# REPORT

# ON

# THE

# FUNDAMENTAL STUDIES ON THE SYNTHESIS OF HEAT-RESISTANT POLYMERS

# TO

# THE NATIONAL AERONAUTICS AND SPACE ADMINISTRATION

# WASHINGTON, D.C.

PERFORMED

UNDER

NASA GRANT NsG339

SEPTEMBER, 1965



DEPARTMENT OF CHEMISTRY

UNIVERSITY OF NOTRE DAME

NOTRE DAME, INDIANA 46556

PROGRESS REPORT NUMBER 8

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## EXPLORATORY STUDIES ON THE SYNTHESIS OF POLYMERIC AZINES

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BY

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## FOREWORD

This report is a summary report of the researches performed under NASA Grant NsG339 for the period 31 January 1965 to 15 September 1965 on the synthesis of heat-resistant polymers. The technical aspect of this grant is administered by Mr. Bernard Achhammer, Office of Advanced Research and Technology, NASA Headquarters, Washington, D. C. 20546.

The research under this grant is being conducted in the Department of Chemistry, University of Notre Dame, Notre Dame, Indiana 46556 under the technical direction of Professor G. F. D'Alelio, principal investigator.

This report covers studies performed by G. F. D'Alelio and Richard Schoenig.

Date September 15, 1965

Signed G. F. D'Alelio

G. F. D'Alelio
Principal Investigator

## ABSTRACT



This report covers the exploratory research on the synthesis and thermal studies of polymeric azines of the general structure, $\{HCArCH=N-N\}_n$, in which Ar represents a divalent aromatic moiety. As prototypes to the study of the azine polymers, the syntheses and study of selected azine monomers were also undertaken. The mechanism, kinetics and temperatures of decomposition of these monomers were investigated and reported.

The conditions required for synthesis of high molecular weight black azine polymers were explored and they were successfully synthesized by melt polymerization techniques. Investigations as to the nature of their thermal behavior were initiated. It was shown that, upon thermal decomposition, the azine polymer yields a species of heat-resistant stilbene-type polymer.

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## I. Introduction.

In a previous report[1] it was shown that Schiff base polymers of the formula, $\{CH\text{-}Ar\text{-}CH{=}N\text{-}Ar\text{-}N\}_n$, have excellent heat-resistant properties. As an analogous extension of this work it was decided[2] to study the syntheses and properties of azine-type polymers, $\{HC\text{-}Ar\text{-}CH{=}N\text{-}N\}_n$. Interest in this type of polymer has been stimulated by the fact,[1,2] that besides eventually giving a heat-resistant polymer, it may very well act as an ablator and at the same time possess semi-conductor properties. The ablative properties are expected to arise out of the following thermal decomposition, the end-product of which should be a polystilbene:

$$\{HC\text{-}Ar\text{-}CH{=}N\text{-}N\}_n \xrightarrow{\Delta} \{HC\text{-}Ar\text{-}CH\}_n + n\ N_2\uparrow \qquad \text{(eq. 1)}$$

It is, therefore, the primary objective of this investigation to synthesize this class of polymers and to study their decomposition reactions. To better understand the behavior of these polymeric aromatic azines, monomeric azines are to be synthesized and their decomposition studied as prototype of the polymers.

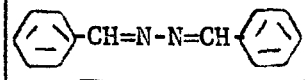
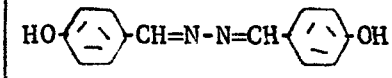
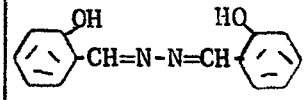
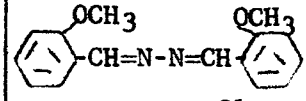
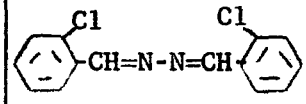
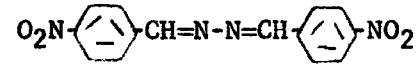
## II. Synthesis of Monomeric Azines.

Before investigations into the synthesis and properties of polymeric azines were initiated, prototype studies into the azine monomers were undertaken with the expectation that they would illuminate the mechanism of decomposition, the kinetics of the reaction, and the effects of substituents on decomposition. Since the polymer structure can be considered as having a segmer which is electronegatively substituted in the benzene ring, $-N = HC\text{-}C_6H_4\text{-}CH{=}N\text{-}N{=}CH\text{-}C_6H_4\text{-}CH{=}$, several appropriately substituted azine

monomers were selected for synthesis in order to study the decomposition in reference to the parent unsubstituted azine. Those selected are given in Table 1.

Table 1

Selected Monomeric Azines

| Compound | Molecular Weight | Melting Point °C |
|---|---|---|
|  | 208.14 | 94 |
|  | 240.14 | 287 |
|  | 240.14 | 219 |
|  | 268.14 | 144 |
|  | 277.05 | 145 |
|  | 338.14 | 307 |

The monomeric azines of Table 1 were synthesized by the direct condensation of the corresponding aldehydes with hydrazine.[1]

A. Experimental.

1. (DA-39-11) Preparation of Dibenzalazine (DBA).

To benzaldehyde, 53 g. (0.50 M) in a beaker was added slowly with stirring anhydrous hydrazine, 8.0 g. (0.25 M). The strongly exothermic reaction yielded a bright yellow solid after several minutes which was removed by filtration. This solid was recrystallized from absolute ethanol to yield 50 g. (96% yield) of bright yellow needles. M.P. 93-94°C, lit. 93°C.[3]

2. (DA-39-12) Preparation of 4,4'-Dinitrobenzalazine (DNDBA).

p-Nitrobenzaldehyde, 5.0 g. (0.033 M) was dissolved in 75 ml. of

benzene. To this solution was added anhydrous hydrazine, 0.52 g. (0.016 M). The benzene was removed by evaporation and the recovered product was recrystallized from dioxane. There was obtained 4.9 g. (91% yield) of golden needles. M.P. 307°C, lit., 303°C.[3]

3. (DA-39-13) Preparation of 4,4'-Dihydroxybenzalazine (p-DHDBA).

p-Hydroxybenzaldehyde, 30 g. (0.25 M) was dissolved in 100 ml. of 95% ethanol. To this solution was added anhydrous hydrazine, 4.16 g. (0.13 M) dropwise with stirring. The ethanol was evaporated from the mixture and the resulting yellow product recrystallized from 95% ethanol. There was obtained 2.8 g. (90% yield) of golden orange crystals. M.P. 287°C, lit., 270°C.[4]

4. (DA-39-14) Preparation of 2,2'-Dihydroxybenzalazine (o-DHDBA).

