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NASA GRANT NsG339

SEPTEMBER, 1966

DEPARTMENT OF CHEMISTRY

UNIVERSITY OF NOTRE DAME

NOTRE DAME, INDIANA 46556

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ON THE

FUNDAMENTAL STUDIES ON THE SYNTHESIS OF HEAT-RESISTANT POLYMERS

EXPLORATORY STUDIES ON THE DIRECT SYNTHESIS OF POLYMERIC SCHIFF BASES

PERFORMED

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BY

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DEPARTMENT OF CHEMISTRY

UNIVERSITY OF NOTRE DAME

NOTRE DAME, INDIANA, 46556

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FOREWORD

This report is a summary report of the researches performed under NASA Grant NsG339 for the period 31 January 1966 to 15 September 1966 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, Richard Schoenig and Thomas Huemmer. The technical assistance of R. Raghunath, P. R. Johnson and D. R. Rao for the period of June 15, 1966 to September 15, 1966 is acknowledged.

Date September 30, 1966

Signed G. F. D'Alelio

G. F. D'Alelio
Principal Investigator

ABSTRACT

Black polymeric Schiff bases, which pass through a fusible stage, have been prepared directly by reacting aryldiamines and aryldialdehydes in benzalaniline or in a mixture of aniline and benzaldehyde. The four isomeric polymers, the meta-meta-, the meta-para-, the para-meta- and the para-para-xylylidenephenylenediamine polymers have been prepared by these direct methods from the appropriate pairs of meta- and para-phenylenediamines and phenylenedialdehydes. The thermogravimetric analyses of these polymers compare very favorably with those of the polymers prepared by the bis-Schiff base exchange method.

TABLE OF CONTENTS

EXPLORATORY STUDIES ON THE DIRECT SYNTHESIS OF POLYMERIC SCHIFF BASES

I. Introduction.

It was shown in previous reports[1-5] that black, fusible polymeric Schiff bases could be prepared by a variety of methods from various reagents. Of these, the bis-Schiff base exchange method was shown to be rather satisfactory. The bis-Schiff base exchange reaction can be expressed as

$$\underset{\text{(I)}}{n\ ArN{=}HCAr'CH{=}NAr} + \underset{\text{(II)}}{n\ ArCH{=}NAr'N{=}HCAr} \longrightarrow$$

$$\underset{\text{(III)}}{ArN{=}\{HCAr'CH{=}NAr'N\}_{\overline{n}}{=}HCAr} + \underset{\text{(IV)}}{(2n-1)\ ArCH{=}NAr} \qquad \text{(eq. 1)}$$

Three steps are involved in this method, namely,

(1) The preparation of monomer (I) from a dialdehyde and a monoamine,

(2) The preparation of monomer (II) from a diamine and a monoaldehyde, and

(3) The reaction of monomer (I) with monomer (II) to eliminate the benzalaniline (IV) with the formation of the polymer (III).

Exploratory studies were undertaken in attempts to simplify this multi-step synthesis of the poly-Schiff bases by the direct syntheses from the dialdehydes, $Ar'(CHO)_2$, and the diamines, $Ar'(NH_2)_2$. It had been shown[1-3] that when the dialdehydes and diamines were reacted in solution in a large variety of solvents under various conditions, including the azeotropic distillation method, only insoluble, infusible, brick-dust polymers were obtained. However, black polymers could be obtained[1] by melting the reactants together in the absence of solvent but under these conditions the reaction is very difficult to control.

In a number of exchange reactions it has been observed[1-5] that when meta-phenylenediamine or dibenzylidene-m-phenylenediamine was used as one of the reagents, the fluid-melt condition during polymerization persisted for longer periods than when the corresponding para-derivatives were used. This result was attributed to the polymer structure resulting from the geometry of the meta isomer. Since the thermal stability of the polymer derived from m-phenylenediamine was of the same order of magnitude as that of the para polymer, consideration was given in this study to the use of the isomeric reagents not only of the diamine but also of the dialdehyde. Thus, four isomeric polymers are possible by reacting meta- or para-phenylenediamine with the meta- or para-arylene dialdehyde. In naming such polymers, the isomeric name of the amine will be used first, thus:

$$(n)\ m\text{-}Ar'(NH_2)_2 + (n)\ m\text{-}Ar'(CHO)_2 \longrightarrow H_2\{NAr'N{=}HCAr'CH\}_n{=}O + (2n-1)\ H_2O$$

meta-meta polymer (eq. 2)

$$(n)\ m\text{-}Ar'(NH_2)_2 + (n)\ p\text{-}Ar'(CHO)_2 \longrightarrow H_2\{NAr'N{=}HCAr'CH\}_n{=}O + (2n-1)\ H_2O$$

meta-para polymer (eq. 3)

$$(n)\ p\text{-}Ar'(NH_2)_2 + (n)\ m\text{-}Ar'(CHO)_2 \longrightarrow H_2\{NAr'N{=}HCAr''CH\}_n{=}O + (2n-1)\ H_2O$$

para-meta polymer (eq. 4)

$$(n)\ p\text{-}Ar'(NH_2)_2 + (n)\ p\text{-}Ar'(CHO)_2 \longrightarrow H\{NAr'N{=}HCAr'CH\}_n{=}O + (2n-1)\ H_2O$$

para-para polymer (eq. 5)

Accordingly the four reactions of equations 2-5 were investigated and the condensations were performed in solution and as melts.

