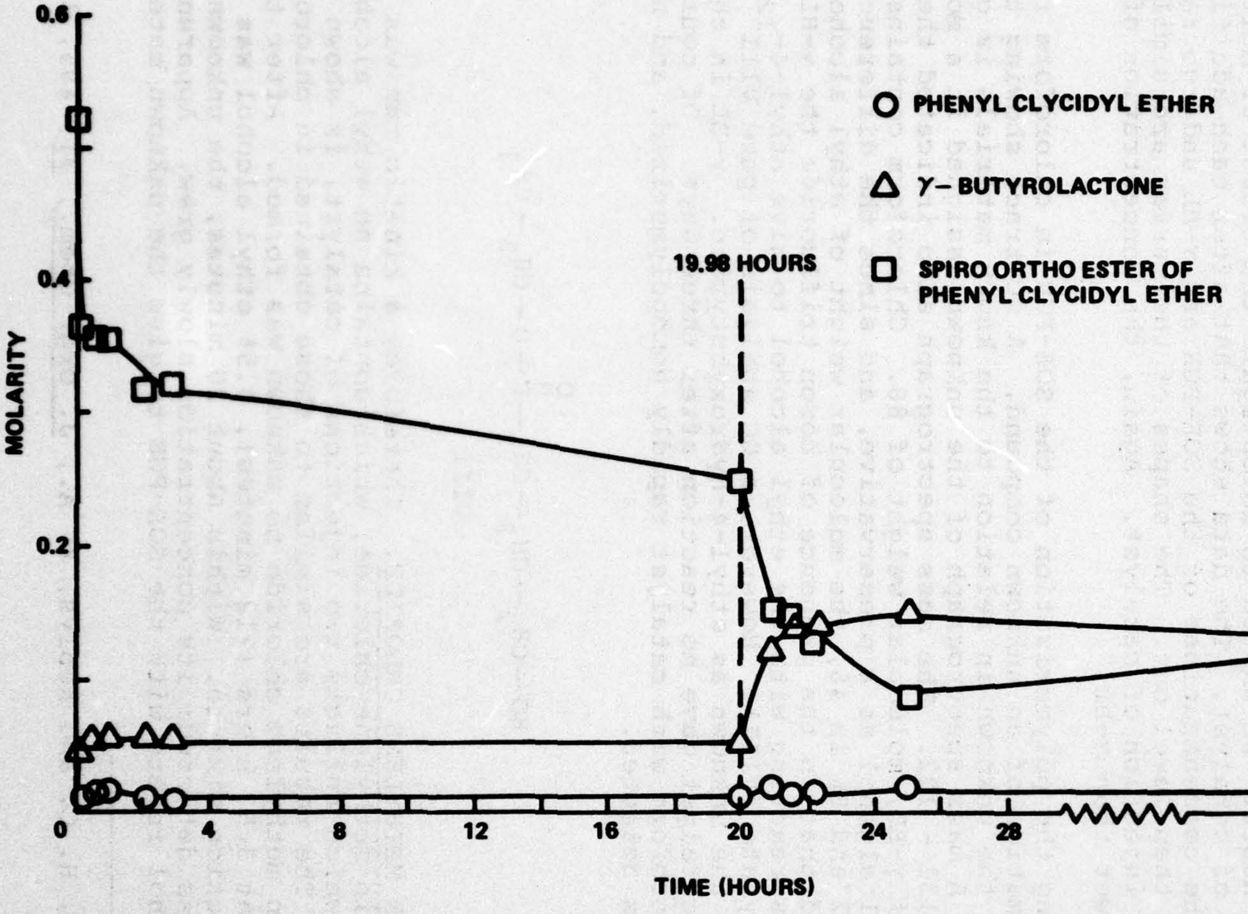

FIG. 4 POLYMERIZATION OF THE SPIRO ORTHO ESTER OF PHENYL GLYCIDYL ETHER IN CHOLOROFORM USING TWO ADDITIONS OF CATALYST

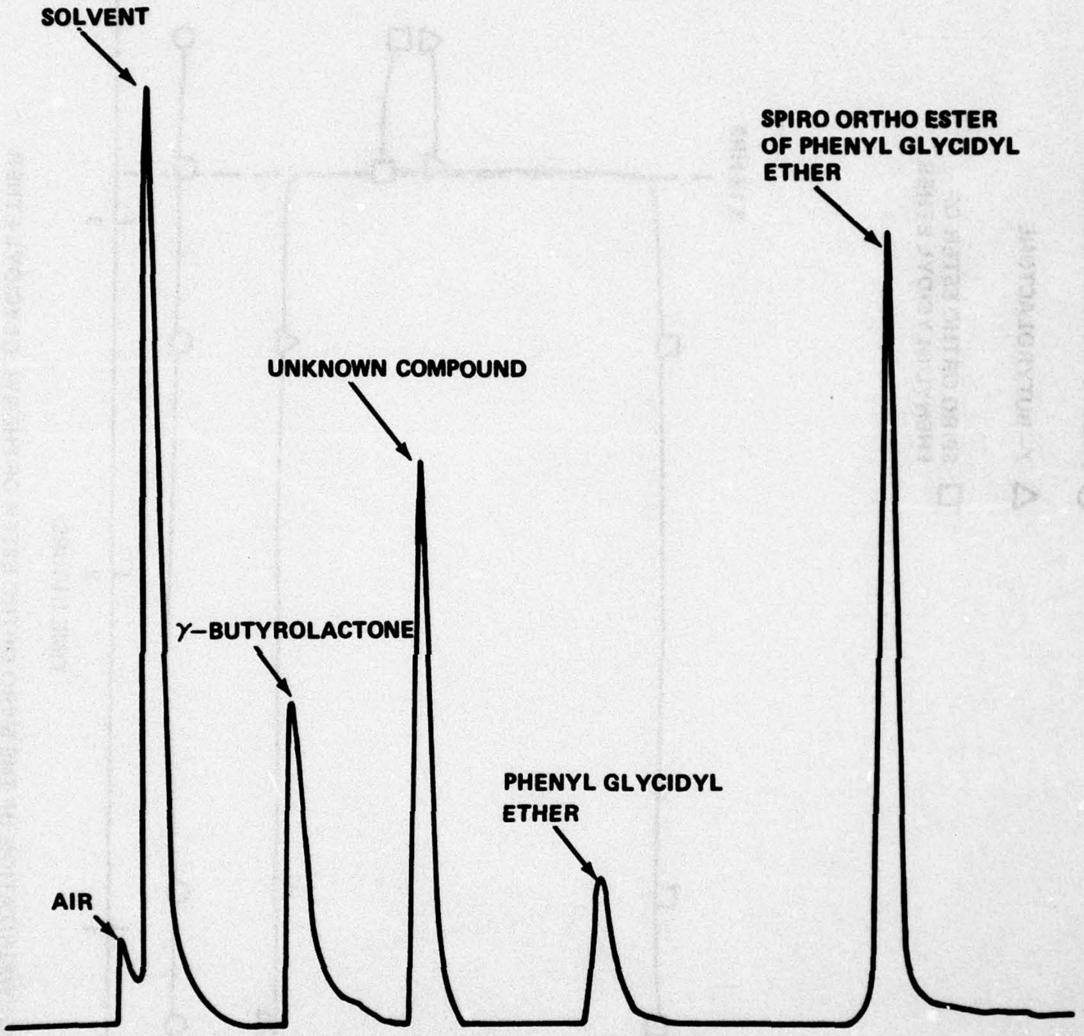

FIG. 5 GAS CHROMATOGRAM INDICATING THE PRESENCE OF THE UNKNOWN COMPOUND

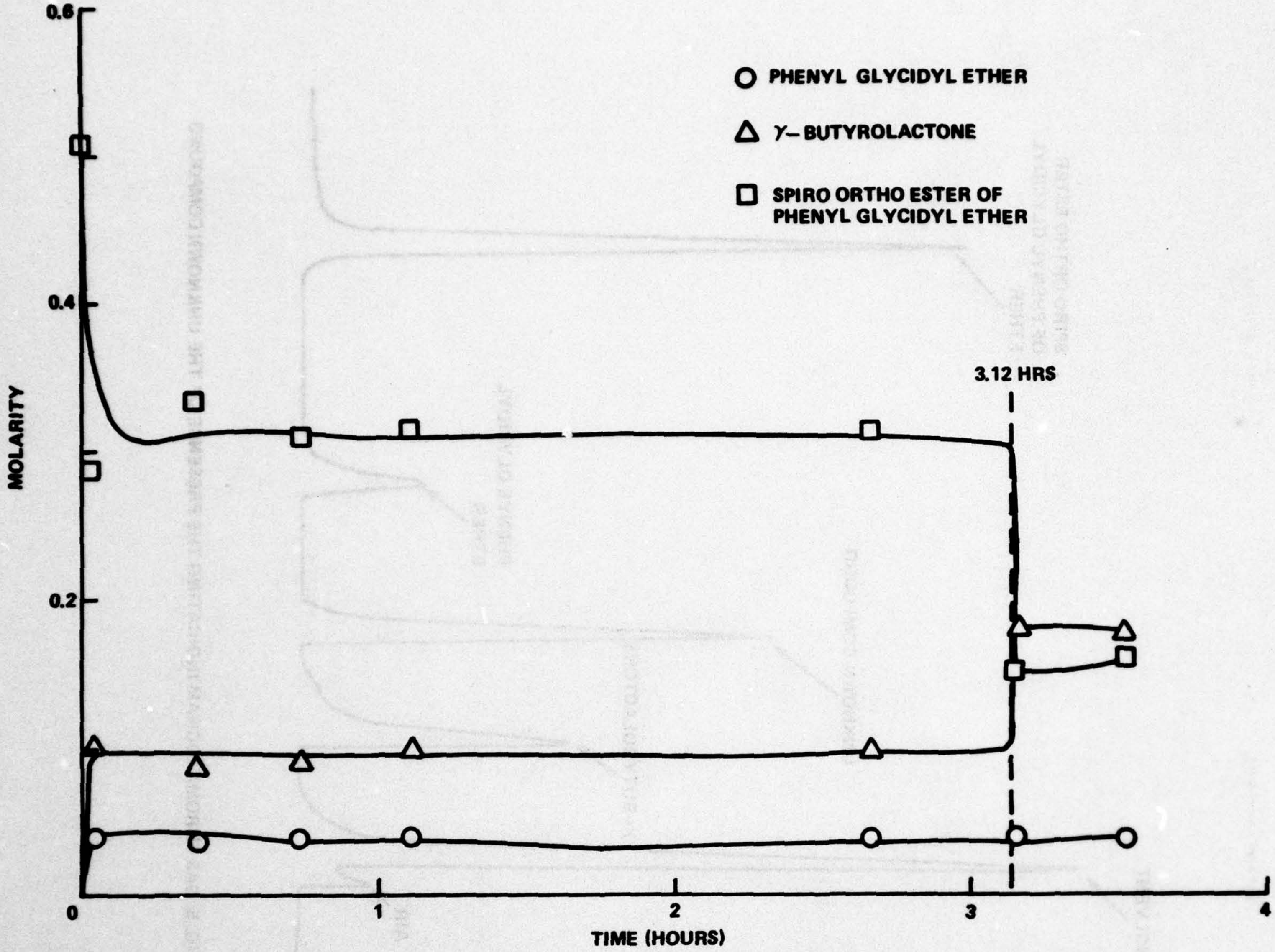

FIG. 6 POLYMERIZATION OF THE SPIRO ORTHO ESTER OF PHENYL GLYCIDYL ETHER IN METHYLENE CHLORIDE USING TWO ADDITIONS OF CATALYST

but further work is required to identify this interesting side product. In any case, future work will be conducted in methylene chloride.

IV. POLYMERIZATION OF THE CRUDE SPIRO ORTHO ESTER OF BISPHENOL A DIGLYCIDYL ETHER (SOE-DGEBA)

Tests indicated that the polymerization of the crude SOE-DGEBA was slow enough to allow the change in the concentration of γ-BL with time to be monitored, at least up to the point where the solution became too viscous to obtain samples. These kinetic experiments were performed in chloroform using 5 mole percent boron trifluoride etherate. Again the same unknown compound (i.e., the same retention times) as was formed during the polymerization of the SOE-PGE was detected. This work was done before we were aware that ethyl alcohol was required to form the unknown. But, the fact that the same unknown is formed in chloroform during the polymerization of both the SOE-PGE and the SOE-DGEBA indicates that the ethyl alcohol reacts with the spiro ortho ester moiety - not the γ-BL or free epoxy - to yield the unknown compound.