To o-hydroxybenzaldehyde, 23.4 g. (0.20 M) was added dropwise with stirring anhydrous hydrazine, 4.0 g. (0.12 M). A solid formed quickly with heat evolution. The yellow solid was recrystallized from petroleum ether. There was obtained 21 g. (88% yield) of a golden yellow solid. Its melting point was 219°C, lit., 216°C.[4]

5. (DA-39-61) Preparation of 2,2'-Dichlorobenzalazine (o-DCDBA).

o-Chlorobenzaldehyde, 10.0 g. (0.07 M) and anhydrous hydrazine, 1.14 g. (0.036 M) were mixed in a beaker. A yellow solid separated out immediately. The yellow solid was recrystallized from 95% ethanol. The yield was quantitative. M.P. 145°C, lit., 141°C.[3]

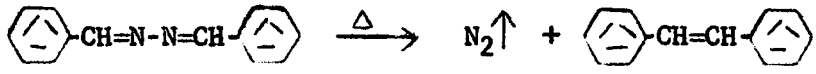
6. (DA-39-63) Preparation of 2,2'-Dimethoxybenzalazine (o-DMDBA).

o-Methoxybenzaldehyde, 5.0 g. (0.019 M) and anhydrous hydrazine, 0.32 g. (0.01 M) were mixed in a beaker. A yellow solid separated out almost immediately; it was recrystallized from 95% ethanol. The yield was quantitative. M.P. 144°C, lit., 143-144°C.[4]

## III. Fundamental Studies of Monomeric Azines.

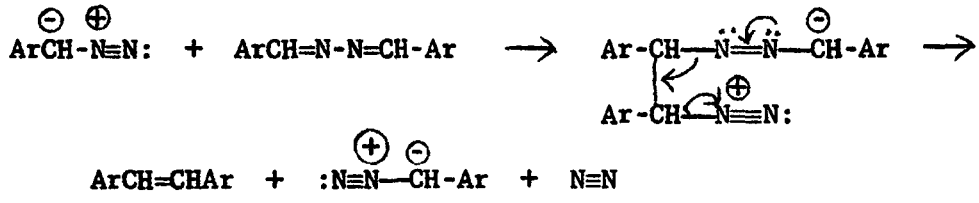
### A. Mechanism of Decomposition.

Curtius and Jay were the first investigators to report the observed decomposition of azine monomers.[5] From an examination of the products of decomposition they concluded that the major reaction was the following:



(eq. 2)

The mechanism of this reaction remained somewhat dubious until it was clarified in 1960 by H. Zimmerman and S. Somasekhara.[6] In their publication, they show the mechanism to be an ionic chain reaction involving an aryldiazomethane molecule rather than a carbene as the chain carrying species; the two propagation steps are given in equation 3:



(eq. 3)

The paper[5] further shows also how this mechanism accounts for most of the other phenomena and by-products observed in the decomposition.

### B. Kinetics of Decomposition.

In proposing the above mechanism Zimmerman and Somasekhara considered[6] the kinetics as determined in 1936 by Williams and Lawrence.[7] These investigators calculated[7] the kinetics from a gas evolution method. They determined that the reaction is indeed a first order decomposition with $k_{607\text{-}608\,^{\circ}K} = 0.15\ min^{-1}$, and an energy of activation, $E_a = 53{,}000$ cal. In light of these facts, then, Zimmerman and Somasekhara proposed the following as the major reaction scheme for monomeric azine decomposition:

Chain Initiation

$$\text{Ø-CH=N-N=CH-Ø} \xrightarrow{k_i} \text{Ø-}\overset{\ominus}{\text{C}}\text{H-}\overset{\oplus}{\text{N}}\equiv\text{N:} + \text{:CH-Ø} \qquad \text{(eq. 4)}$$

Chain Propagation

$$\text{Ø-CH=N-N=CH-Ø} + \text{Ø-}\overset{\ominus}{\text{C}}\text{H-}\overset{\oplus}{\text{N}}\equiv\text{N:} \xrightarrow{k_p} \text{N}_2 + \text{Ø-}\overset{\ominus}{\text{C}}\text{H-}\overset{\oplus}{\text{N}}\equiv\text{N:} + \text{Ø-CH=CH-Ø} \qquad \text{(eq. 5)}$$

Chain Termination

$$\text{Ø-}\overset{\ominus}{\text{C}}\text{H-}\overset{\oplus}{\text{N}}\equiv\text{N:} + \text{X} \xrightarrow{k_t} \text{Y} \qquad \text{(eq. 6)}$$

In this sequence the symbols X and Y represent unknown species in the termination process.

C. Thermal Studies.

1. Thermal Gravimetric Analysis.

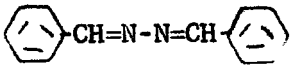
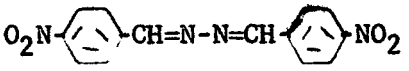
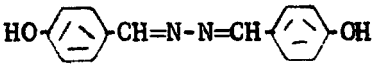
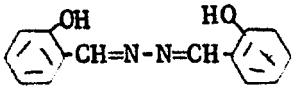
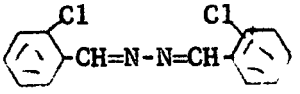
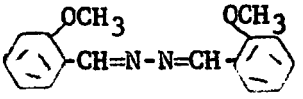
An attempt was made, employing the du Pont 950 Thermogravimetric Analyses (TGA), to check the kinetics, temperatures, and products of decomposition of the azine monomers. The TGA method plots weight loss versus temperature or time. However, this procedure was unsuccessful since losses of weight due to evaporation or sublimation far exceeded, and hence masked, any weight loss data due to decomposition.