A. A Two-Step Synthesis.

The benzalaniline obtained as the by-product of the bis-exchange method is responsible for the polymer remaining in solution.[1-4] This led to considering its use as a solvent in the direct condensation of diamines and dialdehydes. This reaction can be written as

$$n\ Ar'(NH_2)_2 + n\ Ar'(CHO)_2 \xrightarrow{C_6H_5N=CHC_6H_5}$$

$$H_2=\{NAr'N=HCAr'CH\}_n=O + (2n-1)\ H_2O \qquad \text{(eq. 6)}$$

This method would involve a two-step synthesis, namely,

(1) The preparation of benzalaniline (IV) from aniline and benzaldehyde,

(2) The condensation of the diamine with the dialdehyde in the presence of a suitable quantity of benzalaniline to form polymer (III) and to recover benzalaniline (IV).

B. A One-Step Synthesis.

In order to simplify the two-step synthesis even further, it was believed that the separate preparation of benzalaniline could be avoided by using stoichiometric quantities of aniline and benzaldehyde as the reaction medium. In this most direct method, the four reagents, namely, the diamine, the dialdehyde, the aniline and the benzaldehyde would be reacted together in a single step, for which the reaction can be written as

$$n\ Ar'(NH_2)_2 + n\ Ar'(CHO)_2 + m\text{-}ArNH_2 + m\text{-}ArCHO \longrightarrow$$

$$ArCH\{NAr'N=HCArCH\}_n=NAr + (m-1)\ ArN=HCAr + (2n+m)\ H_2O. \qquad \text{(eq. 7)}$$

In the synthesis given in equation 7, equimolar quantities of the dialdehyde and diamine would be used. Aniline and benzaldehyde would also be used in equimolar quantities; but the ratio of diamine-dialdehyde to aniline-benzaldehyde can be varied, if required.

II. Experimental.

A. Material.

The materials used were obtained from commercial sources and purified, when necessary, before use.

Terephthalaldehyde and isophthalaldehyde were purchased from Aldrich Chemical Company; aniline, m-phenylenediamine and p-phenylenediamine were

obtained from Matheson, Coleman and Bell Division of the Matheson Company. Benzaldehyde was purchased from J.T. Baker Chemical Company. The nitrogen used was high purity lamp-grade nitrogen purchased from the Cleveland Wire Division of the General Electric Company.

1. Aniline.

Reagent grade aniline was vacuum-distilled through an eighteen-inch column packed with glass-helices and equipped with a partial take-off head. Distillation was performed under nitrogen using a capillary bleeder at a reflux ratio of six to one. The middle fraction boiling at 87°C/24 mm. was collected, and stored under nitrogen in a brown ground-glass stoppered bottle.

2. Benzaldehyde.

Reagent grade benzaldehyde was vacuum-distilled through an eighteen-inch column packed with glass-helices and equipped with a partial take-off distillation head. Distillation was performed under nitrogen, using a capillary bleeder, at a reflux ratio of six to one. The middle fraction boiling at 76.5°C/21 mm. was collected and stored under nitrogen in a brown ground-glass stoppered bottle.

3. meta-Phenylenediamine.

The commercial grade diamine was very impure and it was purified by distillation at reduced pressure in a nitrogen atmosphere. The middle portion was collected and melted at 62-63°C. The diamine was stored under nitrogen in a brown ground-glass stoppered bottle.

4. para-Phenylenediamine.

The commercial grade was very impure and it was purified by distillation at reduced pressure in a nitrogen atmosphere. The melting point of the purified para-phenylenediamine was 139°C. The diamine was stored under nitrogen in a brown ground-glass stoppered bottle.

5. Terephthalaldehyde.

The reagent grade terephthalaldehyde was recrystallized from distilled water and dried in a vacuum oven at room temperature at 15 mm. Hg. It melted sharply at 116°C.

6. Isophthalaldehyde.

The purchased reagent grade isophthalaldehyde melted sharply at 89.5°C and was used without further purification.

