

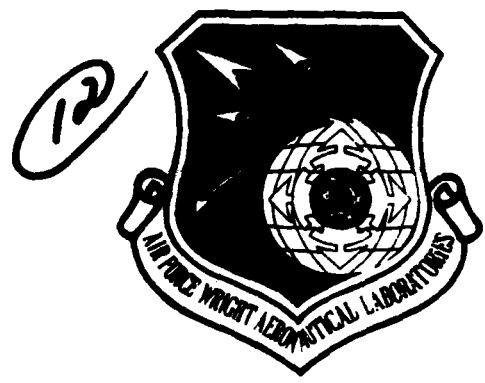
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MOISTURE-RESISTANT ADHESIVES

MIDWEST RESEARCH INSTITUTE
425 VOLKER BOULEVARD
KANSAS CITY, MISSOURI 64110

MAY 1982
FINAL REPORT FOR PERIOD AUGUST 1979 TO DECEMBER 1981



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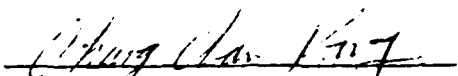
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This technical report has been reviewed and is approved for publication.



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20. (continued)

The resin selected for synthesis and characterization was an acetylene terminated quinoxaline, BA-DAB-BA, and 500 g of this material was synthesized for characterization, modification and sample preparation.

Characterization of BA-DAB-BA was to be the main part of this program. Described in this report is the work performed on:

- . A data acquisition and reduction system;
- . Conversion of heat of reaction data to polymerization rate;
- . Determination of reaction window for BA-DAB-BA;
- . Determination of the viscosity of BA-DAB-BA;
- . Determination of BA-DAB-BA melting points;
- . Initial trial B-Staging of BA-DAB-BA;
- . Precure of BA-DAB-BA;
- . Modified DSC kinetics method; and
- . Modification of a viscosity determination method.

Although significant progress was made on the evaluation of the physicochemical characteristics of BA-DAB-BA, persistent experimental difficulties were encountered which set back the characterization work. Consequently, midway through the project, a change in the scope of work was instituted: from further evaluation of BA-DAB-BA to the synthesis of additional quantities of the oligomer and the end-capper, 4-(3-ethynylphenoxy)benzil. Subsequently, due to re-direction of research funds by the Air Force, another change was instituted in the scope of the project limiting the synthesis of the end-capper of which an additional 1,200 g was synthesized.

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PREFACE

This report was prepared by Midwest Research Institute (MRI) under USAF Contract No. F33615-79-5141, "Moisture-Resistant Adhesives." The work was administered under the direction of the Air Force Wright Aeronautical Laboratories, Research and Technology Division, Air Force Systems Command, with Lt. S. R. Eddy, Mr. M. R. Lucarelli, and Lt. C. C. Kang as project scientists.

This report covers experimental work conducted from August 17, 1979 to December 1981.

The work at Midwest Research Institute was designated Project No. 4829-G and was carried out under the supervision of Dr. C. C. Chappelow, Head, Materials Science Section. Personnel contributing to the experimental work were: Messrs. E. E. Atkins, B. F. Hauber, R. K. Ruckman, T. J. Byerley, and Dr. M. J. Steuck. Mr. H. W. Christie and Mr. R. L. Elliott served as principal investigators on the program.



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SECTION I

INTRODUCTION

The initial goals of the work under the contract were two-fold: first, the selection and synthesis of an acetylene terminated oligomer; second, the development of a systematic series of chemical, physical, and mechanical procedures which would allow timely, technically sound, and cost-effective screening of candidate high-temperature, moisture-resistant resins. These goals were described in MRI Proposal No. L-1544, dated May 23, 1979, which outlines the entire work program.

The final scope of work for the program consisted of three tasks:

- Task I - Resin System Identification
- Task II - Resin Synthesis and Characterization
- Task III - End-Capper Synthesis

This report describes the project activities related to these three tasks. The results obtained on each task are presented and discussed in the next section (Section II). The experimental procedures employed and the work performed on each task are presented in the final section (Section III).

SECTION II

RESULTS AND DISCUSSION

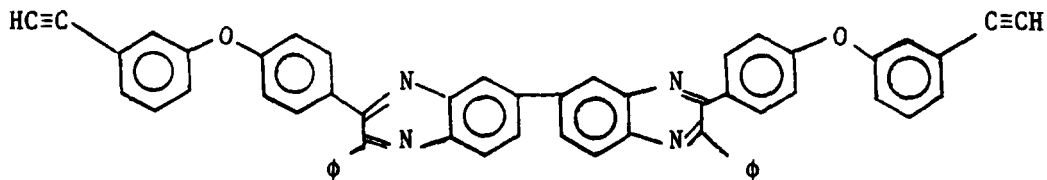
Discussed in this section are the results obtained from the work performed on Task I - Resin System Identification, Task II - Resin Synthesis and Characterization, and Task III - End-Capper Synthesis. Task I was a relatively minor task and has no subdivisions of subject matter. Task II, however, included seven different areas of investigation relating to the synthesis and characterization of the selected resin BA-DAB-BA: synthesis of BA-DAB-BA, data acquisition and reduction system, kinetics of BA-DAB-BA polymerization, melting points of BA-DAB-BA, viscosity of BA-DAB-BA, thermal advancement and the viscosity, and modified DSC kinetics. Task III, the final portion of the work, consisted of the large-scale synthesis of the end-capper, 4-(3-ethynylphenoxy)benzil.

1. Task I - Resin System Identification

Data supplied by AFWAL concerning the thermal stability, mechanical properties, reactivity moisture resistance, and handling properties of nine different acetylene terminated (ATX) polymers were combined with a computerized search of Chemical Abstracts and NTIS literature for literature concerning these ATX polymers to form a base for selection of an oligomer or polymer for synthesis. Several criteria were used in making the selection of the oligomer:

1. Thermal stability of the resultant resin.
2. Hydrolytic stability of the resultant resin.
3. Viscosity of the molten oligomer as it applies to adhesive and composite fabrication application.
4. Ease of synthesis.
5. Amount of information available.

The oligomer 3,3'-bis[4-(3-ethynylphenoxy)phenyl]-2,2'-diphenyl-6,6'-biquinoxaline, identified as "BA-DAB-BA," which has the following structure, was selected.



The thermal, mechanical, and physical properties of BA-DAB-BA have been well described (Reference 1). Arnold and Hedberg have outlined synthesis procedures for making BA-DAB-BA in reasonable yields (Reference 2). This oligomer

has a relatively low (170°C) melting point. In addition, the viscosity of the melt is low enough to make BA-DAB-BA readily amenable to casting and composite sample preparation.

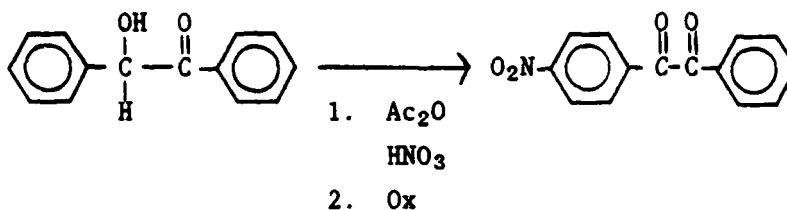
2. Task II - Resin Synthesis and Characterization

Discussed below are the results obtained during the work on Task II. Topics include the synthesis of BA-DAB-BA, the data acquisition and reduction system, kinetics of BA-DAB-BA polymerization, melting points of BA-DAB-BA, viscosity of BA-DAB-BA, thermal advancement and viscosity of BA-DAB-BA modified DSC kinetics.

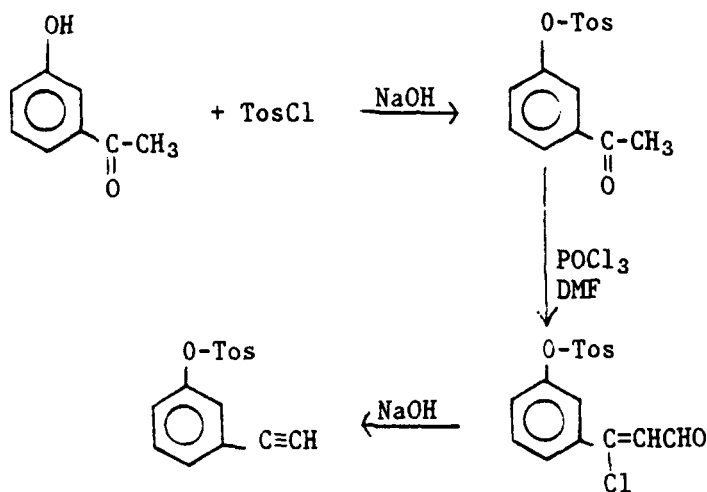
a. Synthesis of BA-DAB-BA: A modification of the Arnold-Hedberg procedure (Reference 2) supplied by AFWAL (Reference 3) was used in preparing 500 g of this oligomer.

In order to make this amount of "BA-DAB-BA," approximately 1,150 g of 3-ethynylphenyl(p-toluenesulfonate) and approximately 1,070 g of 4-nitrobenzil were required. Both of these compounds have been prepared in the past during work on AFML Contract No. F-33615-79-5141, "Synthesis of Monomers and Polymers for Evaluation."

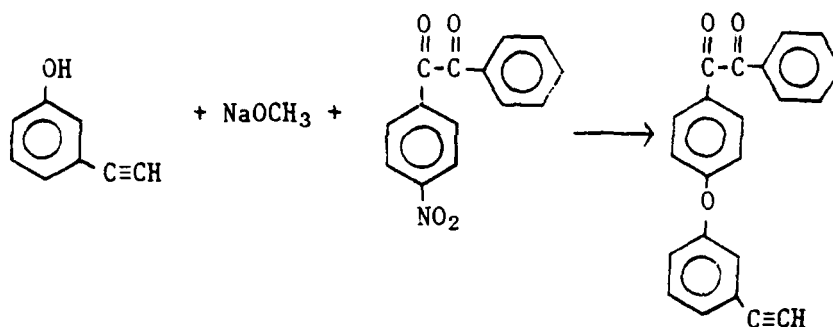
The 4-nitrobenzoin acetate was prepared by nitrating benzoin in acetic anhydride. Yields of 33% of the nitro-acetate were obtained on 11 batches to obtain 1,287 g of product. Conversion of the nitro-acetate to the desired 4-nitrobenzil was accomplished by oxidation in nitric acid in 11 batches with an overall yield of 1,070 g, corresponding to an average yield of 82.3%.



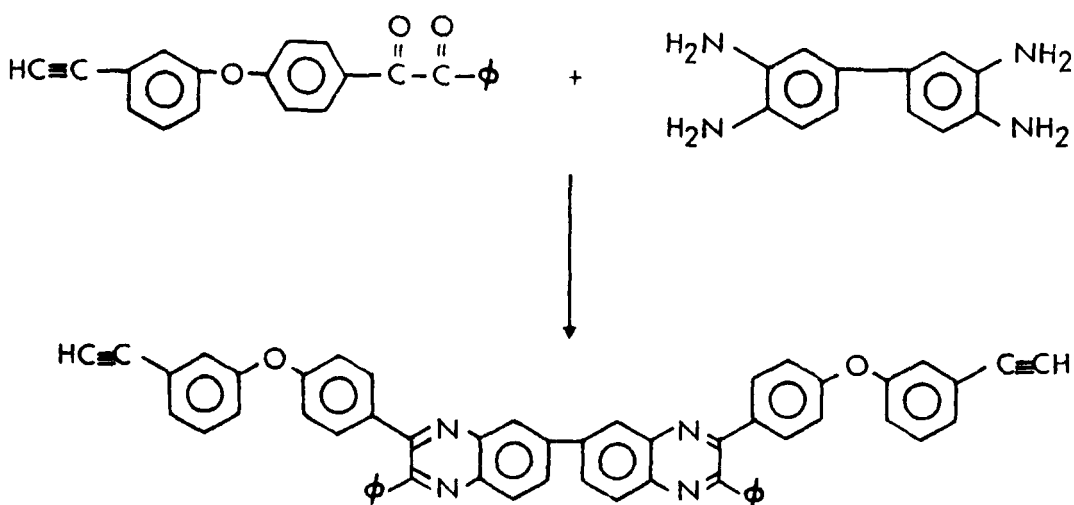
Synthesis of 3-ethynylphenyl(p-toluenesulfonate) began with the preparation of 3-acetylphenyl(p-toluenesulfonate) from 3-hydroxyacetophenone. Treatment of this sulfonate with Vilsmeier reagent gave α -chlorocinnamaldehyde-3-yl-(p-toluenesulfonate), which upon hydrolysis with sodium hydroxide gave the desired 3-ethynylphenyl(p-toluenesulfonate).



The 4-(3-ethynylphenoxy)benzil was prepared by reaction of the sodium salt of 3-ethynylphenol with 4-nitrobenzil in dimethyl sulfoxide.



BA-DAB-BA was prepared by reacting two moles of 4-(3-ethynylphenoxy)benzil with one mole of 3,3'-diaminobenzidine.



Thin layer chromatography (TLC) of the BA-DAB-BA reaction product on silica gel plates showed BA-DAB-BA contaminated with 4-(3-ethynylphenoxy)-benzil (BA) starting material when the plate was developed with methylene chloride, and several trailing spots were present when the plate was developed with either tetrahydrofuran (THF) or ethyl acetate.

A purification procedure was developed which afforded pure single spot (TLC) BA-DAB-BA. Column chromatography on silica gel of the crude reaction product (free of THF) gave a small fraction of recovered BA when eluted with methylene chloride. Further elution with a 40:1 solution of methylene chloride:ethyl acetate gave pure BA-DAB-BA. If more than a trace of THF were present, a BADAB-BA plus BA fraction was obtained. The BA-DAB-BA + BA fractions were retained, combined and rechromatographed as a single fraction (Run No. 11). Consequently, the actual yield of BA-DAB-BA was higher than that reported for some runs.

Progress of BA-DAB-BA down the column could be followed by long wave (365 nm) UV light. It was visible as a brilliant bluish fluorescence. A brilliant yellow fluorescent band was visible (under long wave illumination) trailing the BA-DAB-BA band. If the concentration of ethyl acetate in the elutant were increased, the yellow band migrated into the BA-DAB-BA band. High-performance liquid chromatography (HPLC) of pure BA-DAB-BA showed a single peak.

Details of the synthetic procedures are given in Section III-2-a of this report.

b. Data acquisition and reduction system: Many of the thermal stability, mechanical, physical and chemical properties of the oligomers and resins to be investigated require rather complex test procedures and would be very laborious data-reduction process by hand-methods. The evaluation and characterization of the oligomers and cured resins performed by dynamic mechanical analysis (DMA), thermomechanical analysis (TMA), thermogravimetric analysis (TGA), and differential scanning calorimetry (DSC) require some form of computerized data acquisition.

The system conceived for use on this project consisted of digital multi-meters for conversion of the millivolt and greater electrical analog outputs from the test units to serial binary coded decimal (BCD) signals. These signals, along with the BCD outputs of a DuPont Model 981 DMA unit (when used), are then fed to an 8080A microprocessor based minicomputer for conversion to ASC-II computer compatible format. The ASC-II signals are then fed to paper tape punch/reader for data storage. These data are then fed to a time-sharing computer (United Computing Services, Inc., Kansas City, Missouri) for data reduction and report-page-format printout on an alphanumeric x-y plotter. A more detailed description of this system is given in Section III-2-b of this report.

Initially, the microprocessor, tape punch and accessory were assembled and checked out. Several rather perplexing problems were encountered with both the interfacing of the digital multi-meters to the microprocessor and operation of the punch/reader. The BCD signal level output

from the Tektronix, Model 501/503 multi-meters was not high enough in power to adequately "fire" the microprocessor. This problem was remedied by building buffers for each of the two multi-meters to increase signal strength sufficiently to "fire" the TTL logic of the microprocessor. After a few (2 to 4) hours of operation, the tape punch/reader would stop punching correctly. The cause was finally found to be a mechanical one related to movement of the brackets supporting the electro-magnets that drive the punch. A mechanical "fix" of this problem was attempted without success.

Assembly of the microprocessor was essentially completed, including the insertion into the memory of the unit of the U.S. Bureau of Standards equations for conversion of chromel/alumel thermocouple voltage to temperature. This conversion is necessary for all of the four major tests to be performed as each one has a temperature function. The microprocessor converts the ice bath referenced chromel/alumel thermocouple output (millivolts) to its numerical equivalent in ASC-II format. Other volt inputs are directly converted to ASC-II format for later handling and reduction in the computer.

Several trial runs using an example of DMA data from DuPont were made to determine what modifications of existing x-y plot progresses were required to obtain the desired x-y-y' plot. Only minor modifications were necessary. No difficulty was encountered in transmitting the tape punched data from MRI terminal to the computing service. A detailed discussion of the data acquisition system is presented in Section III-2-b of this report.

However, other problems were encountered with two main components of the data acquisition system. The buffer amplifiers made to increase the power of the binary coded decimal (BCD) signals from the multi-meters worked quite adequately as demonstrated by their ability to drive an "Altair" mini-computer and associated print out equipment. When the multi-meter-buffer amplifier combination was connected to the input board of the Cromomco, Inc. microprocessor the input data appeared as "gibberish" on both the tape punch and Flexowriter output units. This behavior was very disconcerting as all other parts of the data modification and processing system were working well. Examination of the input board indicated that the SN74LS373 octal transparent latch failed to properly process the incoming BCD signals. Once this change was made, the microprocessor properly read and stored the data from the two digital multi-meters.

The DuPont Model 900 Differential Scanning Calorimeter (DSC) was calibrated along with the DuPont Model 941 Thermomechanical Analyzer (TMA) for future use. New calibrations involved setting of the time base generators and adjustment of the temperature rate controls as well as calibration of the x-y plotter. The parallel plate viscometer was attached to the TMA unit and trial runs were performed.

Continuing difficulties with the computerized data acquisition forced a conversion of the experimental procedures to optimum conditions for hand data reduction.

c. Kinetics of BA-DAB-BA polymerization: The polymerization of BA-DAB-BA is a complex combination of internal cyclization and chain extending reactions. For practical use of this oligomer in adhesive and composite material preparation, it is highly desirable to know the gross kinetics of these reactions. Use of DSC required only small (5 mg) samples of the oligomer, and it is readily possible to determine the heat of reaction and the effect of temperature on reaction rate. By use of multiple DSC determinations at six different heat rates (5 to 30°C/min in 5°C intervals), it is possible to determine an effective rate of reaction at 0°C heat rates by extrapolation. The reaction rate at a given temperature is then proportional to the area under the DSC curve (see Section III-2-b of this report).

This procedure called for a minimum of special equipment and was performed using a DuPont Model 900 Thermal Analyzer with a single channel strip chart recorder (L&N Speedomax, 1.0 mv full scale sensitivity) to provide a time-based plot of the differential temperature. Integration of the areas under the curves was done by the "cut and weigh" method. The coefficient of deviation for the heat of fusion of standard pure indium metal was less than 2.0%. The heat of reaction for BA-DAB-BA was found to be 64.6 + 2.6 Kcal/g mol. The activation energy of the gross reaction was 22,960 cal/g mol, and the Arrhenius constant was $1.740 \times 10^7 \text{ sec}^{-1}$. These values were based on the assumption that the reaction was first order, and that the reaction observed was a gross one, that is, a combination of reactions. The first order reaction assumption was validated by the linearity of the semi-log plot of reaction rate and reciprocal temperature. The accuracy of this method was also affected by any nonlinearities in the DSC cell and associated controls. As the data analysis system is essentially a differential one, the slope (E) of log reaction rate versus 1/T was probably more accurate than the Y intercept value (A in the Arrhenius equation).