2. Differential Thermal Analysis.

In view of the failure of the TGA method, differential thermal analytical (DTA) methods were evaluated to establish the thermal properties of the monomeric azines. The method of differential thermal analysis, in which endotherms and exotherms of a compound, indicative of physical or chemical changes in that compound, are plotted versus temperature, proved somewhat more successful than the TGA. The DTA equipment used was the du Pont 900 Model. Accurate melting points (endotherms) as well as decomposition ranges (exotherms) were recorded. The results obtained are given in Table 2 and recorded in the Appendix as Number 1 to Number 6 inclusive.

Table 2

Melting Points and Decomposition
Temperatures °C of Selected Azines

| Exper. No. | Compound | Mol. Wt. | M.P. | Dec. Temp. | Thermogram Appendix Number |
|---|---|---|---|---|---|
| DA-39-11 |  | 208 °C | 94 °C | 324 °C | 1 |
| DA-39-12 |  | 338.14 | 307 °C | 367 °C | 2 |
| DA-39-13 |  | 240.14 | 287 °C | 295 °C | 3 |
| DA-39-14 |  | 240.14 | 219 °C | 381 °C | 4 |
| DA-39-61 |  | 277.05 | 145 °C | 326 °C | 5 |
| DA-39-63 |  | 268.14 | 144 °C | 336 °C | 6 |

D. Discussion.

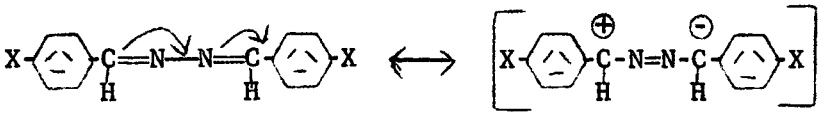
The DTA data above seems to indicate that an electron-donating substituent in the ortho and especially the para position tends to lower the energy required, and hence the temperatures, for decomposition of the azine to nitrogen and the corresponding stilbene.

Although the exact reason for this remains somewhat in question, one explanation is postulated. From the work[6] of Zimmerman and Somasekhara it is known that thermal decomposition involves the splitting of the azine molecule into a carbene and an aryldiazomethane molecule thus:

$$X\text{-}Ar\text{-}CH{=}N\text{-}N{=}CH\text{-}Ar\text{-}X \xrightarrow{\Delta} X\text{-}Ar\text{-}CH: + {:}N{\equiv}\overset{\oplus\ominus}{N}\text{-}CH\text{-}Ar\text{-}X. \qquad \text{(eq. 7)}$$

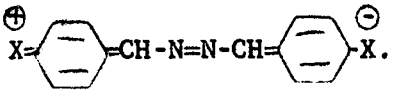
They do not delineate[6] any intermediate steps in the splitting of this molecule. It is possible that this splitting occurs from an excited elec-

tronic state of the azine, thus:



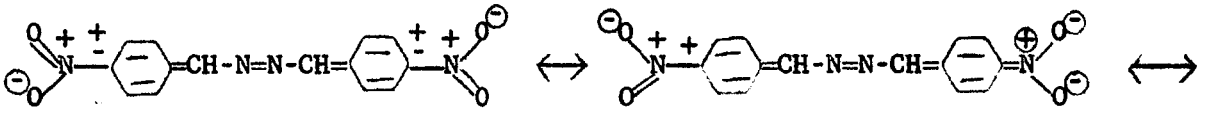
(A) (B) (eq. 8)

Also, then charge interaction with the aromatic rings will vary with the electronic nature of the substituents (X), so that resonance form (B) can assume that of form (C),

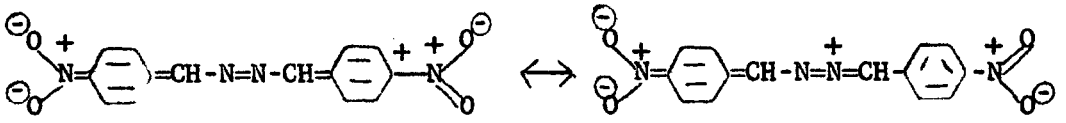


(C)

Further, in the case where X = $NO_2$, more significantly contributing resonance structures can be written than with X = OH, as shown in the comparison of equation 9 with equation 10.

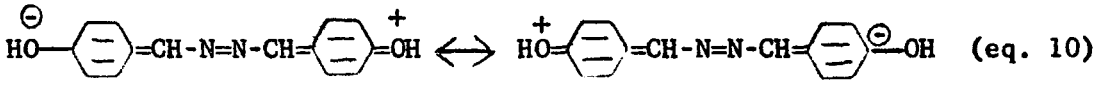


(D-1) (D-2)



(D-3) (D-4) (eq. 9)

versus



(E-1) (E-2) (eq. 10)

Thus, more stability is achieved with the nitro substituent and more energy, that is, a higher temperature, is necessary to cause the fission into the carbene and aryldiazomethane fragments than in the case of the hydroxyl substituent. Further investigation is necessary to substantiate completely this postulate.

The DTA results also reveal that the 2,2'-dihydroxybenzalazine is given added stability to decomposition by the hydrogen bonding with the azine nitrogen as is evidenced by comparing the decomposition temperatures of ortho hydroxy compound with those of the ortho chloro and methoxy derivatives.

The studies on the monomeric azines are not complete and some aspects remain to be examined. Nonetheless, it can be concluded tentatively, at this point, that the rates and temperature of decomposition of monomeric azines are dependent upon their electronic character as well as upon the presence of hydrogen bonding.

IV. Syntheses of High Molecular Weight Polymeric Azines.

The object of this phase of the investigation was to determine the optimum experimental conditions for the synthesis of the required high molecular weight azine polymer: $\{CH\text{-}Ar\text{-}CH{=}N\text{-}N\}_n$. Both solution and melt polymerization systems were investigated.

A. Solution Polymerization.

The method of solution polymerization, previously found not to yield a high molecular weight species with the Schiff base polymers,[1] was re-evaluated in this study for the synthesis of the azine polymers.

1. Experimental.

a. (DA-39-17) Polymerization of Terephthaldehyde (TA) and Hydrazine.