7. Benzalaniline.

Benzalaniline was prepared and purified by procedures previously reported.[1]

B. Polymerizations.

1. Solution Polymerizations (DA-45-3).

Into a 500-ml. three-neck, round-bottom flask equipped with a water condenser, a Dean-Stark trap and a magnetic stirrer was placed 250 ml. of benzene and 0.02 mole of the appropriate diamine. After heating the mixture to reflux, 0.02 mole of the dialdehyde in 150 ml. of benzene was added, dropwise, to the hot diamine solution. The reaction mixture was refluxed for twenty-four hours and the azeotroped water collected in the Dean-Stark trap. During the reaction, the polymer appeared as a precipitate; when water was no longer collected in the trap, the mixture was cooled to room temperature and the precipitate removed by filtration, washed with hot benzene and dried in a vacuum oven at room temperature.

The four polymers, namely, the para-para, para-meta, meta-meta and meta-para polymers were in the form of yellow, insoluble, low molecular weight brick-dusts; they appear to be mixtures of dimers and trimers whose end-groups are aldehydes, amines or both. The analytical data is given in Table I.

Table I

Analyses of Isomeric Low Molecular Weight Polymers

Polymer	% Yield	Analyses*		
		% C	% H	% N
para-para	98.4	74.93	5.24	15.43
para-meta	84.3	75.28	5.64	15.54
meta-meta	91.2	74.21	5.76	15.60
meta-para	82.6	74.76	5.53	15.66

* Per cent calc'd for

$C_{22}H_{20}N_4O$: C, 74.20; H, 5.71; N, 15.70.

$C_{22}H_{16}N_2O_2$: C, 77.60; H, 4.70; N, 8.50

$C_{20}H_{21}N_4$: C, 75.70; H, 6.64; N, 17.65.

2. Melt Polymerizations of Diamines and Dialdehydes.

a. meta-Phenylenediamine and Isophthalaldehyde (DA-45-33).

Purified m-phenylenediamine (0.54 g., 0.005 mole) was ground together with isophthalaldehyde (0.67 g., 0.005 mole) in a mortar and pestle. The mixed reactants were then transferred to a 125-mm. reaction tube equipped with a side-arm to which was attached a condenser, vacuum take-off and receiver. A nitrogen inlet tube was inserted in the top of the reaction tube, and after the oxygen in the system was displaced with nitrogen gas, the tube assembly was inserted into an aluminum block preheated to 300°C. The block was controlled at this temperature by means of a proportional null electronic controller. The reactants immediately softened but did not melt, and a clear, colorless liquid refluxed within the tube. A small amount of sublimed material was also observed in the uppermost portion of the reaction tube. Heating was continued at atmospheric pressure under nitrogen for four hours. Then the pressure was reduced to 5 mm. Hg and heating continued for another two hours at 300°C. A porous,

black polymer (0.993 g., 96.7% yield), was obtained in the lower portion of the reaction tube together with some yellow condensate on the walls of the upper portion of the reaction tube.

b. para-Phenylenediamine and Isophthalaldehyde (DA-45-35).

The procedure of DA-45-33 was repeated except that para-phenylenediamine was substituted for meta-phenylenediamine. No melting of the reactants was observed, and the color of the mixture changed from a brilliant yellow to an olive shade after heating for one hour at 300°C. Heating was continued for another four hours at 300°C at atmospheric pressure, and then the pressure reduced to 1 mm. Hg. After heating for another two hours, the polymer (0.935 g., 91% yield) was removed from the reaction tube; the bottom of the polymer mass was shiny black, and the interior was greenish-brown and not fused to the outer surface.

c. meta-Phenylenediamine and Terephthalaldehyde (DA-45-37).

The procedure of DA-45-33 was repeated except that terephthalaldehyde was substituted for isophthalaldehyde. The reactants did not melt although the solid darkened gradually and some white-yellow condensate appeared at the top of the reaction tube. After heating for four hours at 300°C, the pressure was reduced to 1 mm. Hg. and held there for a period of two hours. The polymer mass (0.831 g., 85% yield) was porous and brown on the top, black on the bottom and in the interior.

d. para-Phenylenediamine and Terephthalaldehyde (DA-45-38).

The procedure of DA-45-37 was repeated except that para-phenylenediamine was used instead of meta-phenylenediamine. The reactants did not melt, although they changed gradually to a yellow-brown color and some yellow condensate formed at the top of the reaction tube. After heating for four hours at 300°C,

at atmospheric pressure; the pressure was reduced to 1 mm. Hg. and held there for a period of two hours. The polymer mass (0.883 g.; 86% yield) was light brown on the top, and porous, dark-brown on the bottom and in the interior.

None of the polymers obtained by the direct reaction of any of the pairs of the isomeric diamines with the isomeric dialdehydes were homogeneous throughout. Only the meta-diamine/meta-dialdehyde pair of reagents softened perceptibly when reacted at 300°C, and even in this case, a clear melt was not obtained though fusion was apparent. However, the meta-diamine/meta-dialdehyde combination afforded the most uniform polymer. The meta-diamine/para-dialdehyde polymer appeared to be more homogeneous than the para-meta polymer, which in turn was better than the para-para polymer. These polymers may be rated in the following order: meta-meta > meta-para > para-meta > para-para.