A reaction window format presentation of the kinetic data was prepared and is shown in Figure 11 in Section III-2-b of this report. The iso-reaction level lines were calculated from the Arrhenius equation values and the logarithmic relationship:

$$k = \frac{1}{t} \times \ln \frac{1}{1-x}$$

where k = reaction rate at temperature
t = time, sec
x = mol fraction reacted at time t

In summary, this method provided a reasonable means for determining reaction kinetics that require the expenditure of a minimum of 30 mg of material.

d. Viscosity of BA-DAB-BA: Use of the micro-parallel plate rheometer attachment to the DuPont Model 941 Thermomechanical Analyzer provided a relatively simple method for determining the viscosity-temperature relationship of BA-DAB-BA. The raw data were collected as an x-y plot of temperature or time versus distance between the parallel plates. These data were then fitted to a polynomial equation with a coefficient of correlation

(r^2) of at least 0.99, or the plate separation was taken directly as "h." Differentiation of the polynomial equation provided the rate of change of height (dh/dt) at a given time or temperature. These values were then used to solve either form 1 or 2 of the Stefan equations to yield the viscosity values. This method required the use of a small (Apple II) computer for curve fitting and rapid data reduction. In addition, only 60 mg of BA-DAB-BA was required per determination.

The viscosity of BA-DAB-BA was found to be quite low at temperatures above the last melting point of 171°C with values of 180 Poise at 180°C and 35 Poise at 190°C. This low viscosity required that these determinations be performed in the temperature scan (10°C/min) mode of operation of the TMA unit. There was not time enough to measure the viscosity at an isothermal temperature above the last melting point. All the sample would flow out of the rheometer before temperature equilibrium was reached. There is some question about the accuracy of the viscosity determinations at these low values, because they are below the normal ranges of utility of the parallel plate rheometer.

The low viscosity of BA-DAB-BA at temperatures above melt indicates that the neat oligomer will not be satisfactory for adhesive applications. The low viscosity would make glue line thickness control very difficult, if possible at all. BA-DAB-BA must be either precured (B-staged) or chemically modified to increase viscosity. A preliminary examination of precure at 167°C (intended to be 175°C-defective thermocouple) showed that indeed the viscosity can be increased by 100-fold before gelation is reached. After heating 50 min at 167°C, the viscosity at 190°C increased from 35 to 5.1×10^3 Poise. It is interesting to note that even after this extended precure time, there was still a sharp inflection in the viscosity-temperature curve at 170°C.

e. Melting points of BA-DAB-BA: Differential Scanning Calorimetry of the oligomer showed two transition or melting temperatures of 95 to 100°C and 140 to 145°C. However, initial trials of the parallel plate rheometer gave indications of three melting points as shown in inflections in the viscosity-temperature curve. The sensitivity of the DuPont Model 900 Thermal Analyzer was increased by use of a high-gain, strip-chart recorder, and four transition or melt temperatures were observed at 103, 141, 163, and 171°C. The fact that they were true melting points was confirmed by visual observation of a small sample of the oligomer in a melt point apparatus. These observations suggest that there may be four stereo isomers whereas high-performance liquid chromatography had earlier shown the presence of only one component.

f. Thermal advancement and the viscosity of BA-DAB-BA: The molecular weight and the viscosity of BA-DAB-BA can be increased by heating BA-DAB-BA. Several different combinations of times and temperatures were used to evaluate this behavior. The temperatures and times were carefully controlled, and small (300 mg) batches of BA-DAB-BA were used to keep exothermic heating to a minimum. Temperatures in the range of 170 to 190°C were used with times ranging from 5 to 60 min. The degree of advancement

was obtained by integration of the area under the DSC curve of 5.0 mg samples of the treated BA-DAB-BA using the heat of reaction value for BA-DAB-BA which had been determined previously. Determination of viscosity of the treated BA-DAB-BA showed substantial increases as the extent of reaction exceeded 10%. As the degree of reaction reaches 45%, the viscosity at 190°C was greater than 10^8 Poise.

The relationship between the degree of advancement and viscosity was found to be logarithmic as follows:

$$\log \eta = 0.159 \left(\frac{A_u - A_t}{A_u} \times 100 \right) + 0.097$$

where A_u = area of DSC plot for 5.0 mg untreated BA-DAB-BA
 A_t = area of DSC plot for 5.0 mg thermally advanced BA-DAB-BA

The first constant is the slope (m, see Figure 1) of the plot of $\log \eta$ versus percent reaction, and 0.097 is $\log \eta$ when the advancement is 0%. A linear regression analysis of the results of 10 different time-temperature treatments of BA-DAB-BA in terms of $\log \eta$ viscosity and percent advancement yielded a correlation coefficient of 0.096 indicating good fit of the experimental data to a semilogarithmic plot.

Several conclusions can be drawn from these observations. Thermal polymerization of BA-DAB-BA is probably linear in nature with very little, if any, side branching or crosslinking occurring. This is indicated by the linearity of the $\log \eta$ /percent reaction plot, and the observation that even at 45% reaction, the product was still soluble in tetrahydrofuran. The polymerization reaction is first order over the range studied which confirms the previously determined kinetic values. The lack of crosslinking indicates that either steric hindrance or the basic stability of the linkage created on condensation of the two acetylenic groups prevents such a reaction.

g. Modified DSC kinetics: By measuring the differential voltage from the Y axis ($\Delta^\circ\text{C}$) of the DuPont Model 900 Thermal Analyzer at 6 sec time intervals it was possible to perform a numeric integration of the DSC plot and obtain heat of reaction, rate of reaction, and reaction kinetics. The data obtained were in good agreement with that obtained previously in terms of heat of reaction and the activation energy ΔE of the Arrhenius equation. There was, however, a substantial difference in the Arrhenius constant (A).

The multiscan-temperature extrapolation method gave an activation energy of 22,960 cal/g mol, whereas the numerical integration method yielded a value of 23,140 cal/g mol. The two Arrhenius constant values were $1.740 \times 10^7 \text{ sec}^{-1}$ for the former method and $5.5968 \times 10^6 \text{ sec}^{-1}$ for the numerical integration method. Of particular importance was the increased sensitivity provided by the numerical integration method. In addition, use of this method made it possible to confirm the order of reaction over a wide reaction range.

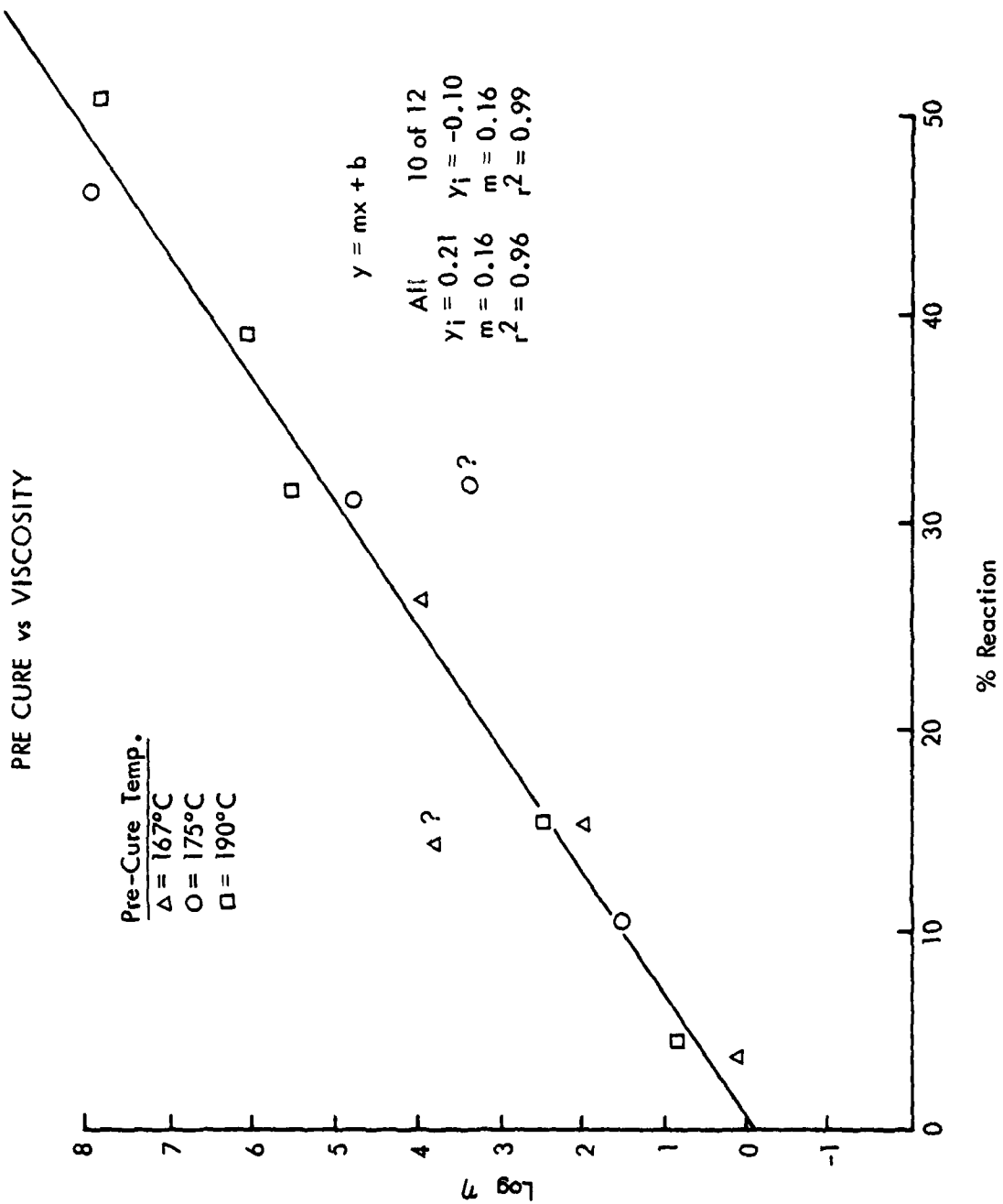


Figure 1 - Effect of Pre-Cure on Viscosity of BA-DAB-BA

By comparing the experimental data as fraction reacted (X) versus time (t) with the same value determined from the following equation:

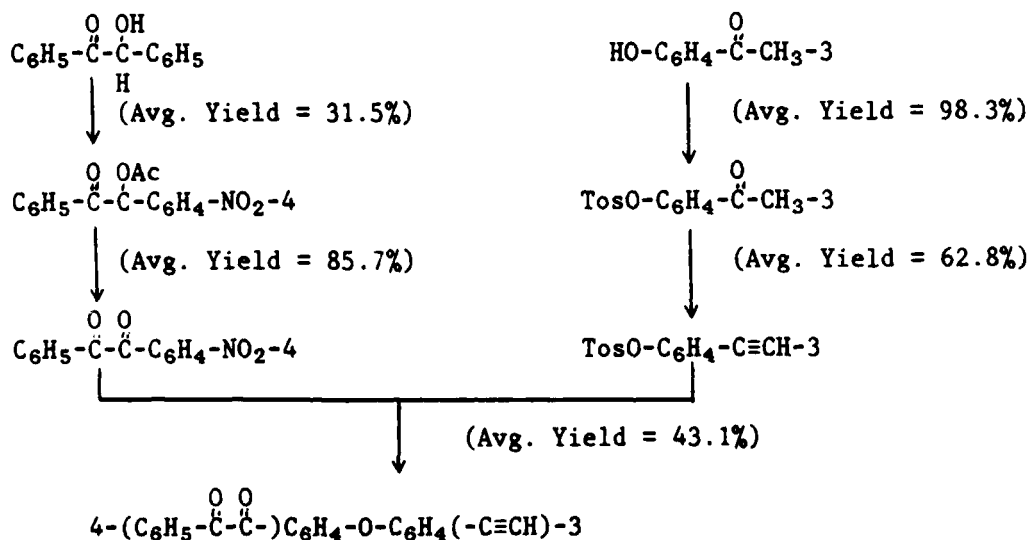
$$k = Ae^{-\frac{E}{RT}} = \frac{1}{t} \ln \frac{1}{1-X}$$

where k = the reaction rate at a given time (t)
 X = the fraction reacted at that time (t)
 T = temperature expressed as a function of time ($T = f(t)$)

It was shown that an excellent agreement exists between the theoretical and experimental values. (Figure 2 shows a plot of the theoretical and experimental values.) The correlation of these two curves by linear regression analysis was very high ($r^2 > 0.99$) throughout the experimental range. These observations show that the reaction is first-order from beginning to end (i.e., from $X = 0$ to $X = 0.99$). Based on these data, it can be stated that the polymerization is linear in nature and that no crosslinking occurs within the accuracy and range of this experiment.

3. Task III - End-Capper Synthesis

The synthesis of 1,200 g of the end-capper, 4-(3-ethynylphenoxy)benzil, involved the batch wise preparation of the indicated amounts of the following four intermediates: (a) 3,226 g of 4-nitrobenzoin, (b) 2,740 g of 4-nitrobenzil, (c) 3,147 g of 3-acetylphenyl(p-toluenesulfonate), and (d) 2,939 g of 3-ethynylphenyl(p-toluenesulfonate). The synthetic route is summarized by the following series of equations:



Details of the synthetic procedure are given in Section III-2-a of this report.

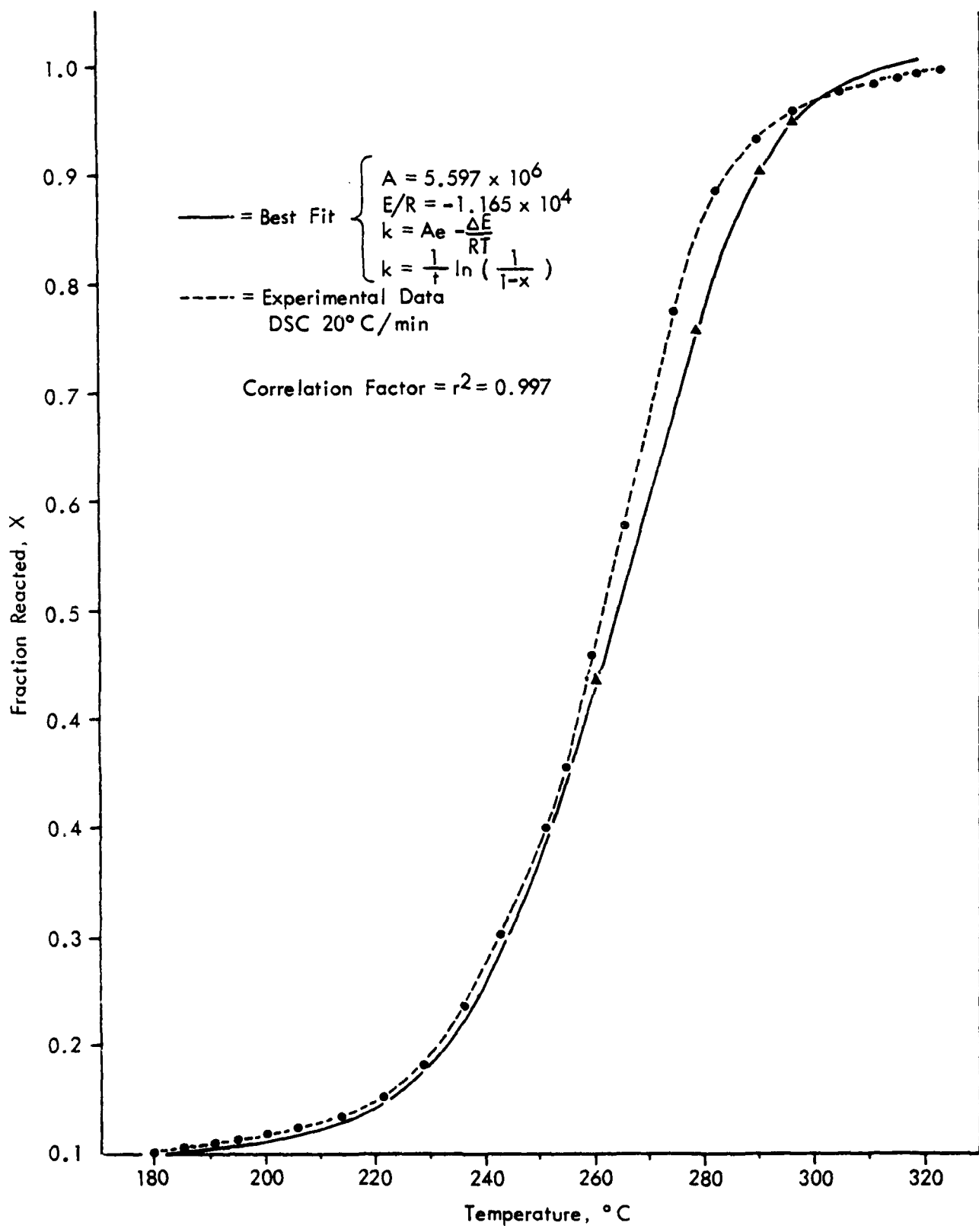


Figure 2 - Fraction BA-DAB-BA Reacted.

SECTION III

EXPERIMENTAL PROCEDURES AND WORK PERFORMED

Described in this section is the work performed on Task I - Resin System Identification, Task II - Resin Synthesis and Characterization, and Task III - End-Capper Synthesis. Major efforts were expended on the synthesis of BA-DAB-BA, [3,3'-bis(4-(3-ethynylphenoxy)phenyl)-2,2'-diphenyl-6,6'-biquinoxaline], in the characterization of this compound, and in the large-scale synthesis of the end-capper, 4-(3-ethynylphenoxy)benzil.

1. Task I - Resin System Identification

Evaluation of the characterization data supplied by AFWAL included mechanical, chemical, and physical data for several resin systems:

- a. Aromatic polysulfone (Union Carbide P-1700).
- b. An acetylene terminated sulfone (ATS) made by reacting a halogenated 4,4'-(dihalo)diphenylsulfone with the potassium salt of *m*-hydroxyphenylacetylene.
- c. A pyrogaly modified acetylene terminated sulfone (PATS).
- d. An acetylene terminated benzylquinoxaline (SBQ).
- e. A low molecular weight acetylene terminated oligomer based on a single bisquinoxaline from diaminobenzidine with two acetylene terminated benzylether structures (BA-DAB-BA).
- f. A general class of high molecular weight acetylene terminated polyquinoxalene (ATQ).
- g. Two acetylene terminated polyimids (Thermid 600 and HR-602).

The technical data supplied to the Midwest Research Institute project staff by AFWAL at the project briefing, held at WPAFB in August 1979, were carefully reviewed. In addition, the verbal technical comments by several of the AFWAL staff were also given serious consideration. A computerized search of Chemical Abstracts and NTIS data banks for publications in the area of interest was completed and evaluated. The oligomer designated "BA-DAB-BA" was tentatively selected as the most effective and cost-efficient oligomer for preparation of Task II and for full characterization. Approval of this oligomer was subsequently received from the AFWAL project monitor. This work was performed during the first month of project activity.

2. Task II - Resin Synthesis and Characterization

Discussed in this section are the procedures and results obtained in the preparation of 500 g of BA-DAB-BA, its characterization, and the equipment and procedures used in its characterization.

a. Synthesis of BA-DAB-BA: Preparation of this oligomer has been described by Arnold and Hedberg in AFML TR-78-142 (Reference 2). The procedure used in this synthesis of BA-DAB-BA was a modification of that procedure provided by AFWAL (Reference 3).