Terephthaldehyde, 0.7024 g. (0.00524 M) was dissolved in 200 ml. of benzene to which anhydrous hydrazine, 0.1677 g. (0.00524 M) was added with stirring. The solution almost immediately precipitated a yellow solid on the side of the flask. The reaction was refluxed in a Dean-Stark apparatus[1,2] and 1.5 ml. of water was collected. After fourteen hours the reaction was terminated and the yellow solid filtered off, dried and weighed. There

was obtained 0.4713 g. (72% yield) of yellow brick dust polymer. M.P. $>$ 300°C.

b. (DA-39-24) Polymerization of p-Xylylidene-dianiline (p-XDA) and Hydrazine.

p-Xylylidene-dianiline 0.9964 g. (0.003505 M) was dissolved in 50 ml. of benzene and to this solution was added 85% hydrazine (aqueous), 0.1320 g. (0.003505 M). A yellow precipitate formed on standing after a few hours. This yellow brick dust polymer was filtered off, dried and weighed. There was obtained 0.45 g. (89% yield) of yellow polymer. M.P. $>$ 300°C.

2. Discussion.

It was confirmed in these studies that solution polymerization yields only the yellow, brick-dust low molecular weight azine polymer. Evidently, the polymer as it grows in length becomes insoluble in the solvent and precipitates out the reaction media in a low molecular weight form and fails to propagate further under the conditions of the experiment.

B. Melt Polymerization.

Melt polymerization consists of heating both monomers to a molten homogeneous solution under an inert atmosphere. Melt polymerizations may be divided[1,2] into three main classifications: amine exchange, carbonyl exchange, and the bis exchange polymerization. Of these, only the carbonyl and bis exchanges processes were studied in melt systems. The amine exchange was found to be inoperative since the hydrazine, which is the lowest boiling constituent in an amine exchange system, distills first from the reaction mixture.

1. Carbonyl Exchange.

The carbonyl exchange can be generalized as:

$$n\ RCOArCOR + n\ ArCH{=}N{-}N{=}CH{-}Ar \rightleftharpoons 2n\ ArCHO + \{CR{-}Ar{-}CR{=}N{-}N\}_n \qquad \text{(eq. 11)}$$

A specific example of the carbonyl exchange is given by the reaction of terephthaldehyde and dibenzalaniline.

$$n\ OHC{-}C_6H_4{-}CHO + n\ C_6H_5{-}CH{=}N{-}N{=}CH{-}C_6H_5 \rightleftharpoons$$

$$2n\ C_6H_5CHO + \{CH{-}C_6H_4{-}CH{=}N{-}N\}_n \qquad \text{(eq. 12)}$$

The carbonyl exchange reaction was evaluated under the different reaction parameters of pressure, temperature, and catalyst.

a. Experimental.

i. (DA-39-16) Polymerization of Terephthaldehyde (TA) and Dibenzalazine (DBA).

Terephthaldehyde 0.4565 g. (0.0034 M) and dibenzalazine 0.7120 g. (0.034 M) were ground finely together in a mortar, placed in a microflask, and its contents were heated under an inert atmosphere of nitrogen. The temperature was raised gradually to 270°C during which time the color of the melt changed from yellow to orange to red to reddish black. At $\sim$ 260°C there was observed a vigorous bubbling and foaming. Benzaldehyde and a basic gas of $NH_3$ and/or $N_2H_4$ were present in the effluent gases. After five hours at 270°C, the reaction was terminated. The black-brown solid obtained weighed 0.63 g. (140% yield). The polymer did not melt in a bunsen flame and was insoluble in the solvents evaluated.

ii. (DA-39-25) Polymerization of TA and DBA with p-Toluenesulfonic Acid as Catalyst.

DBA, 1.0350 g. (0.00497 M) and TA, 0.5275 g. (0.00497 M) were placed along with 0.05 g. p-toluenesulfonic acid, into a microflask and its contents heated, under an atmosphere of nitrogen, to a melt. Then, the temperature was maintained at 160°C at atmospheric pressure. After twenty-four

hours, the pressure was reduced to 0.3 mm. Hg. After thirty-six hours the reaction was stopped. A heterogeneous yellow-brownish polymer, 0.55 g. (108% yield) was obtained which is infusible and insoluble in all the solvents evaluated.

iii. (DA-39-32) Polymerization of TA and DBA.

TA, 0.5417 g. (0.00404 M) and DBA, 0.8403 g. (0.00404 M) were placed in a microflask, and its contents were heated in a nitrogen atmosphere to 205°C and held there for five hours at atmospheric pressure. The temperature was then raised to 230°C and maintained at this temperature for eight hours, after which time the pressure was reduced to 2 mm Hg and the reaction continued for an additional twenty-four hours. Then the reaction was terminated and a brownish-black shiny polymer, 0.56 g. (100% yield) which was insoluble and infusible, was obtained. Heating it for a short period of time to the temperatures in a bunsen flame converts it into a thermally stable black polymer.

iv. (DA-39-42) Polymerization of TA and DBA.

TA, 0.0221 g. (0.00491 M) and DBA, 0.6599 g. (0.00491 M) were placed in a microflask and heated under nitrogen to a temperature of 200°C during the course of which the melt changed in color from yellow to orange to red to brown to black. After forty-six hours the temperature was raised to 250°C. At this point, the pressure of the black viscous mass was reduced to 1.5 mm Hg and the benzalaldehyde of reaction collected. After three additional hours, the reaction was stopped and there was obtained a black, glassy, infusible and insoluble polymer, 0.83 g. (130% yield).

v. (DA-39-29) Polymerization of TA and Di-3-pentylideneazine (D-3-PA).

TA, 0.4725 g. (0.0035 M) and D-3-PA, 0.6124 g. (0.0035 M) were placed

in a microflask and the content heated under a nitrogen atmosphere to 160°C, at which time the clear solution changed successively in color from yellow to gold to orange; after which the reaction was terminated and the yellow-orange polymer removed from the flask. Its weight was 0.61 g. (79% yield). It was infusible and insoluble.

vi. (DA-39-38) Polymerization of p-Xylylidenetetrabutyl Ether (PXDBE) with Dibenzalazine (DBA).

p-XDBE, 1.0001 g. (0.0025 M) and DBA, 0.5281 g. (0.0025 M) were placed in a microflask and heated under inert nitrogen atmosphere to 200°C. After twenty-two hours, the temperature of the orange melt was raised to 250°C. After three more hours the melt was reddish-black, finally becoming black and viscous. At this point, the pressure was reduced to 23 mm Hg and the temperature kept at 270°C, and the butyl acetal of benzaldehyde was isolated as the volatile reaction product. When evidence that no more of the volatile acetal was being eliminated, the reaction was terminated. There was obtained 0.35 g. (79% yield) of black, shiny, infusible and insoluble polymer.