3. Melt Polymerization of Diamines and Dialdehydes in Benzalaniline.

The general procedure used was similar to that used for the direct condensation of the diamine and the dialdehyde (DA-45-33), except that the calculated amount of benzalaniline corresponding to 20% or 33% of the total weight of the reactants was added to the mixture and ground in a mortar and pestle. Then the ground mixture was transferred to the reaction tube and heated for three hours at 300°C before reducing the pressure to 1.5 mm. Hg. for an additional heating period of two and one-half hours. The temperature was then increased to 400°C and heating continued at 1.5 mm. Hg. for eighteen hours.

The conditions in these and in the other following direct syntheses were arbitrarily chosen after a few preliminary experiments and are not necessarily the conditions which would produce the best polymers. The most suitable conditions will have to be determined in a developmental program. The primary purpose of this study was to establish whether or not these new systems would

produce fusible, black polymers which could be converted to the infusible, higher molecular weight polymers.

In those cases in which benzalaniline comprised 33% of the mixture, complete or partial liquifaction of the mixture occurred either on mixing or on heating the reagents. None of the mixtures which contained 20% benzalaniline melted even when heated, although they softened and the color of the reaction mixture darkened rapidly. The results of these reactions are given in Table II and compared to the reactions in which benzalaniline was omitted.

Table II

Effect of Benzalaniline on Yield and Nature of Isomeric Polymers from Diamines and Dialdehydes

% Benzalaniline of Mixture	meta-meta	meta-para	para-meta	para-para
0	96.7% shiny black no melt	85.0% black-brown no melt	91.0% greenish-brown no melt	86.1% brown no melt
20	95.5% shiny black some melting	84.2% black powdery no melt	86.4% black powdery no melt	88.8% dark brown powder no melt
33	105.0% shiny black melt	90.6% shiny black melt	89.8% shiny black melt	101.2% shiny black melt

4. Polymerization of Diamine, Dialdehyde, Aniline and Benzaldehyde.

a. General Procedure.

Equimolar quantities of the diamine and the dialdehyde were weighed on a Mettler Balance to the fourth decimal place, mixed thoroughly in a mortar and pestle, and transferred to the ground-glass reaction tube[1] fitted with a nitrogen inlet and a condenser, and the flow of nitrogen started. The selected amounts of benzaldehyde and aniline were then introduced into the reaction tube

by means of a 0-2 ml. graduated pipette. Then the tube was inserted in the aluminum block[1] already preheated to 120°C, and the mixture heated for one hour at this temperature. Then the apparatus was converted to a distillation system and water and benzylaniline distilled from the mixture. The heating schedule for the polymerizations was as follows:

Time, hours	Temperature, °C	Pressure, Hg.
1	120	atm.
1	200	atm.
4	300	atm.
4	300	1.5 mm.
18	400	1.5 mm.

In all cases, as shown in Table III, black polymers were obtained; however,

Table III

Schiff Base Polymers Prepared by a One-Step Direct Synthesis

Experiment Number	Reactants	Mole Ratio	Per Cent Yield at 400°C
DA-46-72 DA-46-74 DA-46-48 DA-46-49	m-Phenylenediamine, Isophthalaldehyde, Aniline, Benzaldehyde.	1:1:1:1 1:1:1:1 1:1:2:2 1:1:3:3	131.0 133.0 164.0 182.0
DA-46-40 DA-46-46 DA-46-47	m-Phenylenediamine, Terephthalaldehyde, Aniline, Benzaldehyde.	1:1:1:1 1:1:2:2 1:1:3:3	112.0 153.0 181.0
DA-46-41 DA-46-44 DA-46-54	p-Phenylenediamine, Isophthalaldehyde, Aniline, Benzaldehyde.	1:1:1:1 1:1:2:2 1:1:3:3	82.8 79.4 113.0
DA-46-55 DA-46-53 DA-46-42	p-Phenylenediamine, Terephthalaldehyde, Aniline, Benzaldehyde.	1:1:1:1 1:1:2:2 1:1:3:3	127.0 158.0 120.0

when 1:1:1:1 ratio of reactants was used, only the meta-meta system produced a satisfactory melt. The meta-para system was next, followed by the para-meta system, and the para-para system was last. This order parallels that found for the syntheses from the diamine, dialdehyde and benzalaniline. However, all systems produced good melts and shiny, black polymers when the ratio of reactants was at least 1:1:2:2. Ratios intermediate to 1:1:1:1-1:1:2:2, for example, 1:1:1.5:1.5, were not investigated.

The appearance of the meta-meta polymer indicated that the amounts of aniline and benzaldehyde could be reduced below a 1:1 ratio, and this was investigated. The lowest ratio studied which appeared to give suitable melts were 1:1:0.5:0.5, and the data given in Table IV.