(1) 4-Nitrobenzoic acetate: A suspension of 250 g (1.18 moles) of benzoic acid in 930 ml of acetic anhydride was cooled to 15°C and 40 ml of sulfuric acid was added dropwise. The addition caused an exotherm to 35°C and the reaction mixture became clear. After cooling the reaction mixture to -15°C, 60 ml of 90% nitric acid was added dropwise over a 1.2- to 1.5-hr period while the temperature was maintained between -10 and -20°C with a dry ice/isopropanol bath. After the addition was complete, the reaction mixture was allowed to warm to ambient temperature and stand overnight. The resultant solid was collected by filtration and washed with water, and when air dried, weighed 129.5 g and melted at 123 to 127°C. When the solid was slurried in 1,200 ml of methanol, filtered, and air dried, 119.6 g (34% yield) of 4-nitrobenzoic acetate, m.p. 127 to 129°C was obtained.

The overall yield from 11 such reactions gave 1,287 g of product, 33% average yield.

(2) 4-Nitrobenzoic acid: A mixture of 97.9 g (0.327 mole) of 4-nitrobenzoic acetate in 300 ml of concentrated nitric acid (70%) was heated to 85°C. At that temperature, NO_x fumes began to evolve. The solution was heated until NO_x evolution ceased (about 1.5 to 2 hr), then it was cooled and poured onto 1 liter of ice. The solid was recrystallized once from 900 ml of acetic acid and slurried in 1 liter of refluxing methanol. The cooled mixture, when filtered and air dried, gave 61.5 g (74% yield) of 4-nitrobenzoic acid, m.p. 139 to 140°C (reported m.p. 142°C, Reference 4). A total of 907.4 g of this compound was obtained from nine replicate runs with an overall yield of 82.3%.

(3) 3-Ethynylphenyl(p-toluenesulfonate): This compound was prepared by a three-step procedure. 3-Hydroxyacetophenone was tosylated, subjected to a Vilsmeier reaction, and hydrolyzed to the acetylene compound (Reference 5).

(a) 3-Acetylphenyl(p-toluenesulfonate): To a solution of 200 g (1.47 moles) of 3-hydroxyacetophenone and 60.2 g (1.5 moles) of sodium hydroxide in 2,500 ml of water and 1,500 ml of tetrahydrofuran was added all at one time 282 g (1.48 moles) of p-toluenesulfonyl chloride. The mixture was stirred at 25°C for 3 hr, then heated to reflux to distill off 1,400 ml of tetrahydrofuran. The residue was cooled in ice water with rapid stirring until the organic phase solidified. The solid was collected by filtration, washed with water and air dried. The material was dried further by heating at 100°C at 15 mm in a vacuum oven for 2 hr. The weight of

product (pulverized) was 405.1 g (95.1%), m.p. 58 to 61°C (Reference 4, m.p. 52 to 53°C). A total of 2,008 g (94.3% ambient yield) has been prepared.

(b) α -Chlorocinnamaldehyde-3yl-(p-toluenesulfonate): In a 2-liter flask, which was flame-dried under nitrogen, was placed 1 liter of dimethylformamide (Fisher, Spectroanalyzed). To this was added 310 g (2.03 moles of phosphorusoxychloride dropwise while the temperature was maintained between 20 to 25°C with an ice bath. After about 5 to 10 min, a reddish coloration developed. After the addition was complete, the mixture was stirred at 25°C for 1 hr. At this point, the reaction mixture was a deep red color. Dry 3-acetylphenyl(p-toluenesulfonate) was added over a 15-min period, and the mixture was stirred as a slow exotherm raised the temperature to 60°C in about 1 hr. This mixture was heated to 60°C for 3 hr, then cooled. The reaction mixture was added slowly to a solution of 450 g of sodium bicarbonate in 1 liter of water and 1 kg of ice with stirring. After 1 hr, the mixture was filtered, washed three times with water and air dried overnight. The water content was determined on a 20-g sample which had been pumped on at 40°C at 0.1 mm on a rotary evaporator. The remaining material was bottled tightly and used in the next step as soon as possible. The dry weight of product was 301.3 g (87%).

(c) 3-Ethynylphenyl(p-toluenesulfonate): A solution of 62 g (1.55 moles) of sodium hydroxide in 2.5 liters of water and 950 ml of dioxane was heated to 80°C and 261 g (0.775 mole) of α -chlorocinnamaldehyde-3yl-(p-toluenesulfonate) was added as a solution in 500 ml of dioxane. The mixture was stirred at 80°C for 15 min, then cooled in an ice bath to 25°C. The mixture was extracted with three 300 ml portions of methylene chloride. The combined methylene chloride extracts were washed with two 100-ml portions of 1 N sulfuric acid and three 200-ml portions of water. Evaporation of solvent on a rotary evaporator gave a dark oil. The oil was dissolved in 100 ml of methylene chloride and treated with 150 ml of silica gel. After evaporation of the solvent under vacuum, the material was added to the top of a column of 250 g of silica gel and chromatographed with 2:1 hexane-methylene chloride mixture. Evaporation of the eluate on a rotary evaporator gave 101.2 g (48.0%) of 3-ethynylphenyl(p-toluenesulfonate) m.p. 77 to 79°C (Reference 4, m.p. 69 to 70°C).

(4) 4-(3-Ethynylphenoxy)benzil: This compound was prepared by the reaction of the sodium salt of 3-ethynylphenol with 4-nitrobenzil. The synthesis was conducted as follows. To a solution of 18 g (0.45 mole) of sodium hydroxide in 300 ml of methanol under nitrogen was added 60 g (0.22 mole) of 3-ethynylphenyl(p-toluenesulfonate) and the mixture was heated at reflux for 1 hr. Methanol was distilled off until the pot temperature reached 75°C, then 200 ml of dry toluene was added and the distillation was continued until a pot temperature of 90°C was reached. The residue was dried by heating at 40°C at 0.5 mm for 2 hr. The residue was dissolved in 250 ml of dimethyl sulfoxide and added to a stirred solution of 60 g (0.24 mole) of 4-nitrobenzil in 220 ml of dimethyl sulfoxide under nitrogen at 90°C. After the addition was complete (0.5 hr), the solution was allowed to cool to ambient temperature and stirred overnight. The reaction mixture was added to 3 liters of ice water containing 250 g of sodium hydroxide and

extracted five times with 200 ml of methylene chloride. The combined methylene chloride layers were washed with 200 ml of 1 N hydrochloric acid and three times with 300 ml of water. After the solvent was evaporated, the residue was dissolved in 100 ml of 2:1 hexane-methylene chloride and chromatographed on a 12 in. column of silica gel wet packed in hexane. The yellow band was collected by elution with 2:1 hexane-methylene chloride. Evaporation of solvent gave 31.7 g (44% yield) of product, m.p. 83 to 84°C after washing with hexane, (m.p. 79 to 81°C, Reference 4).

(5) Preparation of BA-DAB-BA: A 1-l flask (new with joints sealed with teflon sleeves in place of stop-cock grease) containing 200 ml of tetrahydrofuran was stirred (magnetic stirrer) and purged by bubbling nitrogen through the liquid for 15 min. After 32.6 g (0.10 mole) of 4-(3-ethynylphenoxy)benzil, 10.7 g (0.05 mole) of 3,3'-diaminobenzidine (purified by recrystallization from water and vacuum dried, m.p. 173 to 174°C) and 4 ml of glacial acetic acid were added, the mixture was refluxed for 30 min. A 300-ml solution of 10% sodium hydroxide was added and the mixture was allowed to cool with stirring. The mixture was extracted with methylene chloride (3 x 200 ml) and the combined extracts was washed with distilled water (2 x 400 ml). The solution was passed through a silica gel column, eluting with methylene chloride and finally with THF. The THF solution caused a dark band at the top of the column to move completely down off of the column. The solvents were stripped off and vacuum drying at 60° for 8 hr gave 38.7 g (97% yield) of yellow-orange BA-DAB-BA.

Thin layer chromatography on silica gel plates of BA-DAB-BA is shown in Figure 3. Development with methylene chloride gave only two spots, 4-(3-ethynylphenoxy)benzil (BA) and BA-DAB-BA, with the BA having a higher Rf. Three spots were visible with THF as developer. BA and BA-DAB-BA were not separated and the trailing spots were not identified. Examination of the plate under UV light (short wave, 254 nm) revealed bluish spots, but under UV (long wave, 365 nm) BA-DAB-BA showed a brilliant blue fluorescence and the first trailing spot showed a brilliant yellow fluorescence. With ethyl acetate as developer, five spots were visible. However, the separation of BA-DAB-BA and the trailing spot was greater. TLC in methylene chloride was useful for determining the presence of BA in BA-DAB-BA, and in ethyl acetate it was possible to determine the presence or absence of the trailing spots. It was noted that BA-DAB-BA containing only a small amount of THF (and presumably ethyl acetate) had a much higher Rf when TLC'd in methylene chloride than dry material, that is, solvent free BA-DAB-BA barely moved on the silica gel plates in methylene chloride, but if more than a trace of solvent were present, it moved several inches up the plate.

High-performance liquid chromatography showed BA as a single peak (Figure 4) and that BA-DAB-BA from this first run contained two impurities, BA and an unidentified one (Figure 5).

The preparation of BA-DAB-BA is summarized in Table 1. The first run was a duplicate of the procedure received from AFML and subsequent runs were designed so as to obtain at least 50 g of pure BA-DAB-BA per run.

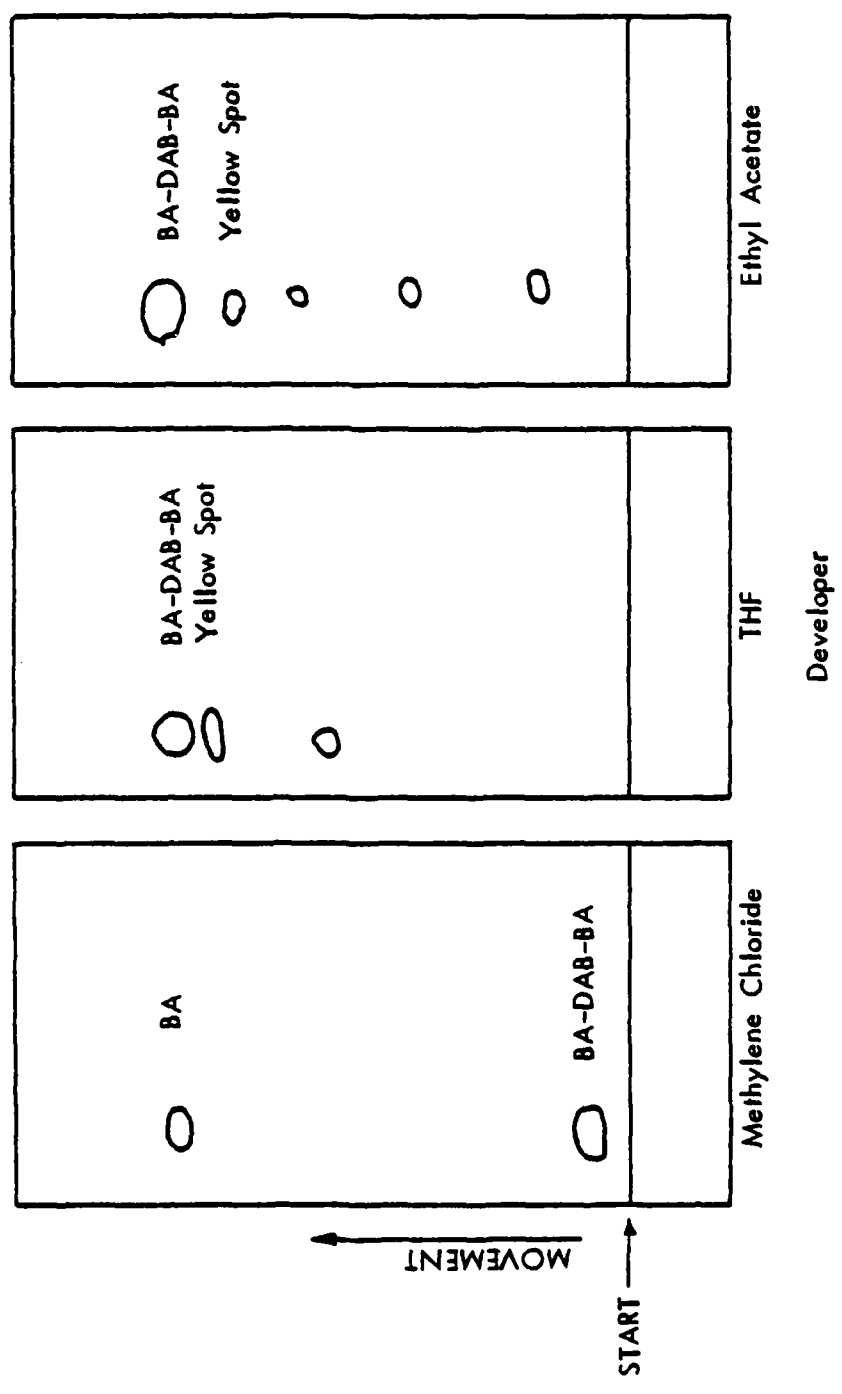


Figure 3 - TLC of BA-DAB-BA (Run No. 1)

Column Conditions
90% CH₃CN/1% HOAc
5 Minute/Inch
1 ml/min
UV at 254 μ m

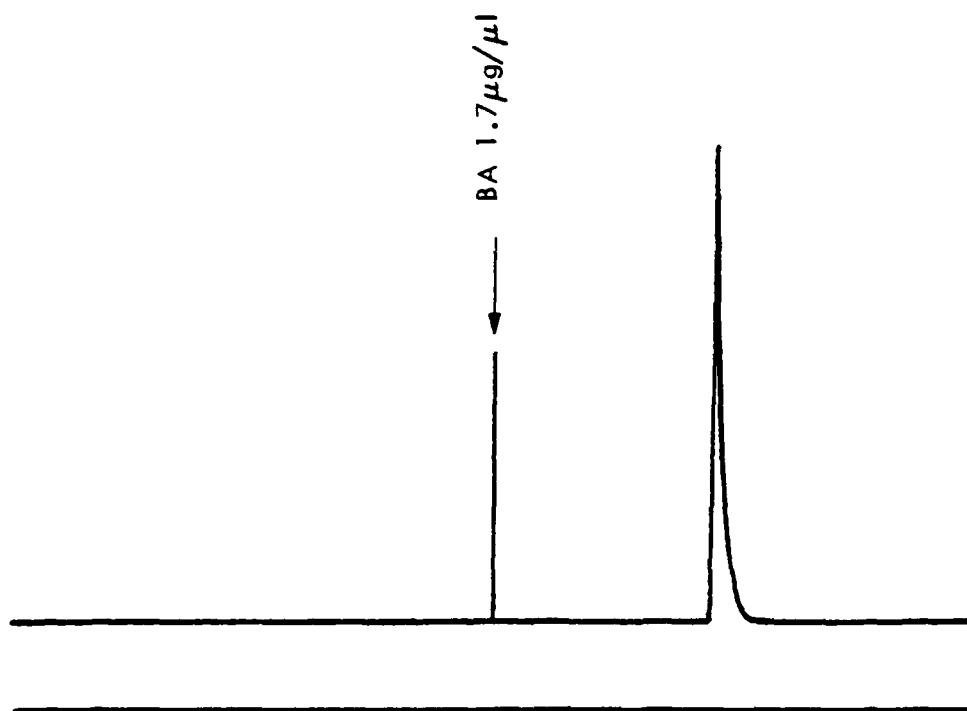


Figure 4 - HPLC of Purified BA

μ Bondapak C18
90% CH₃CN/1%HOAc
5 Minutes/Inch
1 ml/min
Uv at 254 μ m

5 μ l x 2.5 μ g/ μ l in TAF BA-DAB-BA

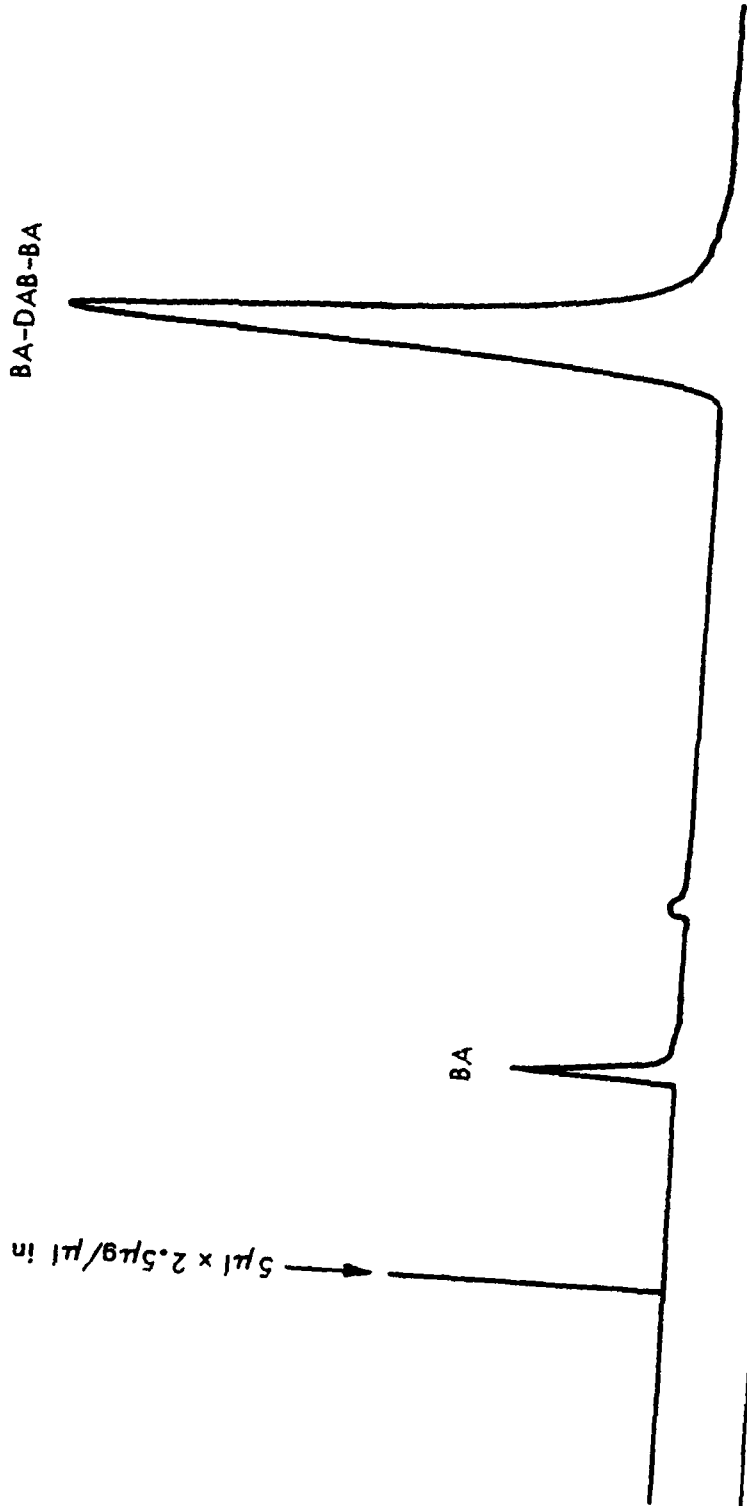


Figure 5 - HPLC of BA-DAB-BA Reaction Product, Run No. 1

TABLE 1

PREPARATION OF BA-DAB-BA

Run No.	BA		DAB		BA-DAB-BA ^{1/}	
	Weight (g)	Moles	Weight (g)	Moles	Weight (g)	Yield (%)
1	32.6	(0.10)	10.7	(0.05)	29.6	75
2	54.8	(0.168)	17.1	(0.08)	54.4	86
3	52.2	(0.160)	17.1	(0.08)	56.5	89
4	52.2	(0.160)	17.1	(0.08)	41.5	65
5	52.2	(0.160)	17.1	(0.08)	43.4	68
6	52.2	(0.160)	17.1	(0.08)	45.2	71
7	52.2	(0.160)	17.1	(0.08)	54.2	85
8	52.2	(0.160)	17.1	(0.08)	54.5	86
9	52.2	(0.160)	17.1	(0.08)	39.9	63
10	52.2	(0.160)	17.1	(0.08)	49.2	77

^{1/} Weight and yield after final purification. TLC, single spot, vacuum dried at 60°C for 24 hours.