Using the equipment and parameters explained in the experimental section, only the changes in γ-BL concentration could be followed and not the changes of free DGEBA, SOE-DGEBA, or resulting polymeric materials. Nevertheless, the data plotted in Figure 7 is informative. Figure 7 is a plot of the change in γ-BL concentration, measured as a percent of the total solids content, versus time. The crude SOE-DGEBA contained 1.9% unreacted γ-BL. The data, although more scattered than desired, shows that more γ-BL is rapidly formed by the reversible reaction upon addition of catalyst. After the rapid initial change, the concentration levels off. The assumption is that the changes in the concentration of the SOE-DGEBA would be similar to those of the SOE-PGE (Figures 2, 3, 4, and 6). Also, if additional γ-BL is formed upon addition of catalyst, then DGEBA must be formed; the free DGEBA can homopolymerize or copolymerize in a manner similar to the PGE formed in the polymerization of SOE-PGE.

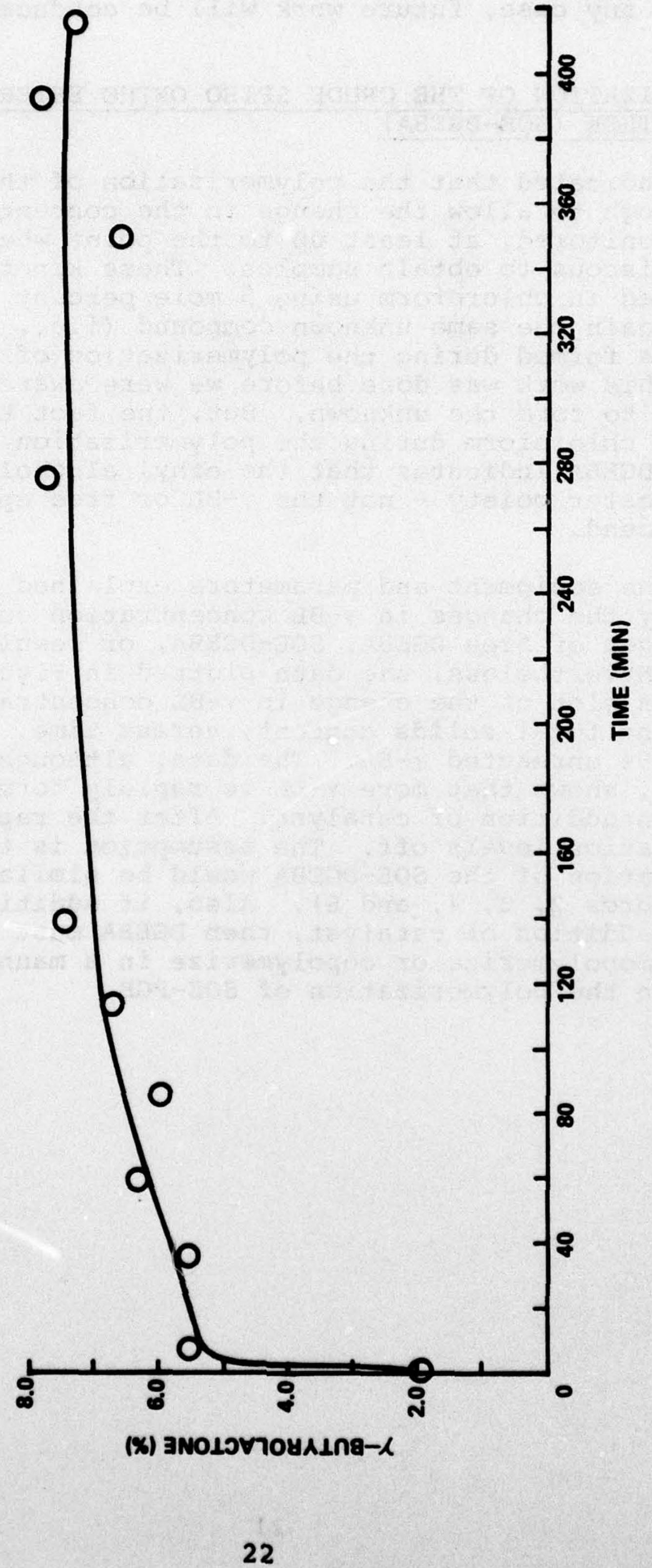

FIG. 7 CHANGE IN THE CONCENTRATION OF γ-BUTYROLACTONE DURING THE POLYMERIZATION OF THE CRUDE SPIRO ORTHO ESTER OF BISPHENOL A DIGLYCIDYL ETHER

CONCLUSIONS

1. The reaction of an epoxide with γ-butyrolactone (γ-BL) to form a spiro ortho ester is a reversible reaction. As a result, during the polymerization of a spiro ortho ester, γ-BL and the epoxide will be formed. However, since the epoxide formed readily homopolymerizes and/or copolymerizes, unreacted γ-BL will be present in any polymeric material formed.