Table IV

Meta-Meta Schiff Base Polymers Prepared at a 0.5:0.5 Aniline to Benzaldehyde Ratio

Experiment Number	Reactants	Mole Ratio	Per Cent Yield at 400°C
DA-46-50	m-Phenylenediamine, Isophthalaldehyde, Aniline, Benzaldehyde	1:1:0.5:0.5	111.0
DA-46-51	m-Phenylenediamine, Terephthalaldehyde, Aniline, Benzaldehyde.	1:1:0.5:0.5	111.0

Representative samples of the polymers prepared at 400°C were powdered in a mortar and pestle, then reduced to a fine powder in a stainless steel vibrator and transferred to a quartz reactor, which was then swept out with deoxygenated nitrogen. The samples were then heated at 600°C for one hour at atmospheric pressure followed by four hours at 1.5 mm. Hg. The weights of each sample

before and after heating at 600°C were determined and the yields of polymer condensed to 600°C calculated from these values are shown in Table V.

Table V

Yield of Polymers After Heating to 600°C

Experiment Number	Reactants	Mole Ratio	Per Cent Yield at 400°C	Per Cent Yield at 600°C
DA-46-72-H600	m-Phenylenediamine,	1:1:1:1	131.0	109.0
DA-46-74-H600	Isophthalaldehyde,	1:1:1:1	133.0	107.0
DA-46-48-H600	Aniline,	1:1:2:2	164.0	132.0
DA-46-49-H600	Benzaldehyde.	1:1:3:3	182.0	114.0
DA-46-40-H600	m-Phenylenediamine,	1:1:1:1	112.0	67.5
DA-46-46-H600	Terephthalaldehyde,	1:1:2:2	153.0	130.0
DA-46-47-H600	Aniline,	1:1:3:3	181.0	155.0
	Benzaldehyde.			
DA-46-41-H600	p-Phenylenediamine,	1:1:1:1	82.8	70.1
DA-46-44-H600	Isophthalaldehyde,	1:1:2:2	79.4	67.8
DA-46-54-H600	Aniline,	1:1:3:3	113.0	93.0
	Benzaldehyde.			
DA-46-55-H600	p-Phenylenediamine,	1:1:1:1	127.0	101.0
DA-46-53-H600	Terephthalaldehyde,	1:1:2:2	158.0	68.4
DA-46-42-H600	Aniline,	1:1:3:3	120.0	99.6
	Benzaldehyde.			

The thermogram of meta-meta polymer, (DA-46-74), prepared from the 1:1:1:1 ratio of reagents condensed to 400°C is shown in Figure 1, and the same polymer, (DA-46-74-H600), postheated to 600°C is given in Figure 2. The thermogram of the para-para polymer, (DA-46-53), prepared from the 1:1:2:2 ratio of reagents condensed to 400°C is shown in Figure 3, and the same polymer, (DA-46-53-H600), postheated to 600°C is given in Figure 4.

In these thermograms,[3] curve 1 is for the polymer heated in a nitrogen atmosphere, curve 2 is for the polymer when recycled in nitrogen and curve 3 is for the recycled polymer heated in air. These thermograms are in excellent agreement with thermograms of the meta-para polymers and in good agreement with the

para-para polymers previously prepared and reported[3] as appendices numbers 1, 3, 7, 9 and 55 in NASA-Report Number N66-11745.

III. Summary and Conclusions.

Previous conclusions have been confirmed, that (1) the solution polymerization of an aryl diamine with an aryl dialdehyde is not a promising method of synthesis of Schiff base polymer, and (2) melt polymerizations of these same reagents is likewise unsatisfactory even though an isomer effect is evident. Two methods for the direct synthesis of poly-Schiff bases from aryl diamines and aryl dialdehydes have been achieved. The first method is a two-step method and utilizes benzalaniline as the reaction medium. The ease of synthesis and the amount of benzalaniline required is related to the structures of the polymer resulting from the isomeric structures of the aryl diamines which are reacted with the aryl dialdehydes. The diminishing order is meta-meta $>$ meta para $>$ para $>$ para-para. The second method is an even more direct one-step synthesis, which has been established by reacting the diamine, the dialdehyde, the aniline and the benzaldehyde in molar ratios varying from 1:1:1:1 to 1:1:3:3. The meta-meta polymers are readily prepared in a 1:1:1:1 ratio and for this polymer this method shows promise also at a 1:1:0.5:0.5 ratio. The ease of synthesis of the isomeric polymers parallels that found for the related synthesis using the diamine and dialdehyde in benzalaniline, and the ratio of reactant 1:1:2:2 is indicated for the meta-para, para-meta and para-para polymers. The polymerization conditions used in the two successful direct syntheses were arbitrarily chosen after a few preliminary experiments and undoubtedly can be improved.

Thermogravimetric analyses of some of the polymers prepared by this direct method, indicate that the polymers compare most favorably with those previously prepared by the bis-Schiff base exchange method.