vii. (DA-39-40) Polymerization of p-Xylylidenetetrabutyl Ether (PXDBE) with Di-3-pentylideneazine (D-3-PA).

p-XDBE, 1.0116 g. (0.0026 M) and D-3-PA, 0.4325 g. (0.0026 M) were placed in a microflask and the contents heated under an inert nitrogen atmosphere to a melt. The temperature was then raised to 200°C and the melt changed from the characteristic yellow color to red. After sixteen and one-half hours the melt became black, bubbly and viscous. At this point the temperature was raised to 300°C and the pressure lowered to 0.1 mm Hg and the dibutyl acetal of 3-pentanone, collected in a dry ice trap as the volatile reaction product. When the collection of volatile by-product ceased the reaction was terminated. There was isolated 0.3 g. (100% yield) of a

black, shiny polymer which was infusible and insoluble.

viii. (DA-39-39) Polymerization of p-Xylylidenetetrabutyl Ether (PXDBE) with Anhydrous Hydrazine.

p-XDBE, 1.1158 g. (0.0028 M) and anhydrous hydrazine, 1.0978 g. (0.0028 M) were placed in a microflask and reacted under an inert nitrogen atmosphere. The temperature was raised to 130°C and after forty-five minutes the solution became yellow and solidified. There was obtained a yellow brick-dust polymer, 0.25 g. (86% yield). M.P. $>$ 300°C.

b. Discussion.

The melt polymerizations involving carbonyl exchange reactions proved to be generally successful, apparently yielding a high molecular weight black, glassy polymers. The two systems, terephthaldehyde plus di-3-pentylideneazine and hydrazine plus p-xylylidenetetrabutyl ether, which do not give black high molecular weight polymers, interestingly enough, have the two most volatile reaction products, that is, 3-pentanone, b.p. 102.7°C and n-butyl alcohol, b.p. 117.7°C respectively. Thus, it may be speculated that at the high temperatures which are used in the polymerizations these systems are too reactive and the volatile products are removed immediately as formed, causing precipitation of the polymer at short chain lengths. Analogously, although terephthaldehyde and dibenzalazine produce a black polymer in a melt polymerization system, the same reagents in the presence of p-toluenesulfonic acid as a catalyst give an orange lower molecular weight polymer. Again, perhaps this is due to the fact that the catalyst increases the rate of the reaction so that the exchange reaction is over before the polymer has a change to attain any appreciable length.

2. Bis Exchange.

The bis exchange can be generalized as:

$$n\ ArCH{=}N{-}N{=}CHAr + n\ ArN{=}CHArCH{=}NAr \rightleftharpoons 2n\ ArCH{=}NAr + \left[N{-}N{-}CHArCH\right]_n \quad \text{(eq. 13)}$$

A specific example of the bis exchange reaction as utilized in this investigation is given by the reaction of p-xylylidenedianiline and dibenzalazine:

$$n\ C_6H_5{-}N{=}CH{-}C_6H_4{-}CH{=}N{-}C_6H_5 + n\ C_6H_5{-}CH{=}N{-}N{=}CH{-}C_6H_5 \rightleftharpoons$$

$$2n\ C_6H_5{-}CH{=}N{-}C_6H_5 + \left[N{-}N{-}CH{-}C_6H_4{-}CH\right]_n \quad \text{(eq. 14)}$$

The bis exchange was evaluated in two specific instances in this investigation.

a. Experimental.

i. (DA-39-43) Polymerization of p-Xylylidenedianiline (PXDA) with Dibenzalazine (DBA).

PXDA, 0.9804 g. (0.0035 M) and DBA, 0.7188 g. (0.0035 M) were placed together in a microflask and heated under inert atmosphere of nitrogen. The reaction temperature for the first four hours was 210°C. The temperature was then raised to 225°C, and after forty-three hours the melt changed in color from yellow to red to black, and a solid black, glassy polymer was recovered. The weight of the infusible, insoluble polymer was 0.65 g. (144% yield).

ii. (DA-39-45a) Polymerization of p-Xylylidenedianiline (p-XDA) with Di-3-pentylideneazine (D-3-PA).

p-XDA, 0.9743 g. (0.0034 M) and D-3-PA, 0.5693 g. (0.0034 M) were placed in a microflask and heated under nitrogen atmosphere. The temperature was raised to 225°C. After twelve hours the pressure was reduced to 2 mm Hg. After twenty-four hours the evolution of volatile reaction product became negligible and the reaction was terminated. There was obtained 0.57 g. (132% yield) of a black, shiny polymer which was infusible and insoluble.

b. Discussion.

The bis exchange as with the carbonyl exchange produced, with a minimum of effort, a high molecular weight azine polymer. The yields, as shown in earlier reports[1,2] were in excess of the 100% theoretical and for the same reasons.[1,2]

C. Post-Treatment of Azine Polymers.

The post-treatment of azine polymers at this time was limited to preliminary solubility studies and to the effects on composition of thermal treatments.

1. Solubility Studies.

Since solubility is an important parameter in polymers some tests were made to evaluate the better-known active solvents up to their boiling points. Two types of polymers were evaluated, namely, the yellow polymer (DA-39-18) and the black polymer (DA-39-42). None of the solvents shown in Table 3 dissolved either the yellow or the black polyazine.

Table 3

Compounds Evaluated as Solvents for the Polyazines

| Solvent[a] | Result |
|---|---|
| $H_2SO_4$ (conc.) | decomposed |
| $CH_3SOCH_3$ | not soluble |
| HCOOH | not soluble |
| $[CH_3-\overset{O}{\overset{\|}{C}}]_2-O$ | not soluble |
| $[(C_2H_5)_2C=N]_2$ | not soluble |
| $[C_6H_5CH]_2$ | not soluble |
| $[C_6H_5CH=N]_2$ | not soluble |
| $C_6H_5CH=N-C_6H_5$ | not soluble |
| $HCON(CH_3)_2$ | not soluble |
| $CH_3CON(CH_3)_2$ | not soluble |

[a] all tested at b.p. of solvent

2. Thermal Reactivity.

This phase of the investigation included some preliminary tests on the behavior of azine polymers at high temperatures.

a. Experimental.

i. DA-39-10.