(6) Purification of BA-DAB-BA: BA-DAB-BA was purified by column chromatography on silica gel eluting with methylene chloride to remove BA, then a 40:1 methylene chloride-ethyl acetate solution to remove the BA-DAB-BA. The crude reaction product could be placed on top of the column either as a methylene chloride solution or as a dry mixture with silica gel. Runs 1 through 7 (see Table 1) were rechromatographed as follows. (These batches had been chromatographed once during the normal work-up.)

The BA-DAB-BA from Run No. 1 (38.7 g and essentially free of THF) was dissolved in 100 ml of methylene chloride and placed on top of a 12-in. column of silica gel wet packed in methylene chloride. Elution with methylene chloride separated the BA completely from the BA-DAB-BA. Evaporation of this fraction gave 1.1 g of BA. Further elution with a 40:1 solution of methylene chloride-ethyl acetate moved the BA-DAB-BA, which was seen as a yellow band on the column under visible light and as a bluish fluorescent band under UV (long wave, 365 nm). BA-DAB-BA was collected in fractions until the trailing yellow spot (long wave, 365 nm) appeared. The trailing spot was visible only on the column as a yellow fluorescent band under UV light (long wave, 365 nm) when ethyl acetate or THF was present. Evaporation of the solvent gave 30.1 g of BA-DAB-BA (single spot by TLC in both methylene chloride and in ethyl acetate). After 20 hr at 60° in vacuum, the BA-DAB-BA weight was 29.6 g (75% yield). Further elution gave 2.7 g of a fraction containing BA-DAB-BA plus the yellow spot.

If the THF was not removed completely from the reaction product, elution with methylene chloride moved the BA-DAB-BA with the BA and a fraction containing both was collected. These fractions were combined with similar fractions and rechromatographed.

Runs Nos. 8 through 10 were worked up differently. After the reaction mixture was washed with water during the normal work-up, the methylene chloride-THF solution was stripped of solvent and dried at 60° in vacuum. The residue was dissolved in a minimum amount of methylene chloride and chromatographed as above.

The results of the column chromatographies of all 10 runs are shown in Table 2. In general, four fractions were collected. The first contained recovered BA, the second fraction was a mixture of BA-DAB-BA and BA and only appeared if the THF was not completely removed from the reaction residue, the third fraction was BA-DAB-BA, and the fourth was a mixture of BA-DAB-BA and the trailing yellow spot. Most of the time the BA-DAB-BA was off the column before the yellow spot appeared.

The lower yields of Run Nos. 4, 5, 6, and 9 should not be compared with the others, since these runs gave a larger than normal BA-DAB-BA plus BA fractions. In order to save time, these fractions were combined and rechromatographed as one fraction rather than as individual fractions.

A HPLC trace of purified BA-DAB-BA is shown in Figure 6.

TABLE 2

PURIFICATION OF BA-DAB-BA BY COLUMN CHROMATOGRAPHY

Run No.	Residue Wt. (g)	BA Wt. (g)	BA-DAB-BA + BA Wt. (g)	BA-DAB-BA Wt. (g)	BA-DAB-BA + Yellow Spot		BA-DAB-BA ^{a/}	
					Wt. (g)	%	Final Wt. (g)	Yield %
1	38.7	1.1	0	30.1	2.7	29.6	75	
2	65.0	7.1	0	55.2	2.7	54.4	86	
3	62.7	4.7	1.2	57.3	0	56.5	89	
4	62.3	4.8	13.7	42.0	0	41.5	65	
5	59.3	4.2	9.0	44.2	0	43.4	68	
6	60.0	5.0	6.1	46.0	2.8	45.2	71	
7	-	5.7	4.0	55.2	0	54.2	85	
8	-	3.5	0.8	55.2	0	54.5	86	
9	64.7	3.9	15.1	40.8	0	39.9	63	
10	64.1	4.1	0	50.3	0	49.2	77	
11 ^{b/}	36.7	1.1	0	33.4	0	32.8	-	

^{a/} The BA-DAB-BA was vacuum dried for 24 hours at 60°C.

^{b/} The combined BA-DAB-BA + BA fractions was rechromatographed.

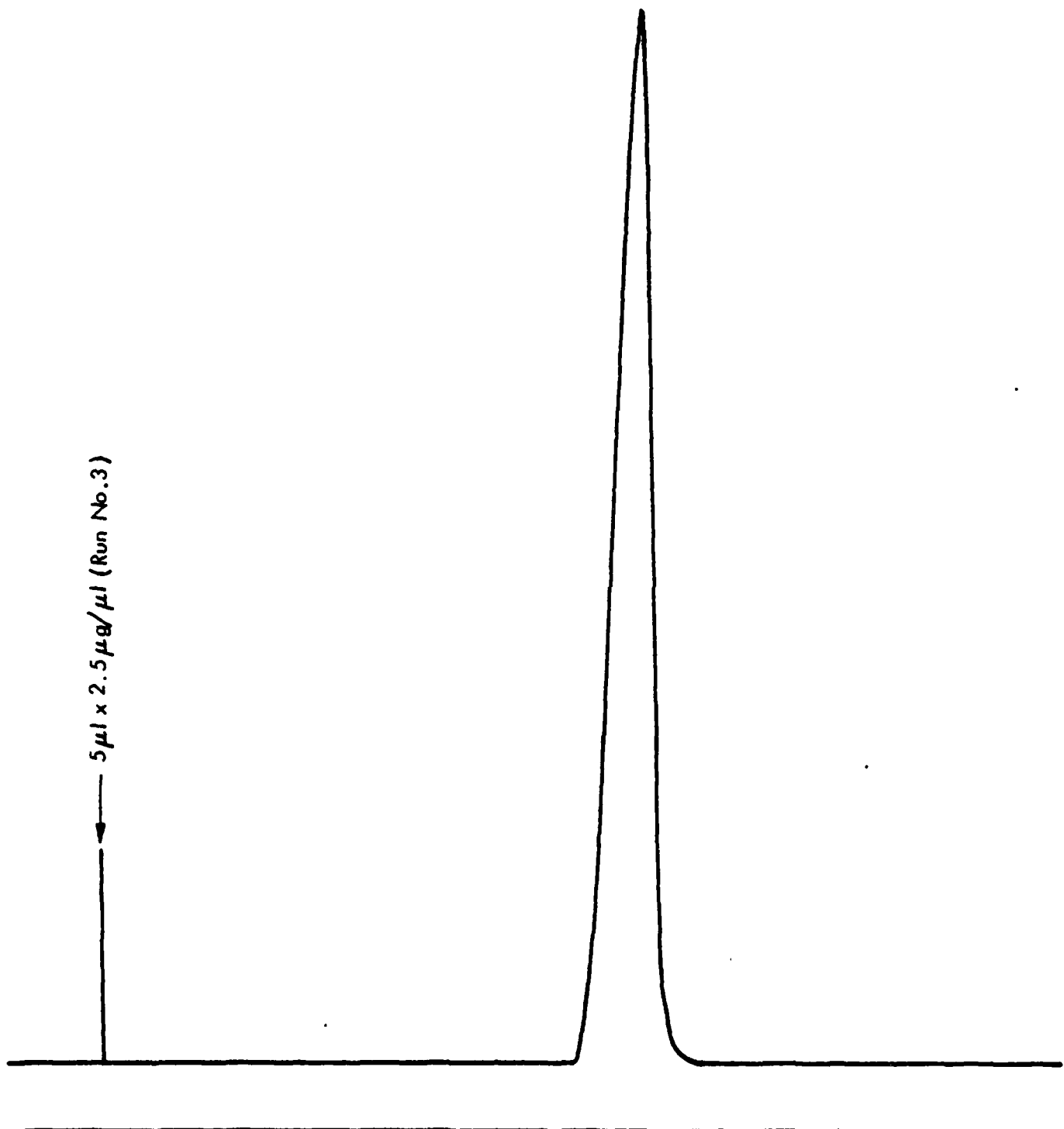


Figure 6 - HPLC of BA-DAB-BA, Purified

Preparation and purification of BA-DAB-BA oligomer was completed. After drying at 60°C under approximately 1 mm Hg pressure, 505 g of product was obtained. Thermogravimetric analysis showed 0.6% volatiles present by weight loss at 140°C.

b. Characterization of BA-DAB-BA: Characterization of BA-DAB-BA was the main part of this program. Work done toward establishing the data acquisition and reduction system and its use, or attempted use, in the determination of kinetics of BA-DAB-BA polymerization, conversion of heat of reaction data to polymerization rate, and determination of reaction window for BA-DAB-BA are reported in this section. In addition, work related to the determination of the viscosity of BA-DAB-BA, determination of BA-DAB-BA melting points, initial trial B-staging of BA-DAB-BA, precure of BA-DAB-BA, a modified DSC kinetic method, and modification of viscosity determination method are presented in this section.

(1) Data acquisition and reduction system: Described below are the different basic tests that require the use of computer data reduction and print-out, and the work performed toward assembling the microprocessor and associated equipment.

(a) Dynamic mechanical analysis: The DuPont 981 DMA unit consists of a resonant double air instrument that applies cycling tensile and compressive loads to the sample under investigation. The electromechanical drive unit can be set to a given amplitude of movement (0.05 to 1.0 mm) depending on the sample configuration and modulus of rigidity. Liquid nitrogen (LN₂) is used as a cooling heating media. The LN₂ is supplied from a large regulated dewar at a controlled flow rate. Thus, an inert gas is used for a heat transfer media. The unit can operate from -150 to 500°C.

The amplitude of movement of the sample support arms is held constant by a feed-back control loop between the linear variable differential transformer (LVDT) and the electromechanical transducer. The amount of energy required to drive the electromechanical transducer is proportional to the energy absorbed by the sample. Thus, a relative damping constant ($\tan \delta$) is made available as a BCD output from the unit. The sample temperature, °C, is supplied by an internally referenced chromel-alumel thermocouple, and the resonant frequency of the sample (and drive unit) are available as BCD output. Both the damping and resonant frequency are displayed on the units LED digital indicators.

The dynamic modulus (E^*) has two components, the real modulus (E') and the loss (E'') component. The phase angle (δ) between stress and strain can be calculated using programs supplied by DuPont, which yield an absolute $\tan \delta$. As $\tan \delta = E''/E'$, the dynamic modulus can be derived $E^* = E' + E''$ from the data obtained. The data acquisition and reduction system described in Section III-C-5 and schematically shown in Figure 7 will perform the calculation required to reduce raw data from the DMA unit to a graphical presentation of the real and loss components versus sample temperature.

SCHMATIC OF DATA ACQUISITION SYSTEM

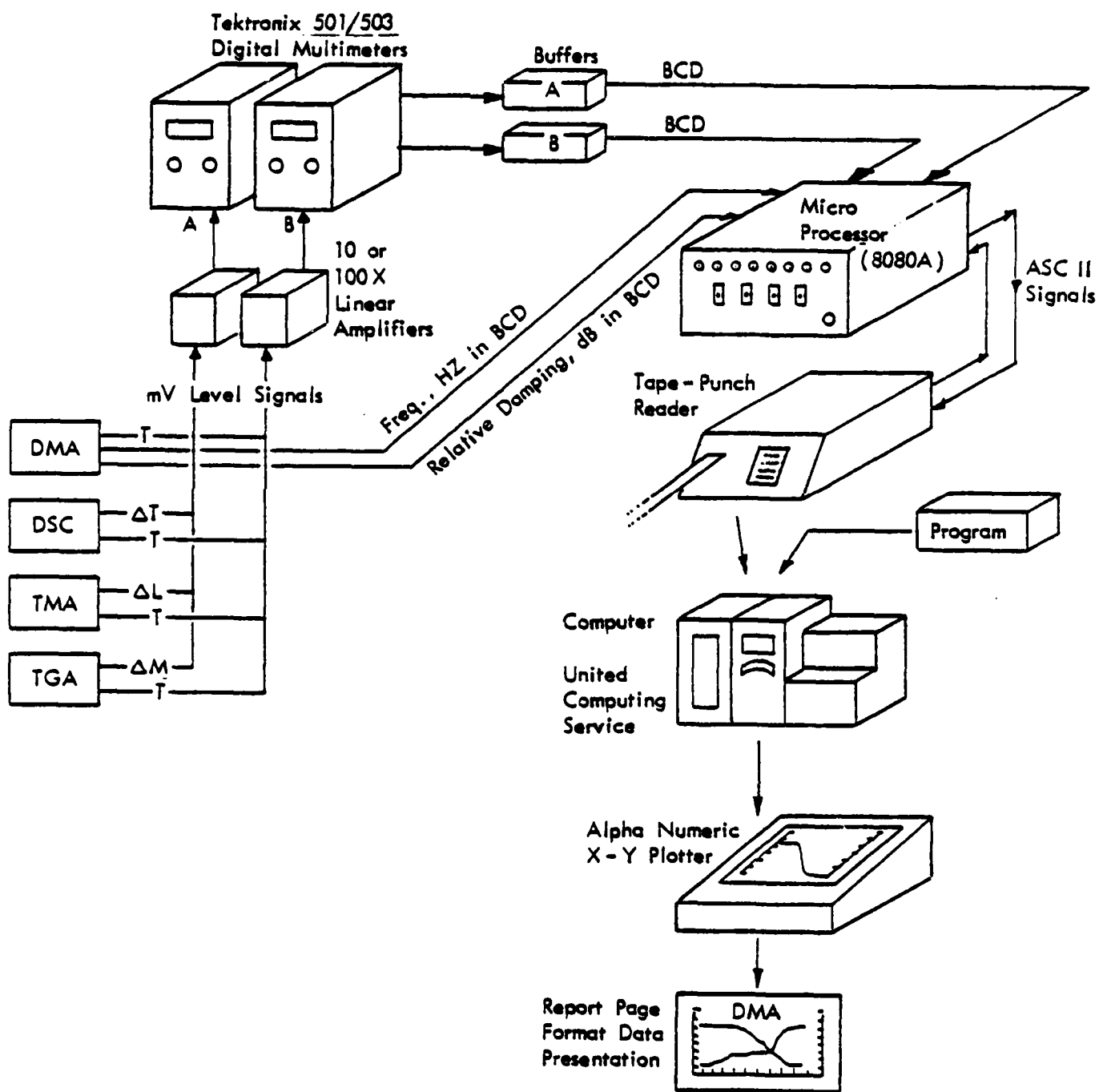


Figure 7

(b) Thermomechanical analysis: A DuPont Model 941 Thermomechanical Analyzer was used for several tests. Basically, the TMA unit consists of a temperature controlled oven, sample-temperature chromel-alumel thermocouple, and a linear variable displacement transducer. All characterization of candidate polymers performed on this device depend upon the relationship between temperature and vertical motion of the load application ram.

For example, when operated in with the thermal expansion fixtures, the sample is heated at a given rate (i.e., $10^{\circ}\text{C}/\text{min}$), and expansion is followed by the movement of the test probe. The LVDT transducer detects the displacement of its core in magnetic coil. The signal from the LVDT is linear with displacement. By plotting the temperature of the sample against displacement, the coefficient of expansion can be determined. The first derivate of the curve (dl/dt) is the coefficient of expansion. A plot of temperature versus dl/dt , (d^2l/dt^2)-the second derivative, will show the temperature at which any phase change occurs.

The parallel plastic rheometer accessory for the TMA unit allows the determination of the effect of temperature of viscosity of polymers. A standard diameter (0.375 in. and 9.53 mm) disc of the polymeric material is made, usually about 0.035 in. (0.89 mm) thick, by pressing or die cutting, whichever method is more applicable to the polymer under study. This "plug" is placed between the parallel plates; the unit is zeroed; and heating is started. An initial thermal expansion will be observed until a phase change or melting occurs. As melting occurs, the polymer begins to flow out between the two parallel plates. The flow-out rate increased with increasing temperature. Displacement of the parallel plates is directly proportional to the flow out, while viscosity at any temperature T is a complex function of the instantaneous plate displacement rate and the distance between the plate. The rates of movement are relatively low. The shear rates of the flowing polymer are in the order of 10^0 to 10^{-3} sec^{-1} ; thus, a nearby static viscosity is determined.

A data acquisition program and data reduction program are supplied by DuPont for the parallel plate rheometer attachment for their Model 491 TMA unit. These programs are designed for their Model 990 thermal analysis system, and require some minor modifications for use with the data acquisition system. This device is of particular use in following the viscosity of a curing resin or oligomer at a series of isothermal conditions. An indication of the rate-of-viscosity increase with time can be obtained. Such an insight into time-temperature-viscosity relationships is of great value in working up optimum cure cycles for composites.

(c) Thermogravimetric analysis: The temperature (milli-volt) and the weight change (volt) signals from a Model TGS-1 Perkin-Elmer thermogravimetric analyzer are fed to the data acquisition-reduction system (see Figure 1). The output data will be plotted as weight loss versus temperature, and, if desired, a derivative plot (dm/dT) versus temperature can be presented.

The thermal stability of oligomers and cured polymers can be readily determined from these data. Derivative presentation of weight loss versus temperature should yield enhance determination of the onset of decomposition as indicated by a rapid change in weight loss or rate of weight loss.

(d) Differential scanning calorimetry: This thermo-analytical technique is very useful in characterizing the phase change temperature (i.e., melting points), heats of fusion and heats of reactions. By proper calibration of the DSC unit (DuPont 900 with 910 self standardizing, constant calometric sensitivity cell), it is possible to determine the kinetics of the polymerization reaction under study. The information obtained allows an intelligent selection of curing temperature for both adhesive and composite applications.

(e) Parallel plate viscometry: The DuPont Model 941 thermomechanical analysis unit was assembled with the parallel plate viscometer attachment. The sensitivity of the linear differential transducer (measurement of displacement of the viscometer plates) was calibrated using a barrel type micrometer to insure that the unit was linear over a movement range greater than 0.040 in. (0.10 cm). In addition, the time base generator which controls the heating rate was calibrated to better than 0.2%.

A trial run was made using a low-density polyethylene ($d = 0.92$) with a load of 30 g on the parallel plates. The sample was run isothermally at 140°C and the flow rate was such that 40 min was required to complete the run. A plot of the plate movement versus time is shown in Figure 8. The plot was smooth, indicating mechanically correct performance of the TMA and its parallel plate viscometer attachment.

(f) Data acquisition from test equipment: The output data from the test units are either in millivolts or in binary coded decimal format (the frequency in Hz and relative damping in db from the DMA unit). The millivolt outputs come from the DSC, DMA, TMA, and TGA units as functions of temperatures, mechanical motion, or change in weight. A schematic of the flow of signals through the data acquisition and processing system is shown in Figure 1. The function of each device in the acquisition-reduction is discussed below.