IV. References.

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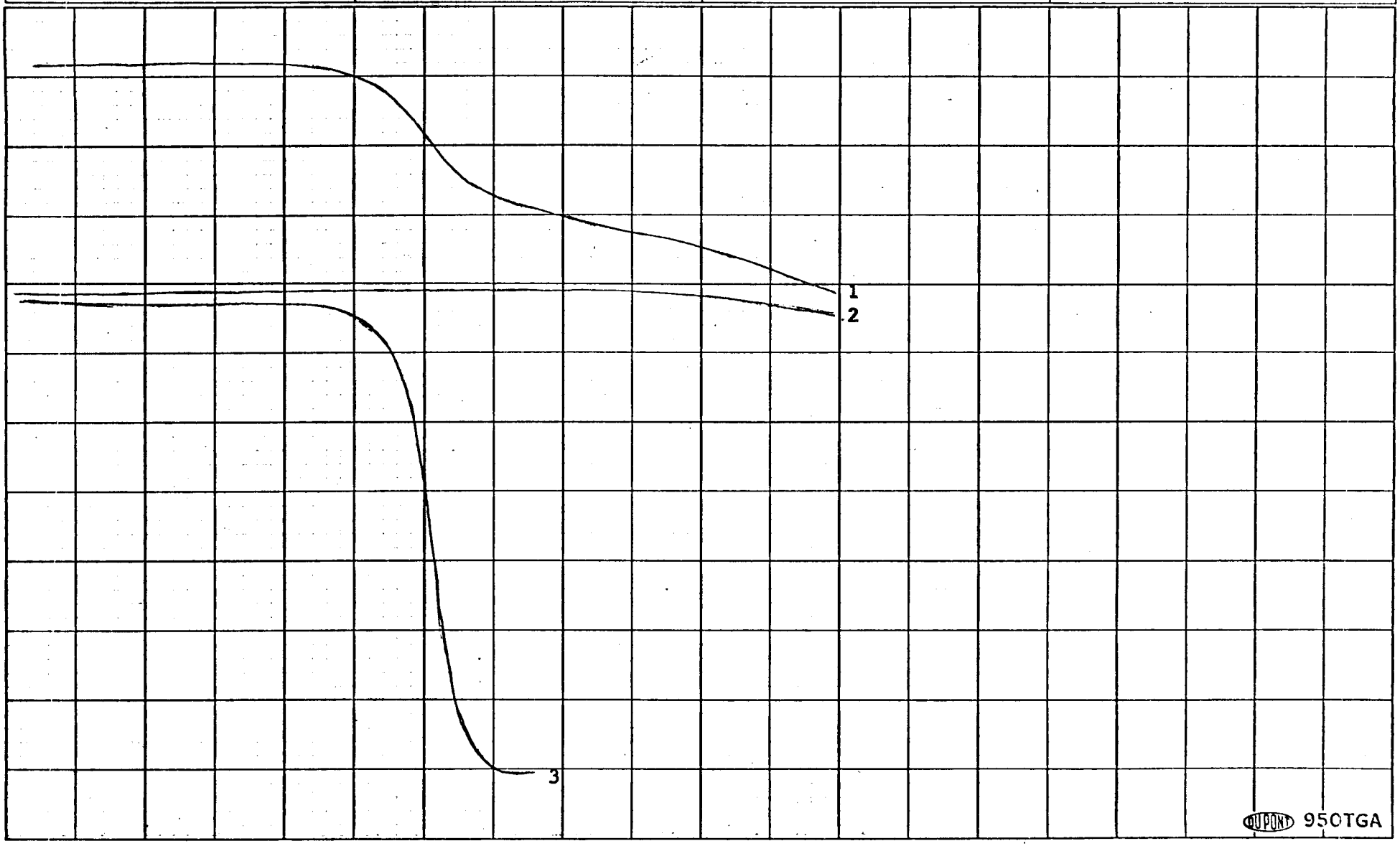
PART NO. 950017

E I DU PONT DE NEMOURS & CO. (INC.)
INSTRUMENT PRODUCTS DIVISION
WILMINGTON 98, DELAWARE

SAMPLE: DA-46-74	X-AXIS	Y-AXIS	RUN NO. ____ DATE ____
m,m-[HCC$_6$H$_4$CH=NC$_6$H$_4$N]$_n$	TEMP. SCALE 200 °C / inch	SCALE 2 mg. / inch	OPERATOR RKS
	SHIFT 0 inch	(SCALE SETTING X 2)	HEATING RATE 15 °C / min.
SIZE 10.59 mg.	TIME SCALE (ALT.) 0	SUPPRESSION 0 mg.	ATM. 1) N_2; 2) N_2; 3) air
			TIME CONSTANT 2 sec.



WEIGHT, mg.