Black azine polymer (DA-39-42) was first ground up and its infrared spectrum recorded (Appendix No. 7). The polymer was then placed on a steel wire gauze and heated in the hottest portion of a bunsen flame. The polymer glowed to a red heat without melting and appeared to fracture with the evolution of a gas. After fifteen minutes of heating at red heat, the sample was removed from the flame, leaving a black shiny polymer which was ground up and its infrared spectrum recorded (Appendix No. 8). This infrared spectrum shows marked changes over the original spectrum of the unheated polymer, and in several regions corresponds to the recorded spectrum of known polyxylylidene oligomer, $\text{-}[\text{CH=CH-C}_6\text{H}_5\text{-}]_n$, recorded by Cameron and Kane.[8]

b. Discussion.

It can be concluded tentatively that the decomposition of the azine polymer to a polystilbene-type polymer does, in fact, occur. The experimental parameters surrounding this reaction as well as the product stability will be the subject of future inquiry and obviously will require elemental analyses, variation in heating temperatures and schedules, etc.

V. Summary and Conclusions.

1. Prototype monomeric azines were successfully synthesized.
2. The mechanism and kinetics of monomeric azine decomposition were reported.
3. Thermal studies including establishing the decomposition

temperatures of azine monomers were conducted.

4. Electronic and structural factors determine decomposition temperatures of azine monomers.
5. Solution polymerization methods for the polyazines yielded only yellow brick-dust polymers.
6. Intermediate fusible black polymeric azines were obtained by melt polymerization techniques.
7. Melt polymerizations yield black infusible, insoluble azine polymers by both the carbonyl and bis exchange reactions as final products.
8. No solvents were found to dissolve highly condensed azine polymers.
9. The decomposition of azine polymers to a stilbene-type polymer was indicated.

VI. Future Studies.

1. Complete the study of azine monomers including differential thermal analyses of an aliphatic azine.
2. A reexamination of the methods of polymerization, including exact yield data and possible determination of degree of polymerization at some intermediate stage in the polymerization.
3. Utilize differential thermal analysis and thermal gravimetric analysis on azine polymers in an attempt to monitor the decomposition while elucidating experimental parameters.
4. The use of mass spectra studies to determine the nature of the products of decomposition will be performed.

5. The thermal stability of the polystilbenes derived from the polyazines will be investigated.

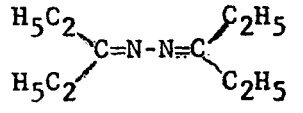
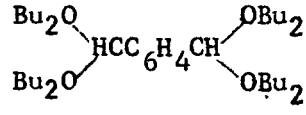
6. Other azine polymers will be synthesized and studied in order to obtain the most thermally stable systems.

## VII. Acknowledgment.

The authors and the University of Notre Dame acknowledge gratefully the financial assistance from NASA for this research. Appreciated also is the general guidance and assistance given by Mr. Bernard Achhammer, NASA Headquarters, Washington, D. C. 20546.

Thanks are also due to James Crivello for assistance in obtaining the thermoanalytical data.

## VIII. Glossary.

| | | |
|---|---|---|
| 1. | DBA | $C_6H_5CH{=}N{-}N{=}CHC_6H_5$ |
| 2. | DNDBA | $4,4'\text{-}O_2NC_6H_4CH{=}N{-}N{=}CHC_6H_4NO_2$ |
| 3. | p-DHDBA | $4,4'\text{-}HOC_6H_4CH{=}N{-}N{=}CHC_6H_4OH$ |
| 4. | o-DHDBA | $2,2'\text{-}HOC_6H_4CH{=}N{-}N{=}CHC_6H_4OH$ |
| 5. | o-DCDBA | $2,2'\text{-}ClC_6H_4CH{=}N{-}N{=}CHC_6H_4Cl$ |
| 6. | o-DMDBA | $2,2'\text{-}CH_3OC_6H_4CH{=}N{-}N{=}CHC_6H_4Cl$ |
| 7. | TA | $p\text{-}OHCC_6H_4CHO$ |
| 8. | p-XDA | $p\text{-}C_6H_5N{=}CHC_6H_4CH{=}NC_6H_5$ |
| 9. | D-3-PA |  |
| 10. | p-XDBE |  |

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| | | | | |
|---|---|---|---|---|
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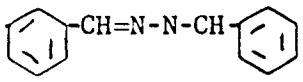
|  | REF. glass beads | | T | △ T | DATE 8-23-65 |
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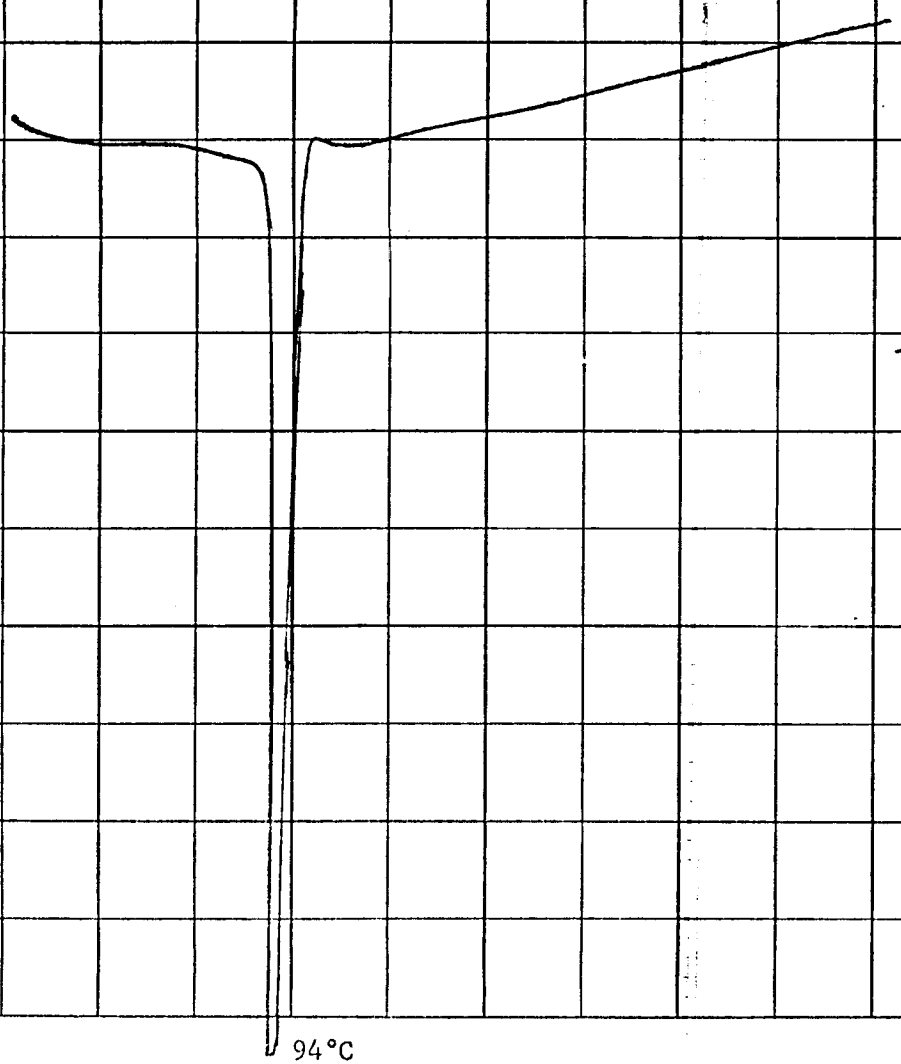
EXO