(i) Linear amplifiers: These units (Omega Eng., Inc., "Omni-Amp II") are multistep (0, 1, 2, 5, 25, 50, and 100x) linear DC amplifiers used to multiply the microvolt signals ($1^\circ\text{C} \cong 40 \mu\text{v}$) of the chromel-alumel thermocouples which determine sample temperature during the various tests. By multiplying by a factor of 100, the sensitivity of the measurement is increased to a point that a signal of $+ 2 \mu\text{v}$ (approximately 0.05°C) is equivalent to the noise level of the amplifiers. This sensitivity readily allows reading temperatures to the nearest 0.1°C if desired.

(ii) Digital multimeter: Two Tektronic Model 501 units with the Model 503 power supply/mounting rack are used to convert the millivolt signals to serial BCD format as well as readout on the LED indicator. The Tektronix Model 501 units are 4-1/2 digit, front LED readout

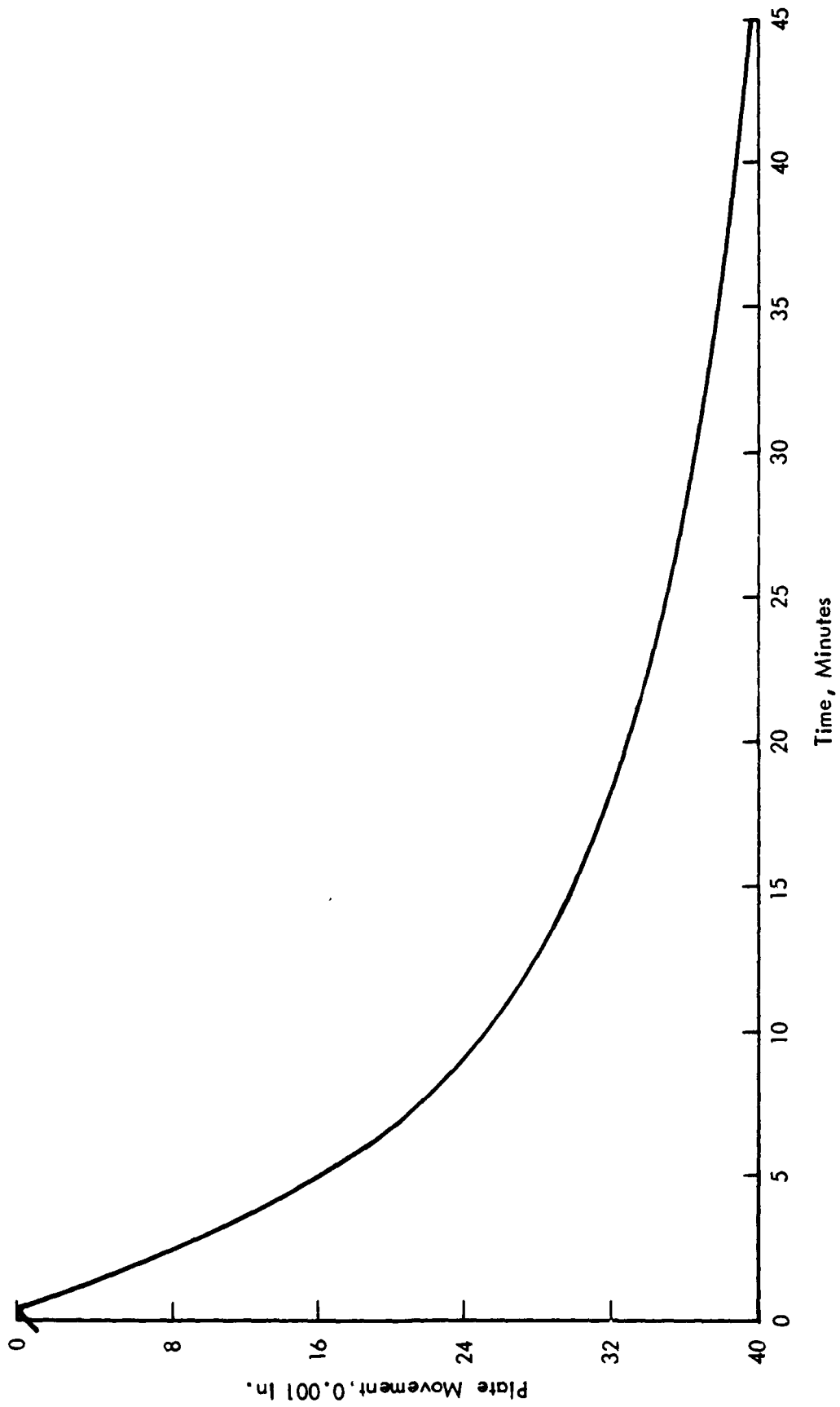


Figure 8 - Plot of Plate Movement Versus Time

with BCD being coded with a clock pulse, polarity and five numbers up to 1.9999. The BCD output of the 501 unit was originally designed to drive low power demanding CMOS inputs. Thus, it was necessary to add a power-amplifying buffer to adequately drive the TTL logic of the microprocessor.

(iii) Direct inputs to microprocessor: There are only two direct inputs to the microprocessor. These come from the DuPont Model 981 Dynamic Mechanical Analyzer, and are serial BCD signals corresponding to the resonant frequency of the unit in Hz and the relative clamping factor in db. These inputs are of sufficient power to drive the microprocessor without buffering.

(iv) Description of the microprocessor: The microprocessor is an 8080A integrated circuit, eight bit microcomputer on the central processing unit board. Also contained in the microprocessor are 7K-8 bit bytes of EPROM (2,708 ICs) and 1K-3 bit bytes RAM (2,102 ICs) for preprogrammed operations. Programs such as conversion of the chromel-alumel thermocouple readings to temperature in °C and identification information for each of up to 15 potential data reduction programs (instructions to the remote computer) are included. The microprocessor has additional in/out ports for TTW (ASC-II teletypewriter) input on a S-100 bus, video readout, and TTW output if desired in the future.

The basic purpose of the microprocessor is the conversion of the BCD data from the DMA unit and from the Tektronic 501 digital multimeters to ASC II format. Once reduced to this computer compatible format, the data were to be stored on punched tape.

(v) Raw data storage: The ASC-II coded data from the microprocessor are punched into paper tape using a Health Model H-10 paper punch/reader in a format compatible with standard tape readers and computer inputs. The punched tape serves as a permanent storage for the data obtained from a given experimental run. The punch reader can also be used to feed program instructions into the microprocessor.

(vi) Data reduction: The Institute has access to several large computers on a time share basis and has the required input software to feed and retrieve data. The services of United Computing Services, Kansas City, Missouri, have been used to provide computer data reduction and plot out of the reduced data. These are a number of rather complex programs to be used:

- Reduction of raw dynamic mechanical analysis data to plots of the modulus of rigidity (E) and damping factor ($\tan \delta$) versus temperature.
- Conversion of thermomechanical analysis data from static parallel plate rheometer to absolute viscosity values versus temperature/time.
- Determination of reaction rates from DSC analysis of oligomers at various heating rates.

unit. Stress relaxation data reduction from the TMA

Many other smaller programs can be readily handled in terms of both data reduction and report-page format printout on an alpha-numeric x-y plotter. Such printouts will require only slight modification of existing programs available from United Computing Services. There are distinct advantages to this total system. Once in operation, it will greatly reduce the man-hours required for data reduction and preparation, by hand, of data plots.

The first attempt to obtain an alpha-numeric plot of simulated DMA data was reasonably successful. Shown in Figure 9 is the result of this initial attempt. The data were extracted from an example of a DuPont analysis of a glass fiber epoxy resin composite. The data are presented as the resonant frequency (hz) of the unit and the damping factor (in relative db) versus temperature. The Y axes are mislabeled, an easily corrected problem. The plot program still had to be modified to get the damping axis moved to the left side of the plot. In addition, the conversion program to reduce these intermediate values to the desired elastic modulus and loss tangent were yet to be placed into the program.

(2) Conditions for determination of polymerization kinetics:
The device used in this determination was a DuPont Model 900 DSC cell. In order to increase the sensitivity of the unit and to provide a time-based X-axis, presentation of the differential temperature (ΔT -Y axis) the output of the Y-axis amplifier was fed to a Leeds and Northrup "Speedomax" single channel recorder. The sensitivity of the recorder can thus be adjusted to provide a full scale presentation of the DSC plot.

The first step required was calibration of the DSC cell using pure indium metal (m.p., 156.6°C), which has a heat of fusion (ΔH_f) of 6.79 mcal/mg. The area under the DSC plot is proportional to the total heat of fusion of the indium sample ($\Delta H = \Delta H_f \times \text{mg}$) by the following relationship:

$$\Delta H = \frac{E \cdot A \cdot \Delta T_s \cdot T_s}{\text{Spl. Wt., mg} \cdot \text{Heat rate, } ^\circ\text{C/min}}$$

where ΔH = total heat of fusion, mcal
E = cell calibration coefficient, mcal/(°C)(min)
 ΔT_s = equivalent Y axis sensitivity, °C/min
 T_s = equivalent X axis sensitivity, °C/in
A = area under curve, in²

Theoretically, the area under the curve is independent of heat rate. This behavior was confirmed by determining the area and corresponding "E" at 5, 10, 15, 20, 25, and 30°C/min heat rates. These determinations were performed under the following conditions:

AFML-MRA-DMA-EXAMPLE-I
TEMP/TIME-10/MIN

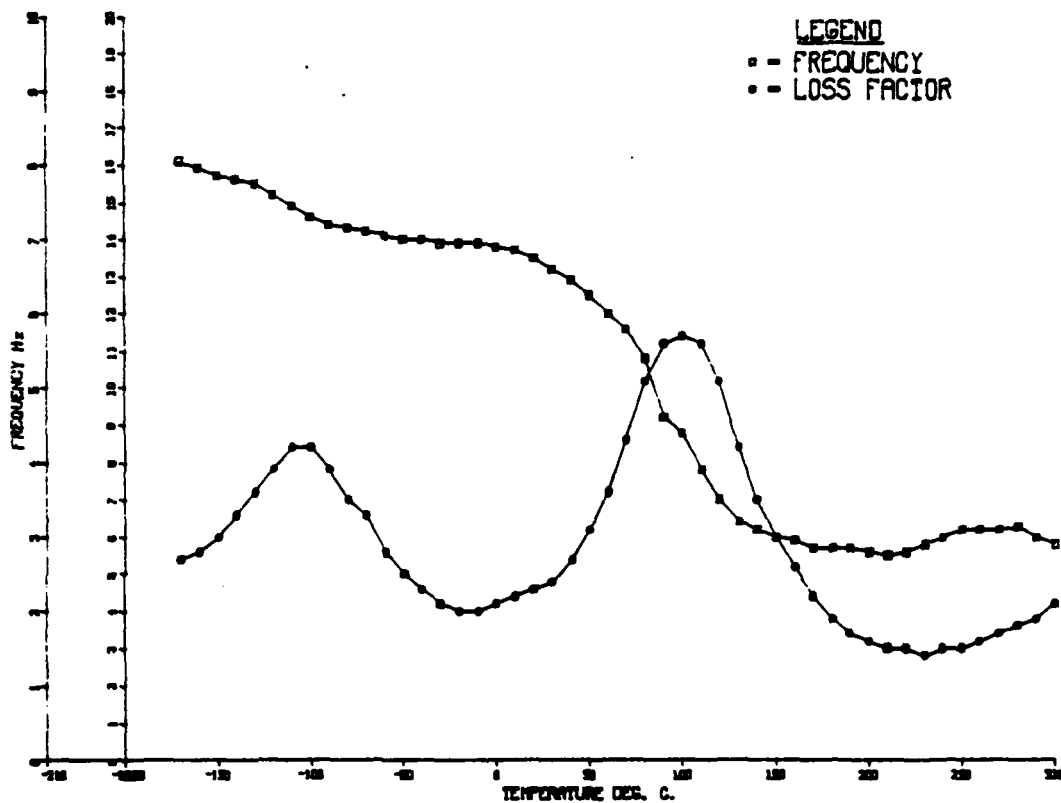


Figure 9 - Trial Alphanumeric Plot of DMA Data

Heat rate - as indicated
 X-Y plotter sensitivity
 X-axis 50°C/in. = 2,000 uV/in.
 Y-axis 0.5°C/in. = 20 uV/in.
 Strip chart sensitivity
 X-axis - 6.0 in/min
 Y-axis - 100 mv/full scale = 10 mv/in.

The strip chart sensitivity is converted to the equivalent sensitivities as follows:

X-axis (Ts) in °C/in. where X = °C/min

$$T_s = \frac{\text{heat rate } ^\circ\text{C/min}}{\text{chart speed in/min}} = \frac{X \text{ } ^\circ\text{C/min}}{6 \text{ in/min}} = \frac{X \text{ } ^\circ\text{C}}{6 \text{ in.}}$$

Y-axis (ΔT_s) in °C/in.

$$\text{Sensitivity} = \frac{10 \text{ Mv/in.}}{40 \frac{\mu\text{v}}{^\circ\text{C}}} = \frac{10,000 \mu\text{V/in.}}{40 \mu\text{v}/^\circ\text{C}} = 250^\circ\text{C/in.}$$

Amplification factor = 1,000

$$\Delta T_s = \frac{250^\circ\text{C/in.}}{1,000 \text{ in/in.}} = \frac{0.25^\circ\text{C}}{\text{in.}}$$

The amplifier in the DuPont 900 units Y-axis circuitry has been set for a gain of 1,000. Thus, the signal fed to the strip chart recorder is 1,000 times greater than the actual voltage difference between the sample and reference cell.

Area under the curve traced on the strip chart recorder was determined by cut and weigh methods. A 2-in. square (4 in²) was drawn of the strip chart recording adjacent to the plot. The plot and standard area were then copied (Xerox) at a 1:1 magnification. A base line was drawn across the base of the two legs of the plot. The area was cut and weighed on an analytical balance. The control area was also cut out and weighed. The area under the curve was calculated as follows:

$$\text{Area, } \mu\text{e}^2 = \frac{\text{Curve area wt, g} \times 4 \text{ in}^2}{\text{Control area wt, g}}$$

The procedure provided a reasonably accurate method for determining the area under the curve while retaining the original data. Shown below (Table 3) are the areas and "E" factors found DSC by analysis of 10.0 ± 0.1 mg samples of pure indium metal.

TABLE 3

DETERMINATION OF "E" FACTOR

<u>Heat Rate</u> (°C/min)	<u>Area Under Curve</u> (in. ²)	<u>"E" Factor</u> (mcal/°C x min)
5	9.61	169.6
10	9.74	167.3
15	9.52	171.2
20	9.60	169.8
25	9.88	164.9
30	9.92	164.3
Mean	9.71	167.9
S.D.	0.163	2.82
C.D.%	1.68	1.68

The reproducibility of the area and "E" factor over the heat rate range of 5 to 30°C/min is indicated by the C.D. (coefficient of deviation) value of 1.68%. This relatively low deviation confirms that all equipment used was operating consistently, and that the "cut and weigh" method of area determination was adequate.

(3) Determination of the kinetics of BA-DAB-BA polymerization:

Using the same equipment setup which was used in the "E" factor determination 5.0 ± 0.1 mg samples of BA-DAB-BA were weighed into DSC pans. Lids were placed on the pans and the samples subjected to DSC analysis at 5, 10, 15, 20, 25, and 30°C/min heat rates. The DSC cell was flooded with nitrogen during these runs. The sensitivity values were:

$$\text{X-axis (Ts)} = \frac{\text{X}^\circ\text{C/min}}{1 \text{ in/in.}}$$

$$\text{Y-axis } (\Delta\text{Ts}) = 0.25^\circ\text{C/in.}$$

Again, the raw data was copied (Xerox) and the area under the curve was determined by the "cut and weigh" integration process. The following results (Table 4) were obtained with the heat of reaction being calculated from the H equation. See Figure 10 for x-y plot of DSC curves.

Although the coefficient of deviation for the heat of reaction (3.98%) was over twice that found with calibration against indium metal (1.68%), it is within reason (less than 5%). As expected, there was no correlation between heat rate and heat of reaction. It should be pointed out that the heat of reaction is a composite for the several reactions that BA-DAB-BA undergoes.

TABLE 4

HEAT OF REACTION OF BA-DAB-BA

<u>Heat Rate</u> <u>(°C/min)</u>	<u>Area Under Plot</u> <u>(in.²)</u>	<u>ΔH</u> <u>mcal/mg</u>	<u>Heat of Reaction</u> <u>Kcal/g mol*</u>
5	9.57	80.34	63.790
10	9.70	81.43	64.660
15	9.76	81.93	65.060
20	10.40	87.31	69.320
25	9.28	77.91	61.860
30	9.46	79.42	63.060
Mean	9.695	81.39	64.625
S.D.	0.386	3.238	2.570
C.D.%	3.980	3.980	3.980

* Molecular weight of BA-DAB-BA is 794.

PART NO 900326

INSTRUMENTS

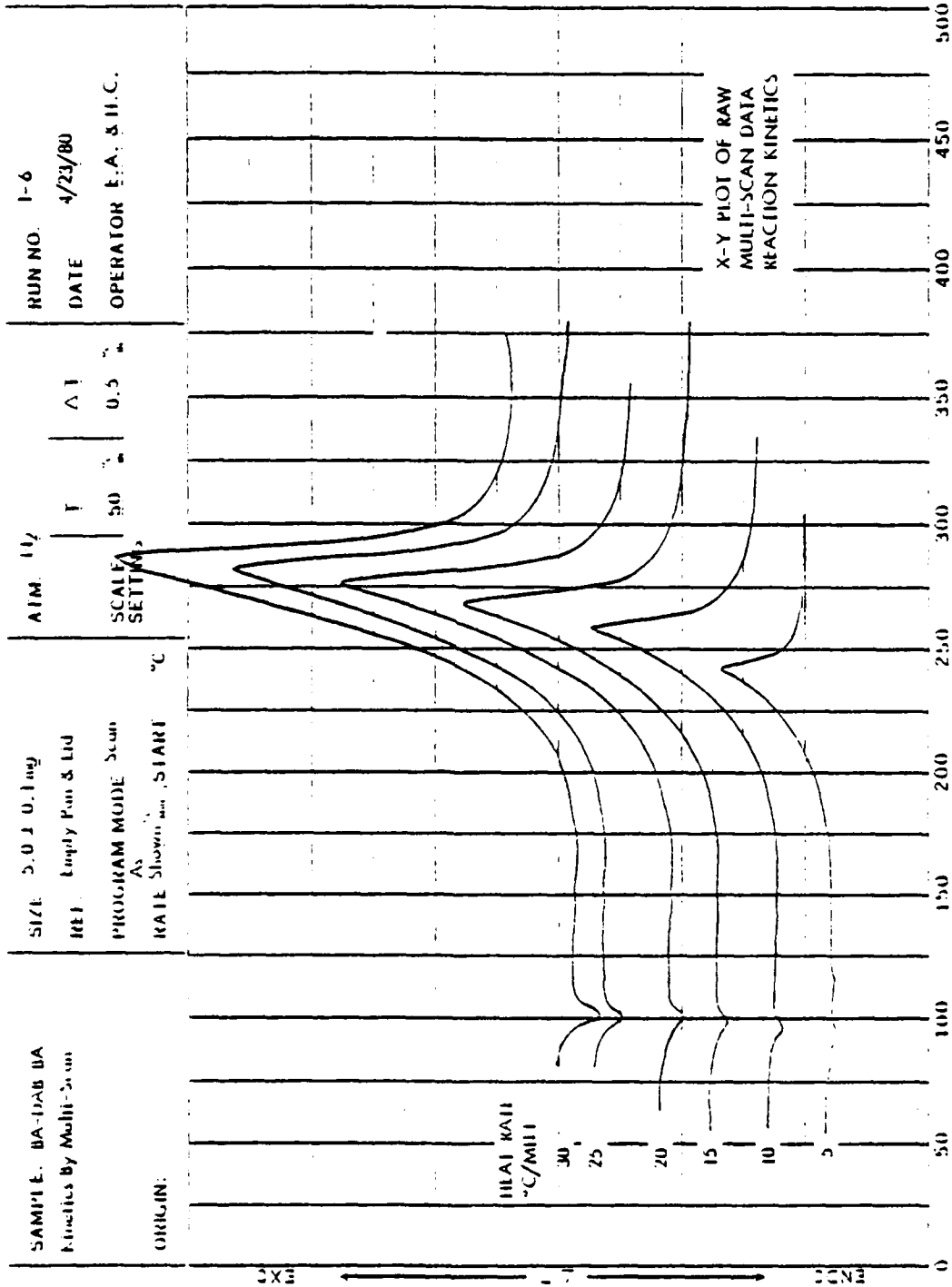


Figure 10 - DSC (CORRECTED FOR CHROMEL-ALUMEL THERMOCOUPLES)

Figure 10 - DSC of BA-DAB-BA at Increasing Temperatures

(4) Conversion of heat of reaction data to reaction rate:
 In order to obtain a realistic figure for reaction rate, it was necessary to consider the following points.