TEMPERATURE*, °C

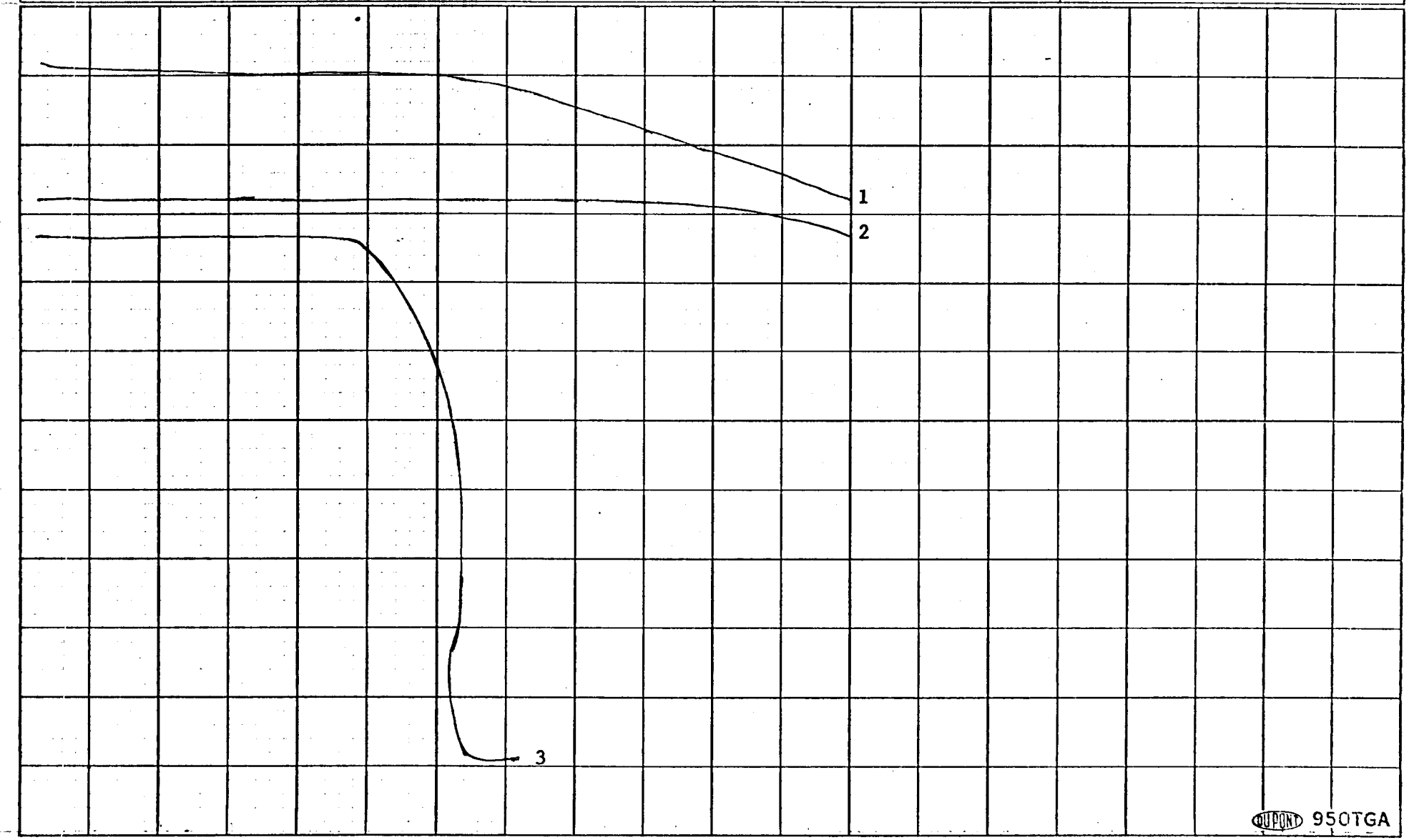
* APPLY CORRECTION FOR NON-LINEARITY OF CHROMEL-ALUMEL THERMOCOUPLES

Figure 1

PART NO. 950017

E. I. DU PONT DE NEMOURS & CO. (INC.)
INSTRUMENT PRODUCTS DIVISION
WILMINGTON 98, DELAWARE

SAMPLE: DA-46-74-H600 m,m=$\{HCC_6H_4CH=NC_6H_4N\}_n$ **SIZE** 10.23 mg.	**X-AXIS** **TEMP. SCALE** 200 °C/inch **SHIFT** 0 inch **TIME SCALE (ALT.)** 0	**Y-AXIS** **SCALE** 2 mg./inch (SCALE SETTING X 2) **SUPPRESSION** 0 mg.	**RUN NO.** ____ **DATE** ____ **OPERATOR** RKS **HEATING RATE** 15 °C/min. **ATM.** 1) N_2; 2) N_2; 3) air **TIME CONSTANT** 2 sec.



WEIGHT, mg.