△ T

ENDO

SAMPLE:

RUN NO.:




DUPONT 900

T, °C (CHROMEL: ALUMEL) *

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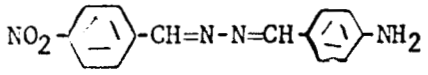
| | | | |
|---|---|---|---|
| SAMPLE: DA-39-12  | SIZE --- | ATM. Air , MM | RUN NO. Appendix No. 2 |
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| | PROG. MODE heat | SCALE: 50 °C/IN. / 0.5 °C/IN. | OPERATOR RKS |
| ORIGIN: | RATE 25 °C/MIN, START °C | SHIFT: 0 IN. / as req. IN. | BASE LINE SLOPE 0 |



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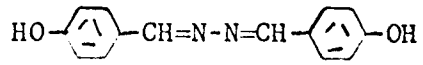
SAMPLE: DA-39-13



ORIGIN:

SIZE -- 

REF. glass beads

PROG. MODE heat

RATE 25 °C/MIN, START -- °C

ATM. air , MM

| | T | ΔT |
|---|---|---|
| SCALE | 50 °C/IN. | 0.5 °C/IN. |
| SHIFT | 0 IN. | as req. IN. |

RUN NO. Appendix No. 3

DATE 8-24-65

OPERATOR JVC

BASE LINE SLOPE 0

EXO

ΔT

ENDO

295°C

287°C

SAMPLE:

RUN NO.:

900

T, °C (CHROMEL: ALUMEL)*

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| | | | |
|---|---|---|---|
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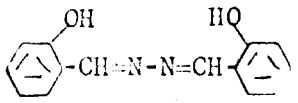
|  | REF. glass beads | T / △T | DATE 8-23-65 |
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| ORIGIN: | RATE 25 °C/MIN, START -- °C | SHIFT 0 IN. as. req. IN. | BASE LINE SLOPE 0 |



T, °C (CHROMEL: ALUMEL)*

*SEE INSTRUCTION MANUAL FOR SCALE CORRECTION

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| | | | | |
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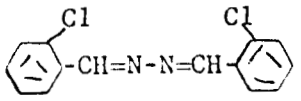
| SAMPLE: DA-39-61  | SIZE --- | ATM. air , MM | RUN NO. Appendix No. 5 | |
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| ORIGIN: | RATE 25 °C/MIN, START -- °C | SHIFT T: 0 IN. ΔT: as req. IN. | BASE LINE SLOPE 0 | |