2. After the rapid initial decrease in concentration of a spiro ortho ester upon addition of catalyst, its polymerization rate is slow at room temperature.

RECOMMENDATIONS

1. The effect of temperature and possibly catalyst on the polymerization and formation rates of spiro ortho esters should be investigated.

2. The chemical composition and changes in composition of the polymer with varying conditions should be determined to further elucidate the reactions occurring during polymerization of spiro ortho esters.

ACKNOWLEDGEMENTS

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APPENDIX A

CALIBRATION CURVES

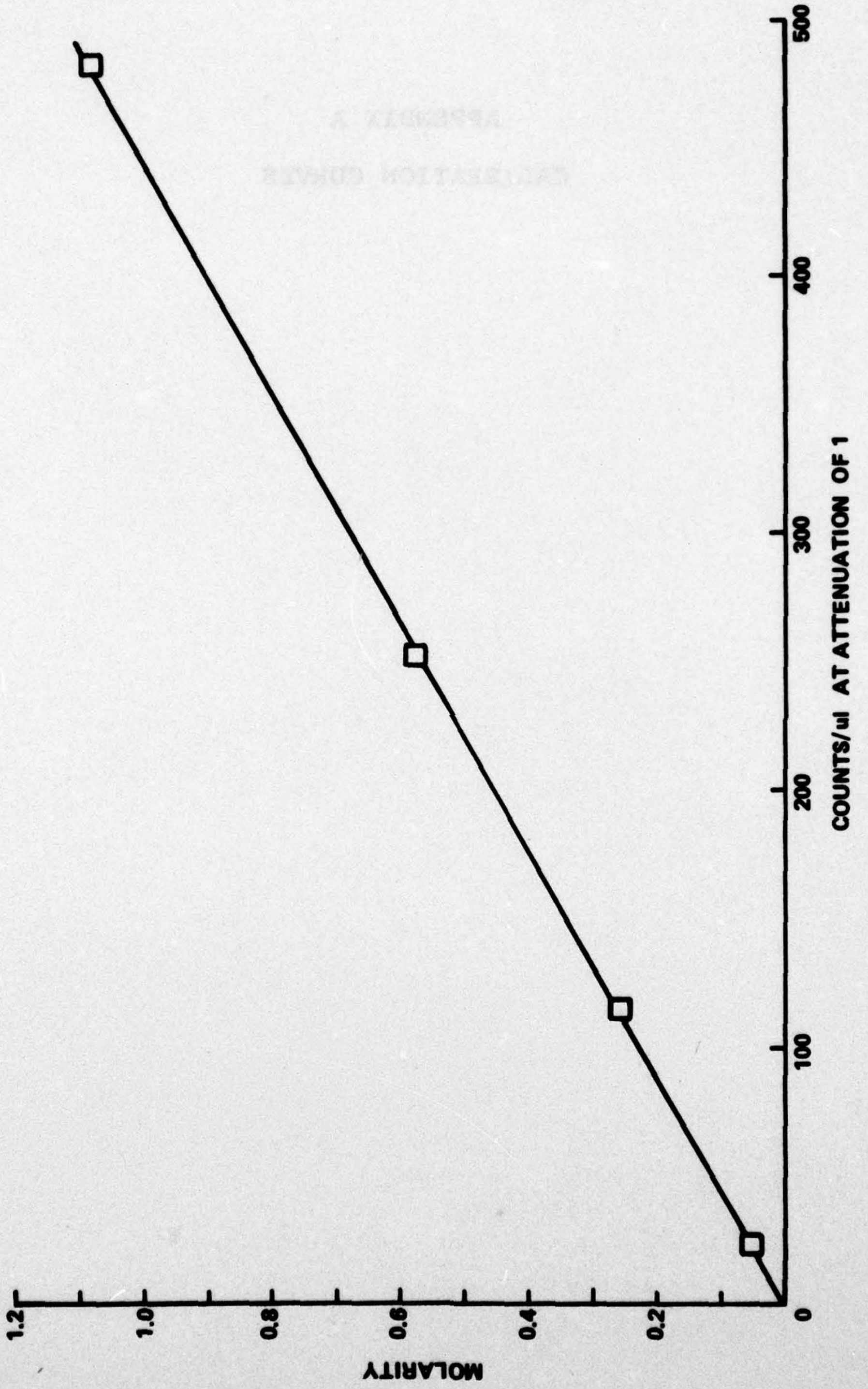