- The area under the DSC plot is proportional to the heat given off (heat of reaction) or absorbed.
- The slope of the rising part of the curve is related to the rate of heat given off at some temperature less than the indicated temperature. This is the "skew" effect of the heat rate and the thermodynamics of the DSC cell.
- Increasing the heat rate increases the skew effect.
- An extrapolated value for height of the DSC curve at an equivalent 0°C/min heat rate can be obtained by measuring the curve height for each heat rate at a set temperature following by graphical extrapolation to 0°C/min heat rate. This procedure eliminates the skew effect of heat rate.
- In the rising part of the DSC curve, the area under a given segment of that curve is proportional to the heat evolved in the corresponding time thus reaction rate.

The vertical height above base line of the DSC plot (from strip chart recorder) was measured at points corresponding to seven increasing temperatures with the following results (Table 5):

TABLE 5
CURVE HEIGHT VERSUS TEMPERATURE

Temp. (°C)	Heat Rate (°C.min)						Extrapolation (0°C/min)
	5	10	15	20	25	30	
197	0.18	0.16	0.14	0.11	0.08	0.08	0.185
207	0.38	0.33	0.30	0.20	0.16	0.14	0.407
217	0.52	0.59	0.56	0.43	0.33	0.32	0.643
227	0.85	0.94	0.87	0.70	0.67	0.66	0.993
236	1.48	1.48	1.50	1.30	1.10	1.20	1.588
246	*	2.10	2.25	2.00	1.80	2.00	2.229
256	*	*	3.10	3.00	2.80	3.10	2.996

* Values meaningless, on cool-down side of peak

The extrapolation was obtained by a computerized least squares fit to a straight line and obtaining the intercept value at 0°C/min.

The area under the DSC curve corresponding to a 6-sec interval of time was determined by multiplying the extrapolated height by 0.1 in. (at a chart speed of 1.0 in/min, 0.1 in. equals 6 sec). Since the area under the curve is proportional to number of calories given off, it is also proportional to the number of moles reacted. From Table 2 the mean square inch value is 9.695, and 5.0 mg of material was reacted; thus, the mol/in.² ratio is:

$$\frac{5 \times 10^{-3} \text{ g}}{794 \text{ g/mol}} \div 9.695 \text{ in.}^2 = 6.495 \times 10^{-7} \text{ mol/min}^2$$

The reaction rate, k', at temperature is then calculated as follows:

$$k' = \frac{(\text{mol/in.}^2) \times (\text{incremental area, in.}^2) \times (\text{mol wt, g})}{(\text{sample weight, g}) \times (6 \text{ sec})}$$

Following the above procedures, the reaction rates for the seven temperatures of Table 3 were calculated and are shown in Table 6.

TABLE 6
REACTION RATES OF BA-DAB-BA

Temp. °C	Incremental Area, in. ²	Reaction Rate k', mol/sec
197	0.0185	3.180 x 10 ⁻⁴
207	0.0407	6.996 x 10 ⁻⁴
217	0.0643	1.105 x 10 ⁻³
227	0.0993	1.707 x 10 ⁻³
236	0.1588	2.730 x 10 ⁻³
246	0.2229	3.937 x 10 ⁻³
256	0.2996	5.150 x 10 ⁻³

These reaction rates are then fitted to logarithmic equations corresponding to the Arrhenius equation:

$$K = Ae^{-E/RT}$$

where K = reaction rate in mols/sec at temperature T in degrees Kelvin
 A = Arrhenius constant (Y-axis intercept at T = ∞), sec
 E = activation energy of reaction, cal/mol
 R = gas constant 1.9869 cal/°K mol
 T = temperature, °K

The following values were obtained.

$$A = 1.740 \times 10^{-7} \text{ sec}^{-1}$$
$$E = 22,960 \text{ cal/g mol}$$

The index of determination (fit factor) from the regression analysis had a value of $r^2 = 0.9875$ which indicates that the fit was quite good (i.e., only 1.25% of the data does not fit the equation).

(5) Reaction window for BA-DAB-BA: A very useful way of expressing the kinetic data developed is the use of a reaction window. This window consists of a combination of reaction temperatures and time that are within the practical processing range, i.e., the temperature should be below 250°C and the time reasonable in terms of processing of adhesively bonded structures and fiber reinforced composites. Shown in Figure 11 is a plot of the degree of reaction (percent of reaction completed) versus reaction temperature and time. The angled lines are iso-reaction levels at 5, 20, 50, 80, and 90% of complete reaction. Any combination of time and temperature falling on the line will give the indicated degree of reaction.

These reaction degrees were calculated as follows. A reaction temperature was selected and the reaction constant k' was calculated from the Arrhenius equation. The degree of reaction was determined, assuming a first order reaction, from:

$$k' = \frac{1}{t} \ln \frac{1}{1-x}$$

where t = time in sec
 x = the fraction reacted

(6) Determination of the viscosity of BA-DAB-BA: The viscosity of BA-DAB-BA above its melting point is important to its performance during use as a structural adhesive and in the preparation of fiber reinforced composites. Changes in viscosity with temperature are very important as well as the increase in viscosity with time at temperature as polymerization occurs. Thus, it is necessary to determine these properties.

The micro-parallel plate rheometer attachment for the DuPont Model 941 TMA can be readily used for such determinations. This instrument consists of temperature controlled oven sample, holder, and a motion measuring transducer. An approximately 0.075 cm (0.030 in.) thick disk of the sample 0.953 cm (0.375 in.) in diameter is placed between two metal plates of the same diameter. As the sample melts and flows out of the cylindrical space between the two plates (held in a metal cage), the two plates move closer together, and the motion detector measures this change. The temperature of the oven is controlled by a DuPont Model 900 Thermal Analyzer either in an isothermal mode or in the scan mode of operation. The raw data are plotted on the x-y recorder of the Thermal Analyzer. The plate motion is on the Y-axis and the temperature or time on the X-axis. These devices are described in the literature (Reference 6).

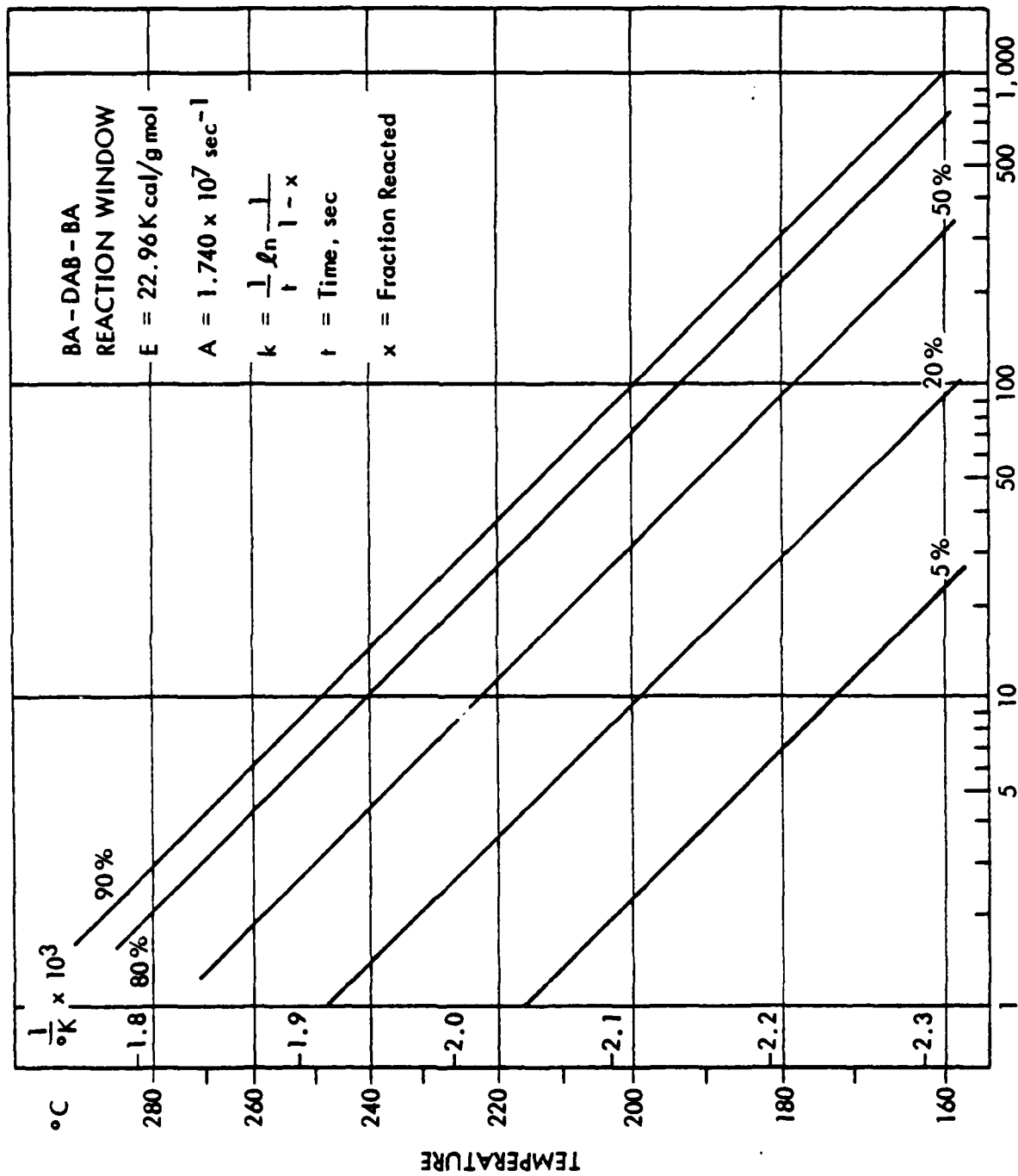


Figure 11 - Reaction Window for BA-DAB-BA

Reduction of the raw data supplied by the x-y plot of plate motion versus temperature/time can be reduced to viscosity following a modification of the method Dienes and Klemm (Reference 7) which is based on work reported by Scott (Reference 8). The technique is based on the Navier-Stokes equation, in vector form, for fluid flow:

$$\rho \frac{\partial V}{\partial t} + \rho V \cdot \Delta V = - \Delta p + \eta \nabla^2 V + 1/3 \eta \Delta \Delta \cdot v$$

where ρ = density of fluid
 V = velocity vector
 p = fluid pressure
 η = viscosity of fluid

Assuming that the fluid is incompressible and that the flow rate is low, then,

$$\nabla \cdot V = 0 \text{ and the square of } V \text{ is very small and can be neglected}$$

The equation then reduces to:

$$\rho \frac{\partial V}{\partial t} = - \Delta P + \eta \nabla^2 V$$

This equation then can be reduced to the simplified scalar partial differential equation:

$$\frac{\partial p}{\partial r} = \eta \frac{\partial^2 v}{\partial z^2}$$

where r = radius of discs
 v = volume of sample
 z = height axis of discs
 η = viscosity of fluid

At this point, Stefan's (Reference 9) derivation is used to further simplify the flow equation to two geometric cases: (1) where the fluid completely fills the space between the plates, and (2) where the fluid does not fill the space, and flow is restricted by the plates.

The DuPont parallel plate rheometer is operated in the case one configuration. Equations of flow then reduce to:

$$F = - \frac{3\pi\eta a^4}{2h^3} \frac{dh}{dt} \quad (\text{Equation 1})$$

where F = force applied to plates in dynes
 a = radius of plates, cm
 h = distance between plates, cm
 η = viscosity in Poise

$\frac{dh}{dt}$ = rate of change in distance between plates, cm sec

Integration of the above equation yields the following:

$$\frac{1}{h^2} = \frac{4F}{3\pi\eta a^4} t + C_1 \quad (\text{Equation 2})$$

where C_1 = constant of integration
 t = time, sec

A plot of $1/h^2$ versus t will yield a straight line (assuming Newtonian flow) whose slope is proportional to η (viscosity) and the intercept is C_1 . This method is referred to as the method of Dienes. Equations 1 and 2 are called the Stefan equations.

In order to rapidly determine the effect of temperature on the viscosity of BA-DAB-BA, it is necessary to operate the parallel plate rheometer in the temperature scan mode. Equation 1 is applicable to this mode as dh/dt is the slope of the curve produced by the analyzers x-y plotter. Thus, the instantaneous slope of the curve yields the dh/dt value and the distance between the plates, h , can also be determined if either the initial separation, h_0 , or the final height (h_f is known).

The initial determination of the viscosity of BA-DAB-BA was made using the temperature scan mode of operation of the parallel plate rheometer. A die was made for pressing the 0.953 cm (0.375 in.) diameter pellets required. Sixty (60) mg of the BA-DAB-BA oligomer powder was placed in the die and pressed at an applied force of 2.7×10^2 MN (30 tons). The pressing force was maintained for 15 min to allow trapped air to escape. The thickness of the pressed pellets was in the range of 0.071 to 0.077 cm (0.028 to 0.030 in.).

There are two methods for handling the raw data (x-y plot): (1) hand measurement of height at incremental times along the curve with calculation of mean slope between these points (i.e., $\frac{dh}{dt} = \frac{h_{t2} - h_{t1}}{t_2 - t_1}$) (this technique is time consuming and subject to mechanical errors); and (2) an alternative method, which involves curve fitting to a polynomial of n^{th} order, and using computerized techniques. Once a polynomial has been found that has a reasonable fit ($r^2 = 0.99$ or better, 99% of data fits equation), this equation is differentiated to obtain dh/dt and a point solution for h corresponding to the dh/dt . The dh/dt and h values are the substituted in Equation 1 and the viscosity determined. All of these manipulations are handled in the computer which saves time and increases accuracy over hand reduction of data.

In the isothermal mode of operation, Equation 2 is most applicable because only the curve height at a corresponding time is required to determine the viscosity values. These values are measured from the x-y plot at regular time intervals along the plot and are then inserted into Equation 2 for determination of the viscosity. Again, the raw data are processed in the computer to save time and assure accuracy.

There are distinct advantages for each procedure, and the method actually used was selected on the basis of each particular determination. When the plot of viscosity versus time or temperature is smooth and without sharp deflections, the curve fitting technique works quite well. However, if there are sharp deflections, the incremental approach for handling the raw data is more accurate. Curve-fitting to irregular shapes leaves some question above the accuracy, even though the coefficient of determination (fit factor, r^2) may be greater than 0.99. The incremental approach can handle relatively sharp changes in slope of the raw data curve with the only limitation being the accuracy to which the curve can be read.

(7) Determination of BA-DAB-BA melting points: The presence of the inflections in the viscosity-temperature plots suggests that there are at least three different melting points observed with the neat BA-DAB-BA sample. Examination of the raw data plot and the viscosity temperature plot (Figure 12) shows three melting points at approximately 105, 140 and 160°C. The increase in viscosity observed at 140 and 160°C are most likely due to compaction of unmelted particles in fluid melt. The first flow is observed at 100 to 110°C. There is an indication of a fourth inflection point between 165 and 175°C, but this change in slope may be due to a true change in viscosity.

In order to confirm these observations, attempts were made to obtain enhanced DSC plots using the bias control on the DuPont Model 900 Thermal Analyzer. The results obtained were poor as the noise level was high when increased sensitivity was used. A second method based on use of an external high gain, strip chart recorder to plot the Δy signal (the differential temperature thermocouple voltage) met with more success.

The Y-axis voltage from the DuPont unit was fed into a Leeds and Northrup Speedomax strip chart recorder at a full scale sensitivity of 1.0 mv. After several trials, a good trace of the differential voltage (differential temperature) was obtained as shown in Figure 13. There were four inflections in the trace at 103, 141, 163, and 171°C which correspond closely with inflections in the temperature-viscosity plots. In order to further confirm the existence of multiple melting points, a small sample of BA-DAB-BA was heated at approximately 2°C/min in a melting point tube and observed under five times magnification. Shrinkage was observed at approximately 95 to 100°C with the particles appearing wet. Melting points were observed at 130 to 135°C with complete melting to a clear liquid occurring at 170 to 175°C. Thus, the visual melting points observed were in fair agreement with both DSC and the parallel plate rheometer. The inflection in the viscosity-temperature curve of BA-DAB-BA at approximately 175°C corresponds to the 171°C melting point shown by DSC. Thus, this point is a