T, °C (CHROMEL: ALUMEL) *

* SEE INSTRUCTION MANUAL FOR SCALE CORRECTION

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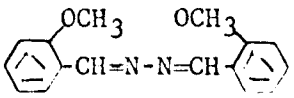
| | | | | |
|---|---|---|---|---|
| SAMPLE: DA-39-63  | SIZE --- | ATM. Air , MM | RUN NO. Appendix No. 6 | |
| | REF. glass beads | | DATE 9-14-65 | |
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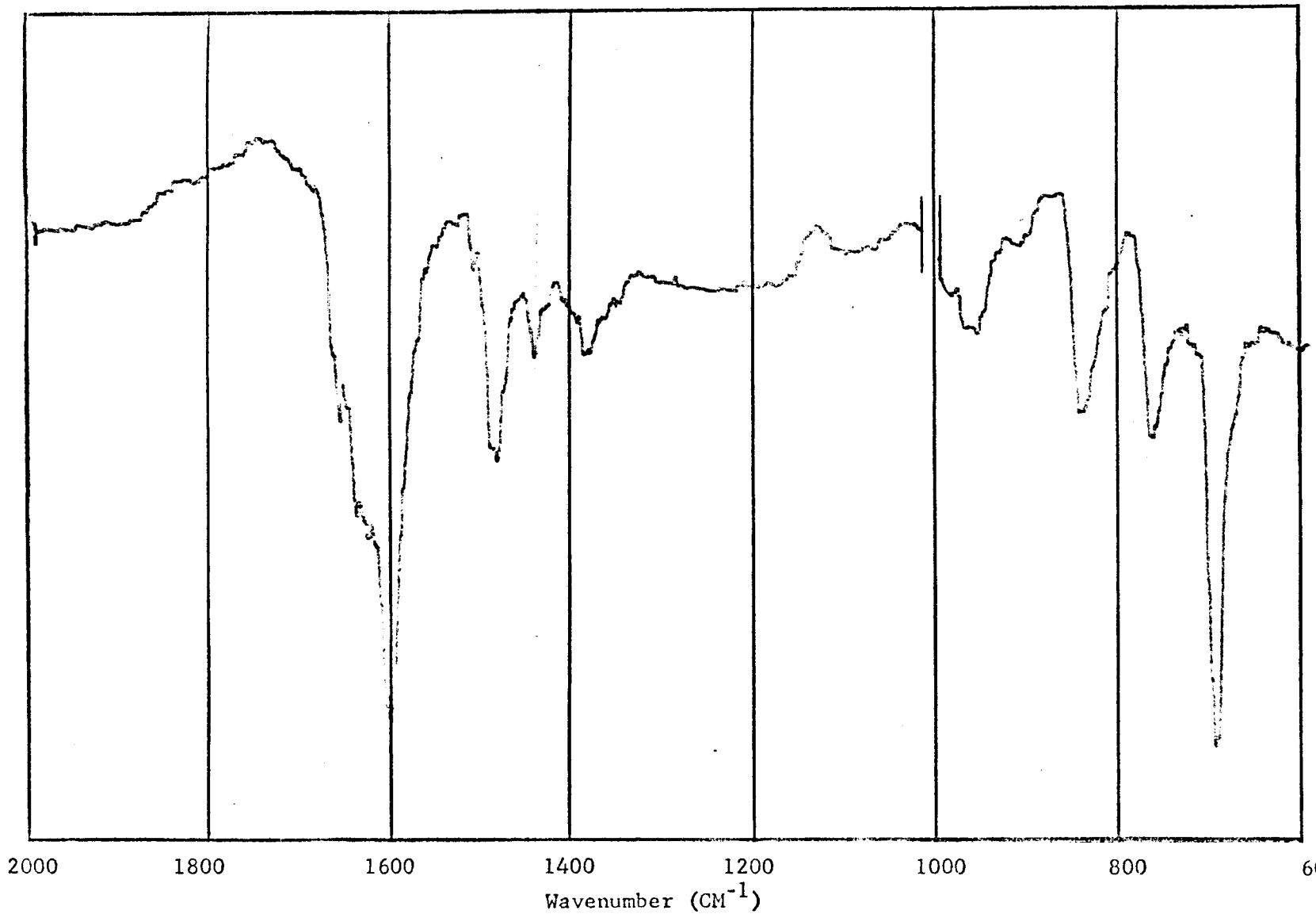
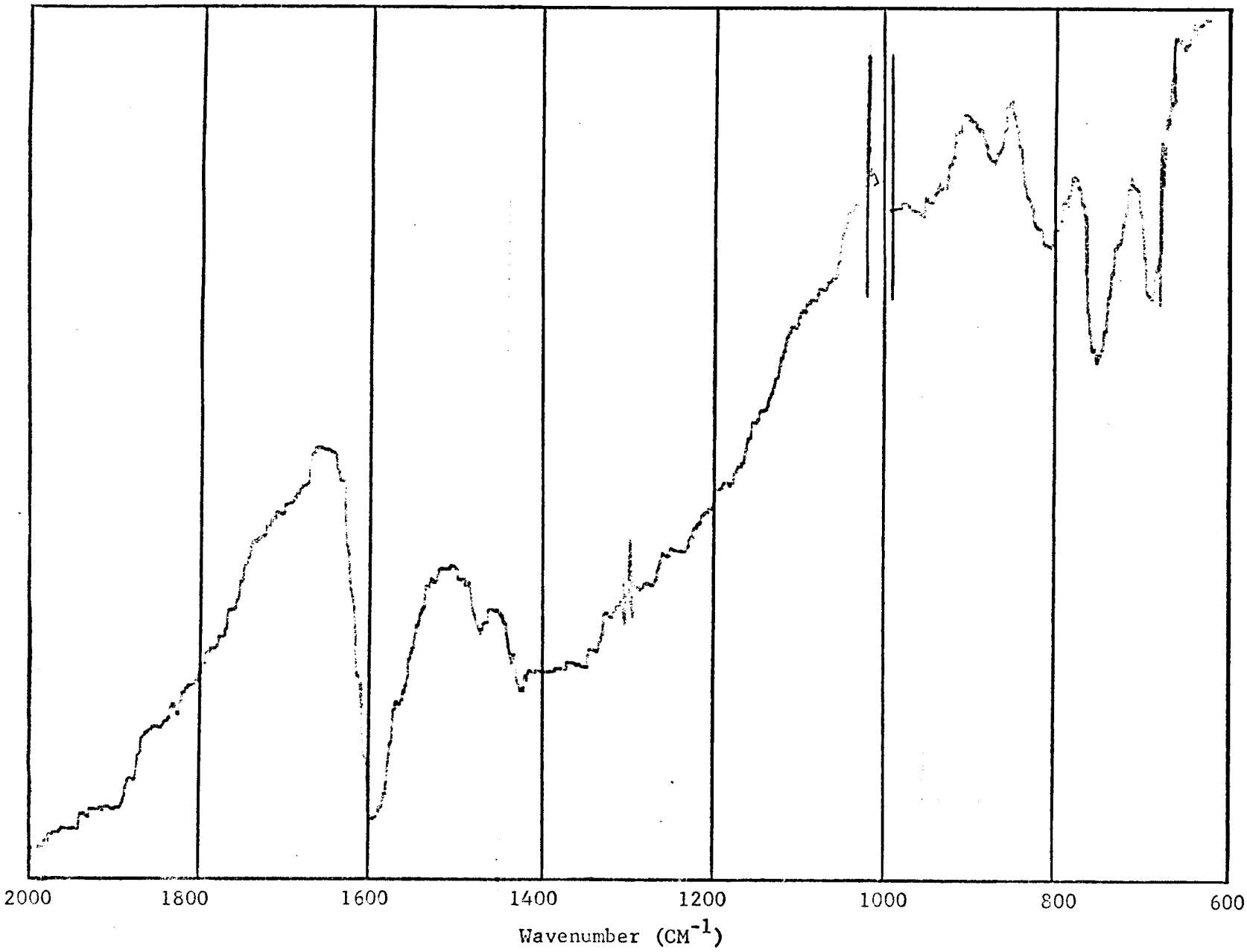
* SEE INSTRUCTION MANUAL FOR SCALE CORRECTION




Infrared Spectrum of Polymer DA-39-42 $\{HC\text{-}C_6H_4\text{-}CH{=}N\text{-}N\}$

Appendix No. 7




Infrared Spectrum of Polymer DA-39-10 $\{HC\text{-}C_6H_4\text{-}CH{=}N\text{-}N\}$

Appendix No. 8