FIG. 8 CALIBRATION CURVE FOR PHENYL GLYCIDYL ETHER

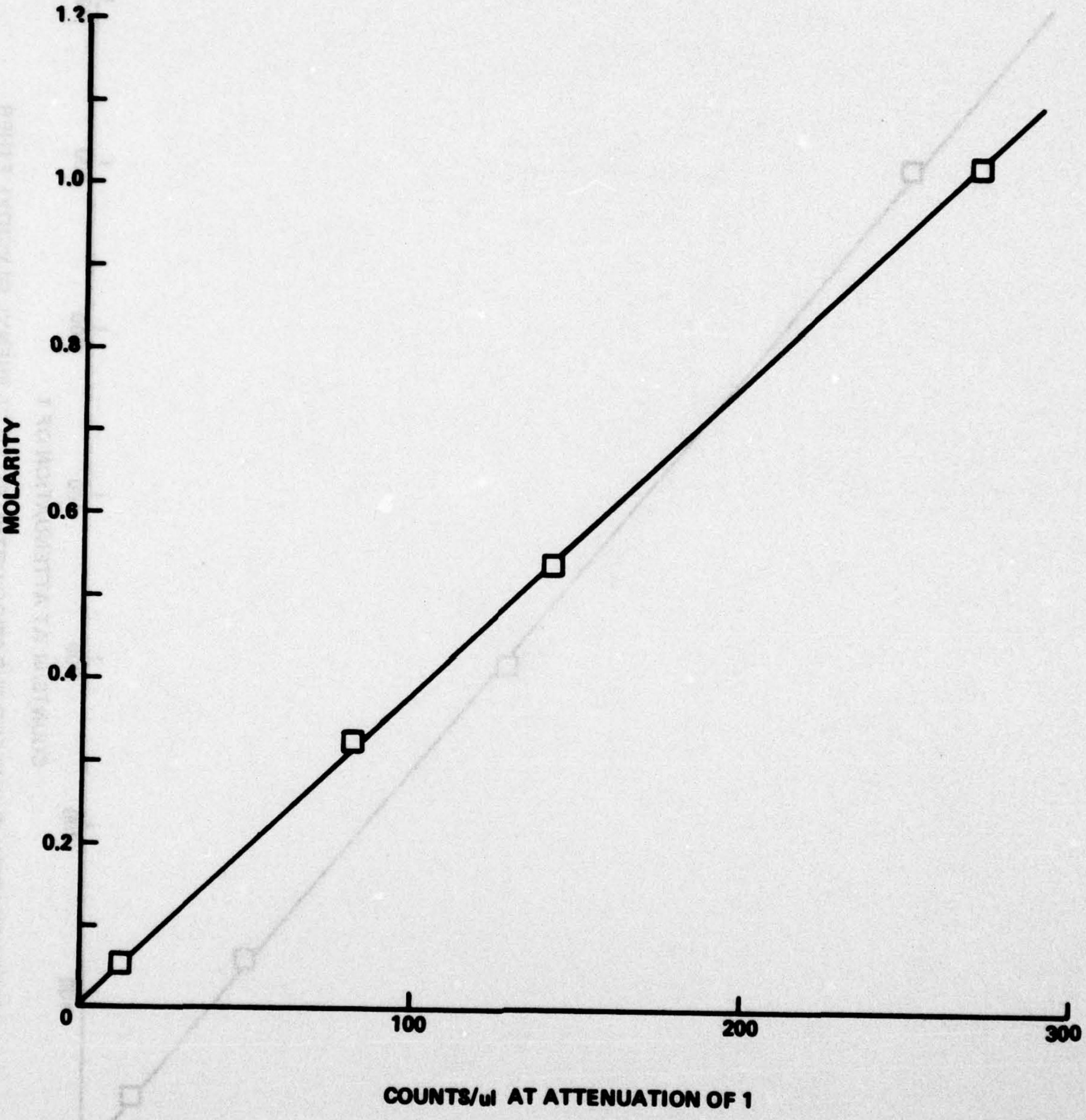

FIG. 9 CALIBRATION CURVE FOR γ–BUTYROLACTONE

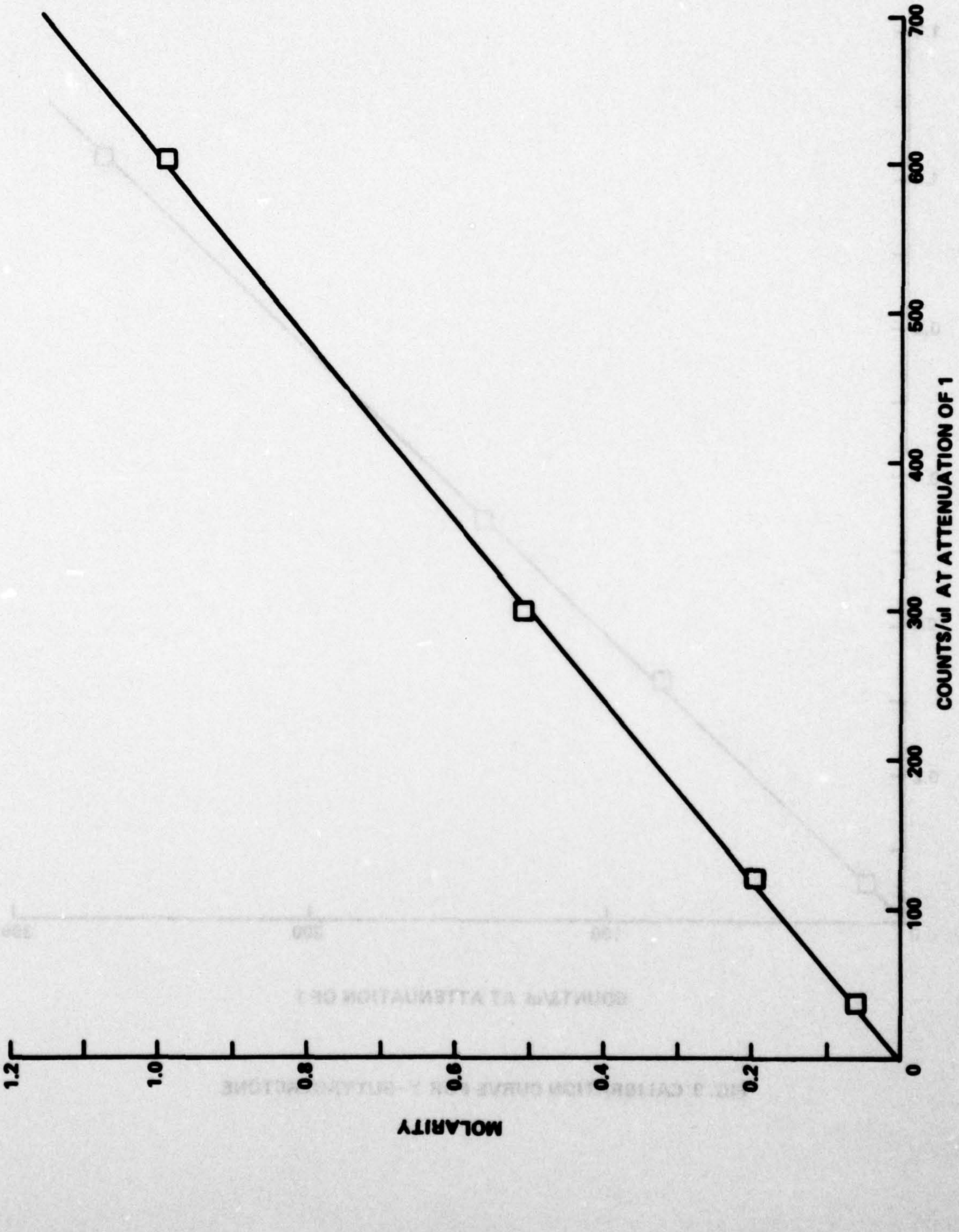

FIG. 10 CALIBRATION CURVE FOR THE SPIRO ORTHO ESTER OF PHENYL GLYCIDYL ETHER

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