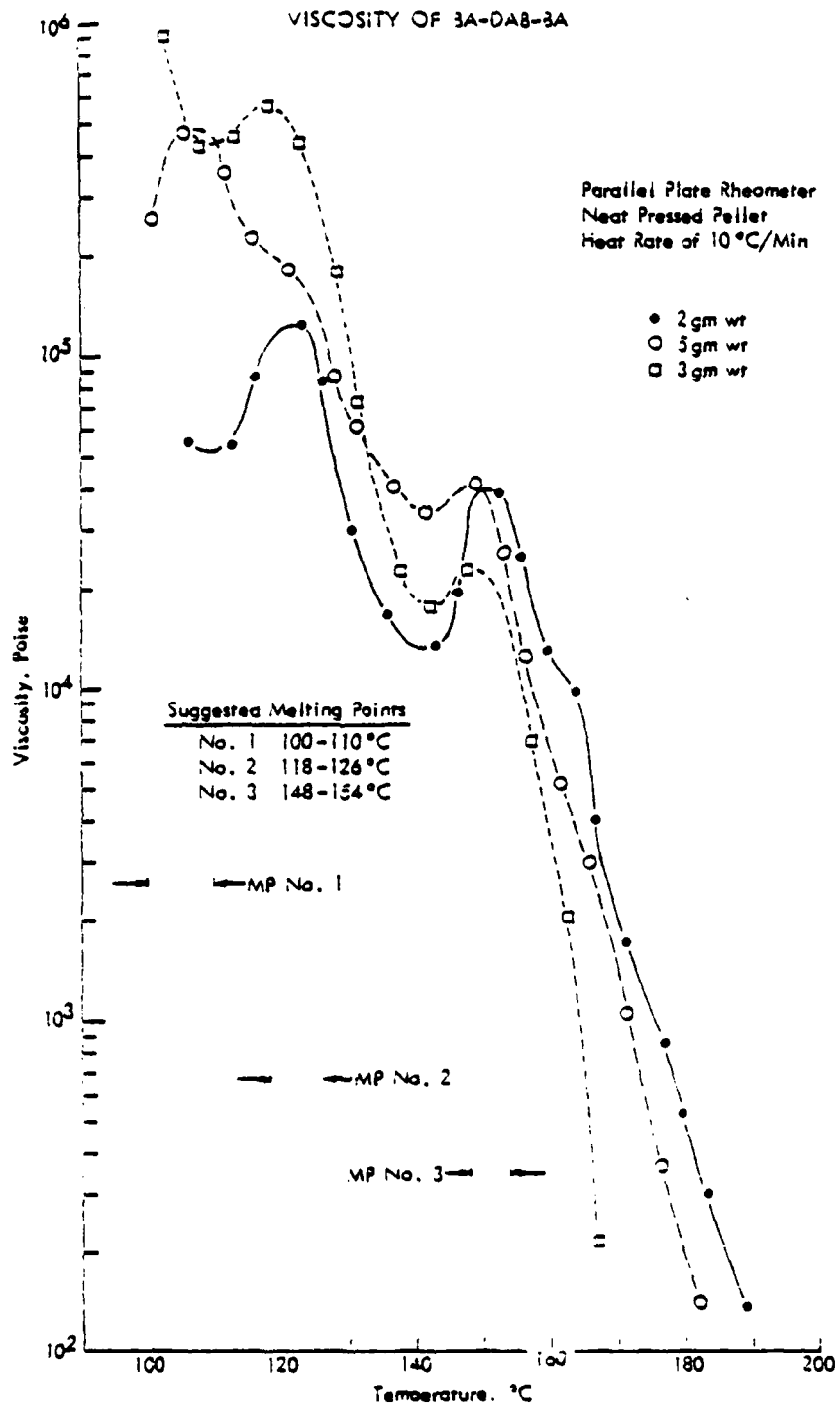


Figure 12 -
Effect of Load Weight on Viscosity Determination for BA-DAB-BA

MELTING POINTS OF BA-DAB-BA BY EXPANDED SCALE DSC

Spl Wt = 5.0mg
Heat Rate = 20°C/Min

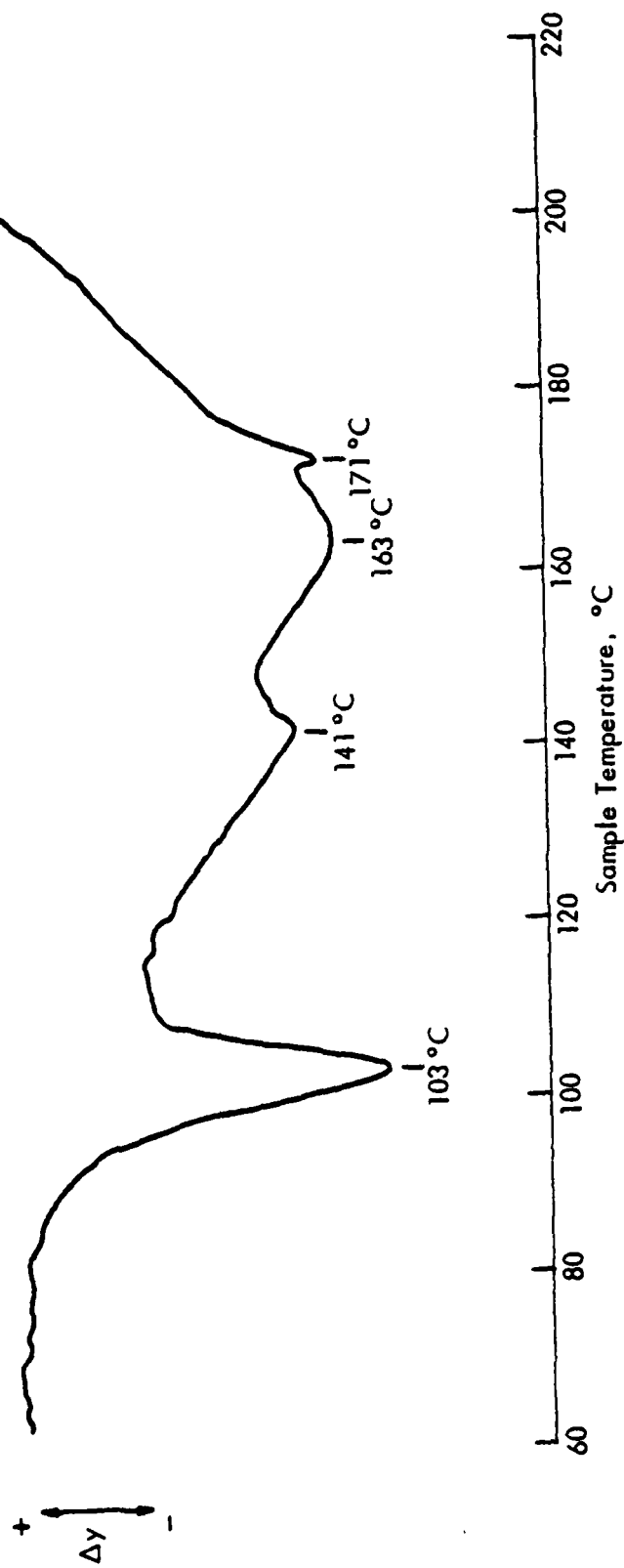


Figure 13 - Expanded Scale DSC of BA-DAB-BA

true melting point, and the melt is not a homogeneous fluid until that temperature is exceeded.

(8) Trial B-staging of BA-DAB-BA: Since the viscosity of the molten BA-DAB-BA was quite low, a brief examination of the effect of precuring or B-staging was performed at the end of this reporting period. Four, 100-mg batches of neat BA-DAB-BA were weighed into 15 x 45 mm glass vials (1 dram). These vials were then placed in a preheated aluminum block bored so that the vials were surrounded by metal. The aluminum block was a 2-in. (5.0-cm) cube. A thermocouple was placed into a small well in the block for temperature monitoring. The entire assembly was heated in a forced air oven. The oven temperature was set so the temperature of the block was 175°C. The sample-containing vials were withdrawn at 15, 35, 50, and 60 min after insertion. The cured BA-DAB-BA was then removed from the vials, which has been previously coated with "Freekote 33" release agent and ground for pellet preparation. The 60-mg pellets were then used in the parallel plate rheometer for viscosity determination. The viscosity-temperature plots of the data obtained are shown in Figure 14.

Even after extended periods of precure, the inflection points corresponding to melting points of the BA-DAB-BA were still present. There were substantial increases in viscosity as was expected. After this first run was completed, it was found that the alumel chromel-thermocouple had a cold weld junction, and that the correct cure temperature was 167°C, rather than the desired 175°C.

(9) Precure of BA-DAB-BA: Thermal advancement of precure of BA-DAB-BA was found to be a successful method for increasing its viscosity. Additional precure data were obtained by heating small samples ($\cong 200$ mg) under nitrogen at $190 \pm 1^\circ\text{C}$ for 5, 10, 15, and 20 min. Heating was accomplished in a thermostated oil bath. The viscosity at 190°C was determined using a microparallel-plate rheometer. A modified method of raw data collection was used and is described in the following section of this report. The amount of polymerization taking place was estimated by comparing the area (A_u) under the DSC trace of neat untreated BA-DAB-BA and that area (A_t) for an equal (5.0 ± 0.1 mg) weight of precured material. That is represented by the following equation:

$$\% \text{ Reaction} = \frac{A_u - A_t}{A_u} \times 100$$

The data obtained is presented below in Table 7 and as a plot of log viscosity versus percent reaction in Figure 1.

The plot of log viscosity against percent reaction was shown in Figure 1 was derived by subjecting the viscosity and percent reaction to a limited curve fitting on a Texas Instrument TI-59 calculator. The best overall fit was obtained with a semilogarithmic relationship:

$$\log \eta = m(\% \text{ reaction}) + b$$

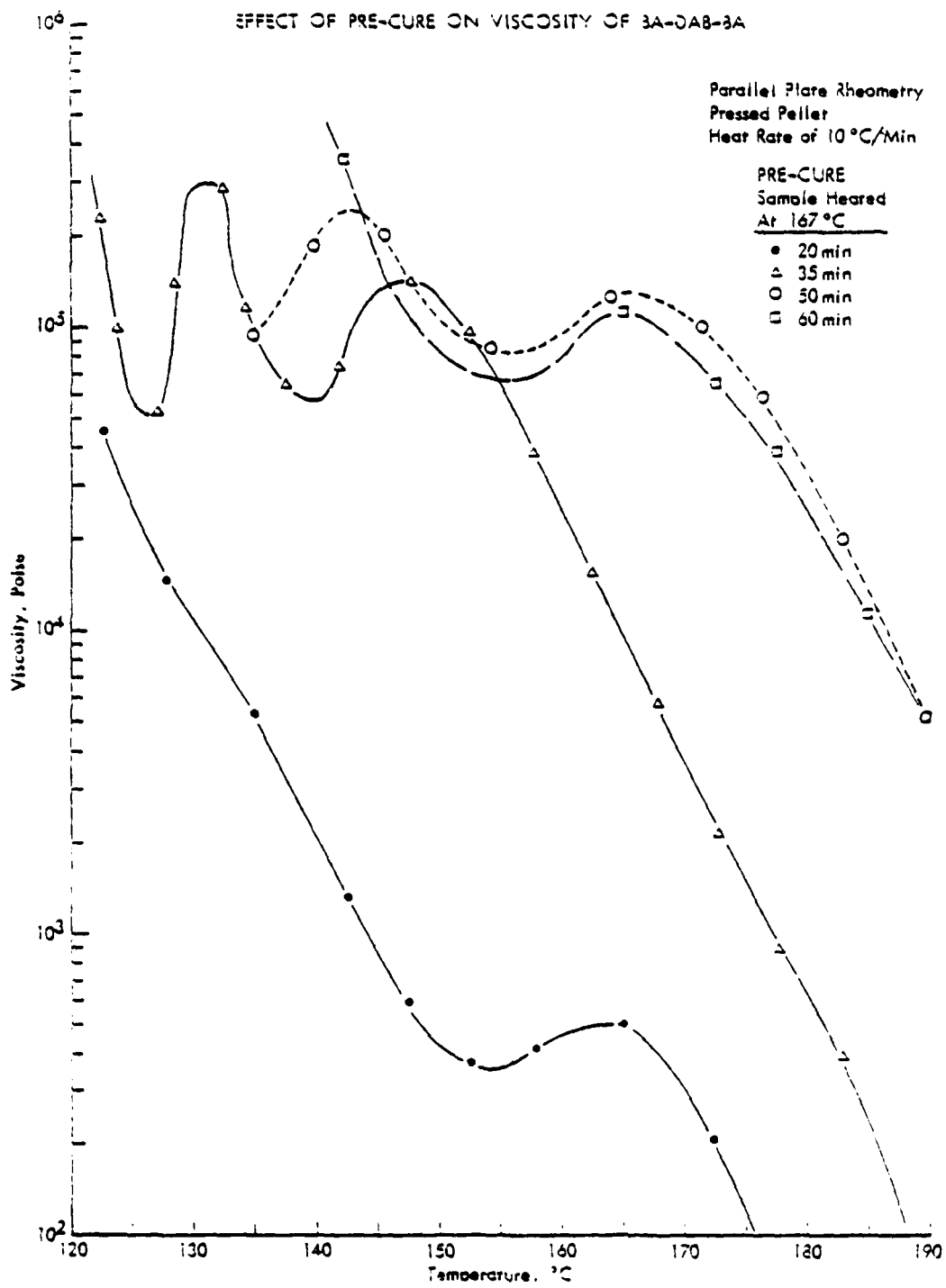


Figure 14 - Viscosity of Precured BA-DAB-BA

TABLE 7

PRECURE OF BA-DAB-BA

<u>Temperature (°C)</u>	<u>Time (min)</u>	<u>Reaction (%)</u>	<u>Viscosity as 190°C, η (poise)</u>
167	20	3.9	10
167	35	14.8	85
167	50	13.9	6×10^3
167	60	26.4	8×10^3
175	20	10.2	35
175	35	31.6	2×10^3
175	50	34.1	6×10^3
175	60	45.6	7×10^8
190	5	4.9	6
190	10	15.0	2×10^2
190	15	36.3	3.2×10^5
190	20	39.0	1.2×10^6

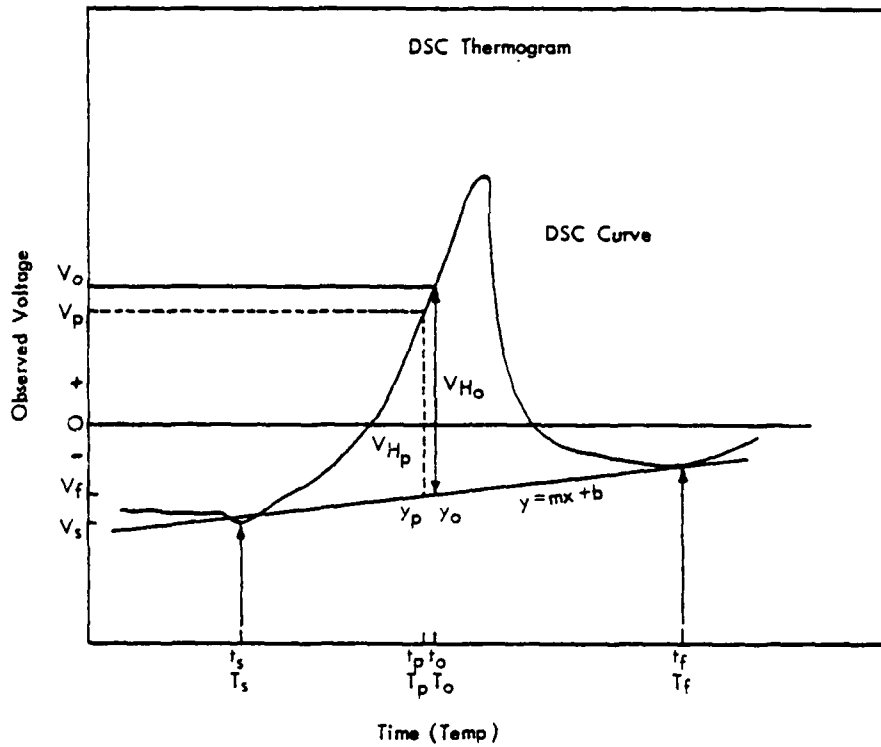
All 12 sets of data were used in a linear regression analysis to yield:

$$\begin{aligned} b(\text{y axis intercept}) &= 0.205 \\ m(\text{slope of plot}) &= 0.146 \\ r^2(\text{correlation coefficient}) &= 0.938 \end{aligned}$$

As shown in Figure 15, two of the data points were under question because the order of viscosity and degree of cure did not fit well even by visual examination. Removal of these two points yielded the following plot parameters:

$$\begin{aligned} b &= 0.097 \\ m &= 0.159 \\ r^2 &= 0.986 \end{aligned}$$

This relatively good fit indicates that some conclusions about polymerization of BA-DAB-BA can be drawn: (a) polymerization is probably a linear function with very little side branching or crosslinking occurring as indicated by the linearity of the $\log \eta/\%$ reaction plot, and the complete solubility of the precured material in tetrahydrofuran; (b) thermal precure can be used to increase viscosity in a reliable manner if mass-exothermic effects are considered; and (c) the viscosity of neat, uncured BA-DAB-BA is quite low, being on the order of one poise at 190°C as indicated by the y-axis intercept value ($\log \eta = -0.097$). These conclusions are valid only in the range of the experiment.



Base Line - $y = mx + b$

$$m = \frac{V_f - V_s}{t_f - t_s}, \quad b = V_s - m t_s$$

Heat Rate - $^{\circ}\text{C}/\text{sec}$

$$= \frac{T_f - T_s}{t_f - t_s}$$

Effective Incremental Area - A_e , V-sec

$$A_e = \left[\frac{(V_{y_o} - V_o) - (V_{y_p} - V_p)}{2} + V_p \right] \times (t_o - t_p)$$

$$\text{Total Area, } A_t = \sum_{t_s}^{t_f} A_e, \text{ Volt sec}$$

Sample Temperature, T_s , $^{\circ}\text{K}$

$$T_s \text{ } ^{\circ}\text{K} = (t_o - t_s) \left(\frac{T_f - T_s}{t_f - t_s} \right) + T_s \text{ } ^{\circ}\text{C} + \Delta T + 273.2$$

$$\Delta T = V_{H_o} \cdot T_s = (V_{y_o} - V_o) \Delta T_s$$

Where $\Delta T_s = ^{\circ}\text{C}/\text{Volt}$ (sensitivity of y axis)

Figure 15 - Integration of DSC Plot.

(10) Modified DSC kinetic method: The area under the DSC curve is directly proportional to the energy given off or absorbed. Calibration of the DSC either by heat of fusion or by heat-capacity methods provide a calibration coefficient which has the dimensions of cal/(time x temperature). Thus, it is possible to calculate the total heat of reaction by determining the area under the curve.

(a) Collection of DSC data: A Hewlett-Packard Model 3465-B digital multi-meter (4-1/2 digit readout) was connected to the external axis (ΔT) output of the DuPont Model 900 Thermal Analyzer. This voltage output is the differential thermocouple voltage amplified 1,000 (60 dB) times. The digital multi-meter was range switched so that at least four digits were indicating the voltage. An audible alarm that sounds a brief note every 6 sec was used to inform the operator when to record the voltage reading.

The thermal analyzer was set to the desired heat rate and y-axis sensitivity for each experimental run so that both an x-y plot and the digitized readings could be obtained simultaneously. Recording of the digital readings was normally started at 80°C as indicated on the x-y recorder. The finish time was recorded after the run was completed and the temperature corresponding to this time recorded. These values were used to calculate the heat rate over this range.

(b) Integration of DSC plot: It was necessary to determine a base line for the DSC plot. It was assumed that the base line was linear as shown in Figure 15. This figure is a sketch of the DSC plot and base line. Also, it shows the terminology used in developing the integration and data reduction routines.

The data was collected on the form shown in Figure 16, then reduced to k and x values using a Texas Instrument TI-59 calculator. The data reduction programs are presented in Appendix A and B. The procedure used for base correction and integration of the DSC curve are described and the integration and data reduction program is presented in Appendix A. Determination of the Arrhenius constant A and the activation energy E were calculated by linear regression analysis of the k and 1/T values. Eighty to ninety individual determinations were made. The correlation coefficients indicated that excellent linearity was obtained.

The shape of the curve produced by integration of the energy of reaction of BA-DAB-BA as shown in Figure 17 indicate that the reaction is first order. If so, the following statement can be made:

$$k = Ae^{-\frac{E}{RT}} = \frac{1}{t} \ln \frac{1}{1-X}$$

where X = the fraction of material reacted or the fraction of energy given off in time t.