TEMPERATURE*, °C

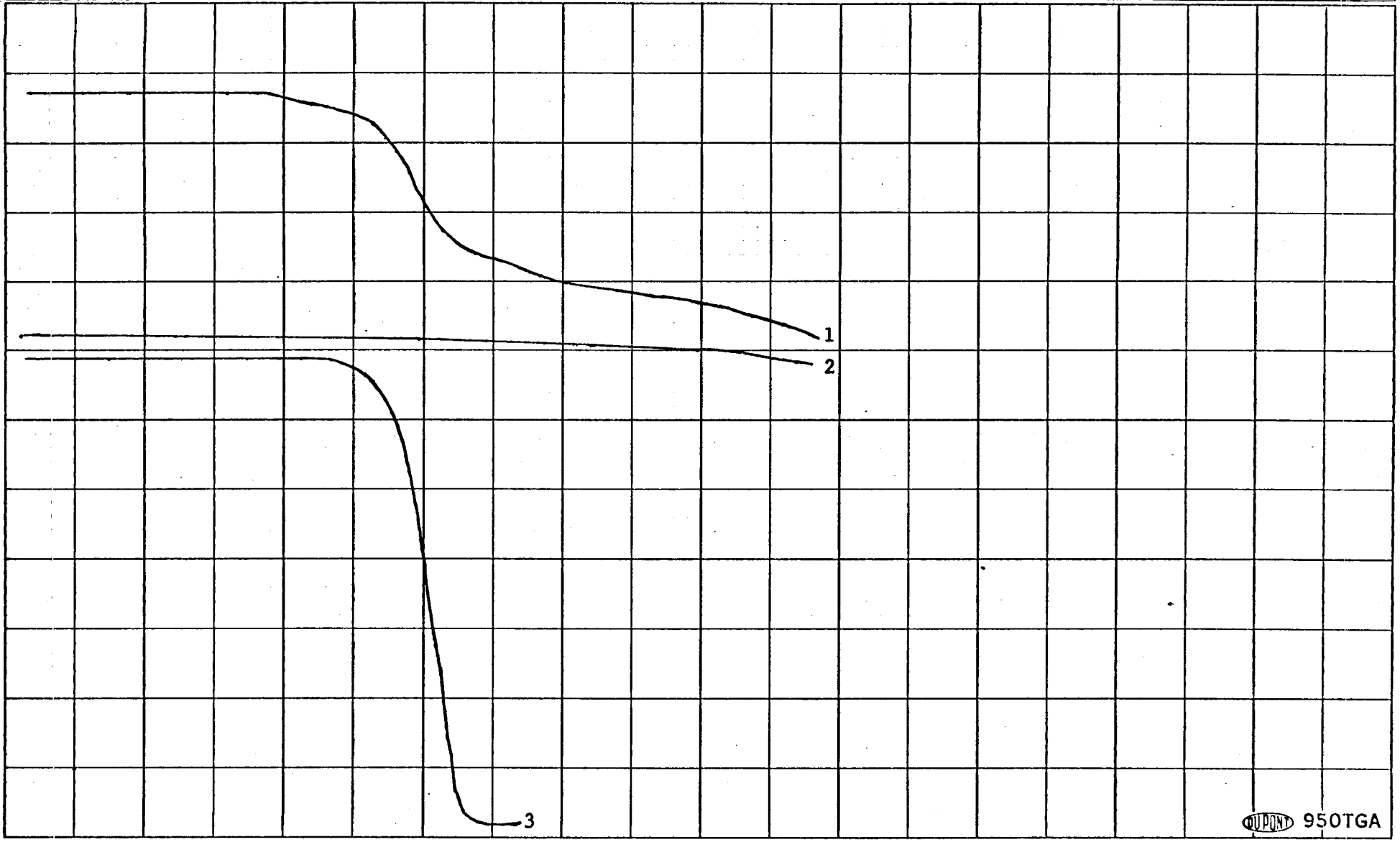
* APPLY CORRECTION FOR NON-LINEARITY OF CHROMEL-ALUMEL THERMOCOUPLES

Figure 2

PART NO. 951071

E. I. DU PONT DE NEMOURS & CO. (INC.)
INSTRUMENT PRODUCTS DIVISION
WILMINGTON 98, DELAWARE

SAMPLE: DA-46-53	X-AXIS	Y-AXIS	RUN NO. ____ DATE ____
p,p=[HCC$_6$H$_4$CH=NC$_6$H$_4$N]$_n$	TEMP. SCALE 200 °C / inch	SCALE 2 mg. / inch	OPERATOR RKS
	SHIFT 0 inch	(SCALE SETTING X 2)	HEATING RATE 15 °C / min.
SIZE 10.83 mg.	TIME SCALE (ALT.) ____	SUPPRESSION 0 mg.	ATM. 1) N_2; 2) N_2; 3) air
			TIME CONSTANT 2 sec.



WEIGHT, mg.

TEMPERATURE*, °C

* APPLY CORRECTION FOR NON-LINEARITY OF CHROMEL-ALUMEL THERMOCOUPLES

Figure 3