The goodness of fit of the experimental curve and a plot of a theoretical curve was checked by calculating X as a function of time

TIME/ SEC.	MULTIMETER	TIME/ SEC.	MULTIMETER	TIME/ SEC.	MULTIMETER	TIME/ SEC.	MULTIMETER
6	-.0120	174	-.0067	342	+.0249	510	-.0045
12	-.0120	180	-.0061	348	+.0122	516	-.0046
18	-.0121	186	-.0053	354	+.0125	522	-.0046
24	-.0121	192	-.0049	360	+.0082	528	-.0047
30	-.0121	198	-.0041	366	+.0055	534	-.0048
36	-.0120	204	-.0034	372	+.0036	540	-.0048
42	-.0120	210	-.0025	378	+.0022	546	-.0049
48	-.0119	216	-.0015	384	+.0011	552	-.0049
54	-.0117	222	-.0005	390	+.0004	558	-.0049
60	-.0117	228	+.0006	396	-.0003	564	-.0049
66	-.0115	234	+.0017	402	-.0009	570	-.0049
72	-.0114	240	+.0030	408	-.0013	576	-.0048
78	-.0113	246	+.0044	414	-.0017	582	-.0048
84	-.0112	252	+.0058	420	-.0020	588	
90	-.0111	258	+.0075	426	-.0024	594	
96	-.0108	264	+.0090	432	-.0027	600	
102	-.0107	270	+.0108	438	-.0029	606	
108	-.0106	276	+.0125	444	-.0031	612	
114	-.0105	282	+.0146	450	-.0033	618	
120	-.0102	288	+.0165	456	-.0035	624	
126	-.0100	294	+.0187	462	-.0037	630	
132	-.0096	300	+.0210	468	-.0038	636	
138	-.0093	306	+.0236	474	-.0040	642	
144	-.0090	312	+.0261	480	-.0041	648	
150	-.0085	318	+.0288	486	-.0042	654	
156	-.0082	324	+.0312	492	-.0043	660	
162	-.0076	330	+.0321	498	-.0049		
168	-.0071	336	+.0298	504	-.0045		

Figure 16 - DSC Time/Voltage Data for Neat BA-DAB-BA

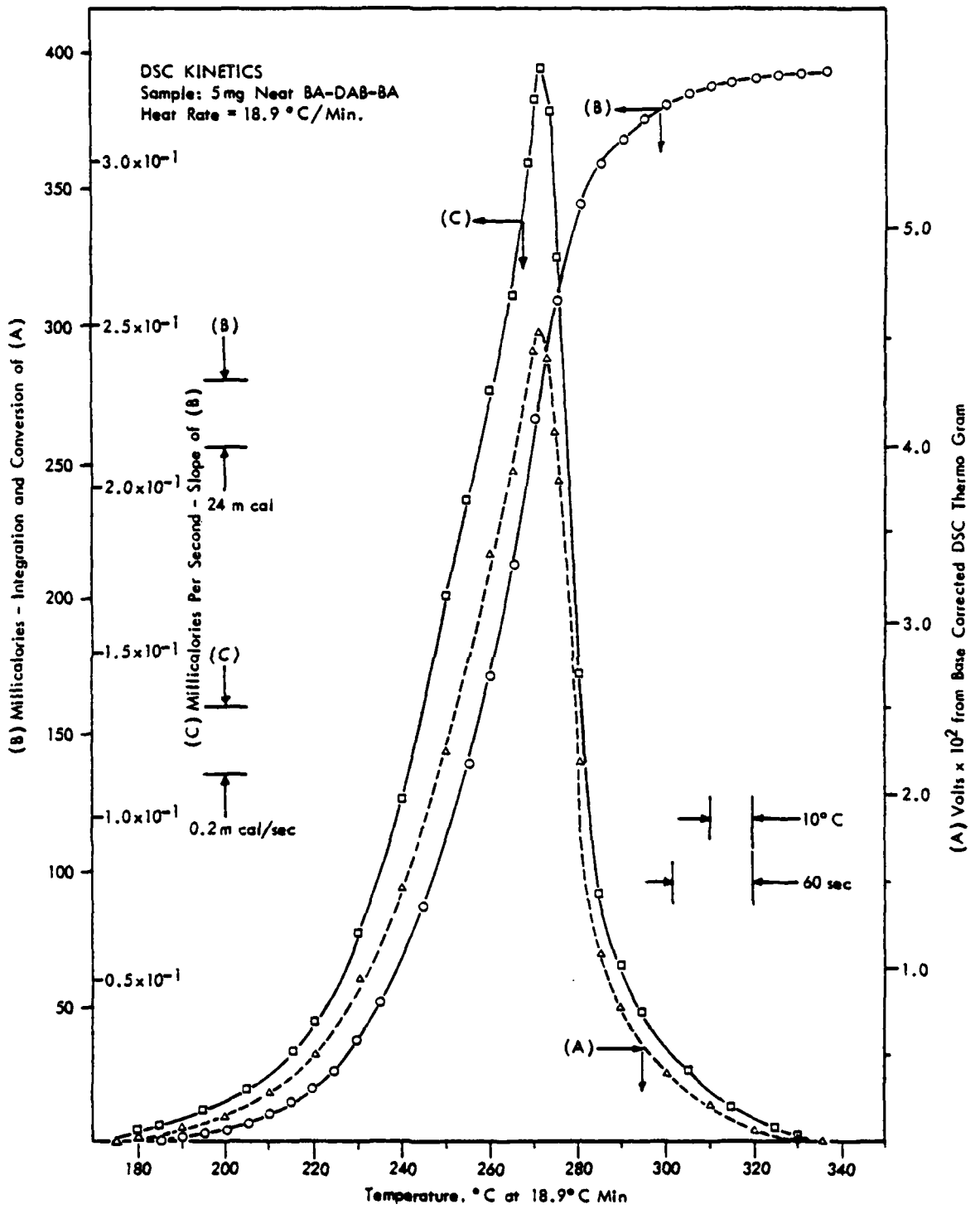


Figure 17 - Integration of DSC Plot.

by replacing the T value in the Arrhenius equation with $T = f(t)$ as the temperature is increasing linearly with time. From Figure 15, the value of the experimental T_0 is $T_s + (t_0 - t_s) \times \text{°C}_s$ (start temperature plus the product of elapsed time in Seconds_0 and the heat rate_s). A correction of ΔT must be added to this value to provide a correct sample temperature. Thus, T in the Arrhenius equation is replaced by:

$$\{[T_s + (t_0 - t_s) \times \text{°C}_s + \Delta t] + 273.2\} = f(t)$$

and then:

$$Ae^{-\frac{E}{Rf(t)}} = \frac{1}{t} \ln \frac{1}{1-X}$$

This equation can then be solved for X as a function of time. The experimental curve and the derived curve are shown in Figure 2, and the only major differences occurred at X values above 0.5. At this point, the experimental rate of reaction is somewhat faster than theory. However, a linear regression analysis of the theoretical and experimental X values indicates an excellent fit with the correlation coefficient, r^2 , being greater than 0.99 at all points along the curves and the overall $r^2 = 0.9974$. It can thus be said that the reaction of BA-DAB-BA is first order to completion within a 1% error. Table 8 shows the experimental and theoretical X values, and the correlation coefficients at regular intervals along the two curves of Figure 2.

TABLE 8
CORRELATION OF EXPERIMENTAL AND DERIVED REACTION DATA

Observation Time t Sec and (T° C)	Elapsed Time t - t _s , Sec and (data point N _o)	Fraction Reacted, X		Correlation Coefficient, r ²
		Experimental	Theory	
402 (183.3)	24 (5)	2.709 x 10 ⁻³	1.482 x 10 ⁻³	0.996
432 (192.8)	54 (10)	8.182 x 10 ⁻³	5.451 x 10 ⁻³	0.999
456 (200.3)	78 (14)	1.468 x 10 ⁻²	1.149 x 10 ⁻²	0.996
498 (213.5)	120 (21)	3.609 x 10 ⁻²	3.30 x 10 ⁻²	0.996
546 (228.6)	168 (29)	8.984 x 10 ⁻²	8.945 x 10 ⁻²	0.999
594 (243.7)	216 (37)	0.2055	0.2057	0.999
642 (258.8)	264 (45)	0.4603	0.4046	0.994
690 (273.9)	312 (53)	0.7751	0.5314	0.997
738 (289.0)	360 (61)	0.9347	0.8863	0.997
786 (304.1)	408 (69)	0.9786	0.9840	0.994
810 (315.4)	432 (73)	0.9897	0.9934	0.997
828 (321.1)	444 (75)	0.9949	0.9985	0.995
840 (324.9)	456 (77)	0.9990	0.9991	0.997
882 (332.4)	504 (85)	0.9998	0.9999	0.997

(11) Modification of viscosity determination method: The method of measuring the plate separation and time parameters of the x-y plot obtained from the DuPont Model 900 Thermal Analyzer and the Model 941 Thermomechanical Analyzer were described in Section II-B-6. The method of measuring these values was changed with an increase in sensitivity being obtained. A Hewlett-Packard Model 3465-B digital multi-meter was used to measure the output voltage of the linear differential motion transducer in the thermomechanical analyzer. This voltage is directly proportional to the distance between the plates of the micro-parallel plate rheometer. The temperature/time output was recorded on the x-y plotter of the Model 900 Thermal Analyzer. The output voltage of the motion transducer was recorded manually once every 6 sec on key from an audible alarm timed by a synchronous timer motor. The tabular data thus collected were then fed into an Apple II minicomputer for data reduction and print out on fan fold paper. At a scan rate of 10°C/min, it was possible to record data for determining viscosity once every 1°C, or 10 data points per minute.

This procedure allowed measuring the experimental parameters more accurately as the multi-meter had a 4-1/2 digit readout. The viscosity can be determined either in the isothermal or temperature-scan mode, because the time is consistent through the recording period.

3. Task III - End-Capper Synthesis

Described below is the work done on the synthesis of 1,150 g of additional end-capper, 4-(3-ethynylphenoxy)benzil.

a. Synthesis of end-capper intermediates: The procedures used in the synthesis of additional quantities of 4-(3-ethynylphenoxy)benzil were the same described in Section III-B-1. The intermediates prepared, their total weights, and the average yields are summarized in Table 9.

TABLE 9

PREPARATION OF END-CAPPER

<u>Intermediate</u>	<u>Weight (g)</u>	<u>Average Yield (%)</u>
4-Nitrobenzoin acetate	3,226	31.5
4-Nitrobenzil	2,740	85.7
3-Acetylphenyl(p-toluenesulfonate)	3,147	98.3
3-Ethynylphenyl(p-toluenesulfonate)	2,939	62.8

b. Synthesis of 4-(3-ethynylphenoxy)benzil: This compound was prepared by the reaction of the sodium salt of 3-ethynylphenol with 4-nitrobenzil. The synthesis was conducted as follows. A solution of sodium methoxide was prepared by adding 20.8 g (0.90 g atom) of freshly cut sodium of 300 ml of methanol in a 1-1 one-necked flask under nitrogen. After the

sodium had reacted, the flask was placed in a water bath at 25° and 120° g (0.44 mole) of 3-ethynylphenyl(p-toluenesulfonamide) was added portion-wise. The mixture was heated to reflux for 1/2 hr; then most of the methanol was removed on a rotary evaporatory at 55°C. About 30 ml of toluene was added to the residue to help remove the remaining solvent while the rotary evaporation was continued. After 3 hr at 55° and 0.1 mm of Hg, the solid was dissolved in 400 ml of dimethyl sulfoxide and added in 1/2-hr to a solution of 120.0 g (0.47 mole) of 4-nitrobenzil in 300 ml of dimethyl sulfoxide at 90° under nitrogen. The solution was allowed to cool to ambient temperature with stirring overnight. The reaction mixture was added to 3 liters of ice water containing 250 g of sodium hydroxide and extracted four times with 200, 200, 100, and 100 ml of methylene chloride. The combined methylene chloride extracts were washed with 250 ml of 1 N hydrochloric acid and three times with 300 ml of water. After the solvent was evaporated, the residue was dissolved in 200 ml of 4:1 hexane-methylene chloride and chromatographed on an 8-in. column of wet packed silica gel. The yellow band was collected by elution with 4:1 hexane-methylene chloride. Evaporation of solvent gave 67.1 g of product that contained traces of impurities (by TLC on silica gel plates in methylene chloride). After the yellow solid was washed with hexane and recrystallized from 200 ml of methanol, 58.3 g (40.5%) of 4-(3-ethynylphenoxy)benzil, m.p. 84 to 85°C (m.p. 79 to 81°C, Reference 4) with a single spot (TLC) was obtained. A total of 1,200 g of material was prepared with an average yield of 34.1%.

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APPENDIX A

DEVELOPMENT OF INTEGRATION PROCEDURES

TABLE A-1

DATA INPUT

<u>Key</u>	<u>Description</u>
2nd-A'*	Activate system constant and operating value subroutine, program steps 000 through 056.
A	Enter t_0 , sec. Program steps 057-061.
B	Enter V_0 , volts. Start program routine steps 062 through 162.
*Data Registers	The constants and operating values are inserted initially and are described in Table A-2.
*Linear Regression Analysis	After the constants are entered the linear-regression analysis subroutine is activated by the following key strokes: 2ND, PGM, 1, SBR, CLR. Storage registers 00 through 06 are used in this subroutine. On starting a new batch of data, storage registers 25 and 29 must be cleared.

TABLE A-2

DATA OUTPUT

Key

C	Reaction rate in mol/sec from $k = \frac{1}{t} \ln \frac{1}{1-x}$ for t_0 and T_0 corrected.
D	y intercept value, mol/sec, from linear regression analysis.
E	Slope, m from linear regression analysis = E/R from Arrhenious equation.
2ND E' + X ²	Correlation coefficient, r of regression analysis, must be squared, to be fit factor.
2ND B'	t_0 in sec for next data set.

TABLE A-3

DATA STORED IN REGISTERS

<u>Register No.</u>	<u>Symbol</u>	<u>Description</u>
<u>A - Loaded prior to data analysis</u>		
00	-	Used in linear regression analysis.
through	-	
06	-	
07	t_s	Time, sec at start of reaction. Data taken from raw time, voltage data sheet.
08	t_f	Time, sec at end of reaction.
09	T_s	Temperature, °C, at t_s .
10	T_f	Temperature, °C, at t_f .
11	V_s	Voltage, volts, at t_s .
12	V_f	Voltage, volts, at t_f .
13	$V^\circ C$	Voltage generated by 1°C, uv/°C.
14	A_f	Amplification factor for recorders normally set for 1,000 x.
19	Cc	Calibration coefficient of DSC cell, mcal per volt x sec = 68.5956 mcal/V sec.
20	-	273.2°K, 0°C in °K.
27	ΔH_s	Heat equivalent of 1 mol/sec reaction rate for a 5.0 mg sample = $\Delta H/\text{mol weight} + 5.0 = 406.96 \text{ mcal/sec}\cdot\text{mol}$.

TABLE A-3 (continued)

<u>Register No.</u>	<u>Symbol</u>	<u>Description</u>
<u>B - Placed in registers during program</u>		
15	$^{\circ}C_s$	Heat rate for DSC cell, $\frac{T_f - T_s}{t_f - t_s}$, $^{\circ}C/sec.$
16	Δt_s	$^{\circ}C/volt$ equivalent for y-axis of recorder = $(V_c \times A_f)^{-1}$
17	BL_m	Base line slope, $m = \frac{V_f - V_s}{t_f - t_s}$, volt/sec.
18	BL_y	Intercept value of $y = mx + b$ equation of base line, $[V_s - (BL_m \times t_s)] = BL_y$.
21	t	Time, sec, of observed point.
22	V_o	Voltage, volt, at observed point.
23	R_o	Reaction exotherm rate for $t_o = [(BL_m \times t_o) - (BL_y - V_o)] \times C_c^o$, m cal/sec.
24	R_i	Incremental exotherm in 6 sec corrected from previous reading = $\frac{R_o - R_p}{2} + R_p \times 6$, mcal in 6 sec.
25	R_s	Sum of all R_i 's determined = ΔH , in cal.
26	T_s	Corrected sample temperature, $^{\circ}K$, $[(t_o - t_s) \times C_s + \frac{R_o}{C_c} \times \Delta T_s] + T_s + 273.2 = ^{\circ}K$.
28	R_m	Reaction rate at t_o in mol/sec.
29	R_p	The R_o value from previous data set entry, mcal/sec.
30	X	Fraction reacted at t_o , $\frac{R_s}{\Delta H_s}$
31	R_t	Reaction rate from $k = 1/t \ln 1/1-X$

APPENDIX B

PROGRAM FOR TI-59 CALCULATOR

TI-59 PROGRAM WORKSHEET

AUTHOR HWC

DATE 10/5/80

ENTRY NO. 000
TO 099

SHEET 1 OF 3 SHEETS

PROGRAM TITLE DSC Kinetics

000	2nd LBL	25	1/X	50	+	75	=
1	2nd A'	26	STOR	51	RCL	76	-
2	RCL	27	16	52	11	77	RCL
3	10	28	RCL	53	=	78	22
4	-	29	12	54	STOR	79	=
5	RCL	30	-	55	18	80	X
6	09	31	RCL	56	R/S	81	RCL
7	=	32	11	57	2nd LBL	82	19
8	÷	33	=	58	A	83	=
9	(34	÷	59	STOR	84	STOR
10	RCL	35	(60	21	85	23
11	08	36	RCL	61	R/S	86	-
12	-	37	08	62	2nd LBL	87	RCL
13	RCL	38	-	63	B	88	29
14	07	39	RCL	64	STOR	89	=
15)	40	07	65	22	90	÷
16	=	41)	66	RCL	91	2
17	STOR	42	=	67	17	92	=
18	15	43	STOR	68	X	93	+
19	RCL	44	17	69	RA	94	RCL
20	13	45	X	70	21	95	29
21	X	46	RCL	71	=	96	=
22	RCL	47	07	72	+	97	X
23	14	48	=	73	RCL	98	6
24	=	49	+1-	74	18	99	=

← ENTRY NO.

← OPERATION

← CODE NO.

TI-59 PROGRAM WORKSHEET

AUTHOR HWC

DATE 5/10/80

ENTRY NO. 100
TO 199

PROGRAM TITLE DSC Kinetics

SHEET 2 OF 3 SHEETS

105	STOR		25	X \rightleftharpoons t		50	\div		75	RCL	
1	24		26	=		51	RCL		76	07	
2	SUM		27	+		52	27		77)	
3	25		28	RCL		53	=		78	1/X	
4	RCL		29	09		54	STOR		79	=	
5	21		30	=		55	28		80	STOR	
6	-		31	+		56	RCL		81	31	
7	RCL		32	RCL		57	25		82	LNx	
8	07		33	20		58	\div		83	2nd Σ +	
9	=		34	=		59	RCL		84	R/S	
10	X		35	STOR		60	27		85	2nd LBL	
11	RCL		36	26		61	=		86	C	
12	15		37	RCL		62	STOR		87	RCL	
13	=		38	23		63	30		88	31	
14	X \rightleftharpoons t		39	STOR		64	+/-		89	R/S	
15	RCL		40	29		65	+		90	2nd LBL	
16	23		41	RCL		66	1		91	D	
17	\div		42	26		67	=		92	2nd OP	
18	RCL		43	1/x		68	1/x		93	12	
19	19		44	X \rightleftharpoons t		69	LNx		94	R/S	
20	=		45	RCL		70	X		95	2nd LBL	
21	X		46	24		71	(96	E	
22	RCL		47	\div		72	RCL		97	X \rightleftharpoons t	
23	16		48	6		73	21		98	R/S	
24	+		49	=		74	-		99	2nd LBL	

ENTRY NO.

OPERATION

CODE NO.

TI-59 PROGRAM WORKSHEET

AUTHOR HWC

DATE 5/10/80

ENTRY NO. 200
TO End

PROGRAM TITLE DSC Kinetics

SHEET 3 OF 3 SHEETS

200	2nd E'		25			50			75		
1	2nd OP		26			51			76		
2	13		27			52			77		
3	R/S		28			53			78		
4	2nd LBL		29			54			79		
5	2nd B'		30			55			80		
6	RCL		31			56			81		
7	21		32			57			82		
8	+		33			58			83		
9	6		34			59			84		
10	=		35			60			85		
11	STOR		36			61			86		
12	21		37			62			87		
13	R/S		38			63			88		
14			39			64			89		
15			40			65			90		
16			41			66			91		
17	.		42			67			92		
18			43			68			93		
19			44			69			94		
20			45			70			95		
21			46			71			96		
22			47			72			97		
23			48			73			98		
24			49			74			99		

← ENTRY NO.

← OPERATION

← CODE NO.