NASA CR-134463
SN-281-F

FLAME RETARDANT POLYPHOSPHAZENES

prepared by

K. L. PACIOREK, D. W. KARLE, and R. H. KRATZER

ULTRASYSTEMS, INC.
Newport Beach, California

prepared for

NATIONAL AERONAUTICS AND SPACE ADMINISTRATION

NASA Lewis Research Center
Contract NAS3-16768

Tito T. Serafini, Project Manager

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FOREWORD

This Final Report describes the work performed by the Chemicals and Materials Research Department, Ultrasystems, Inc. during the period from 26 June 1972 to 27 July 1973 under Contract NAS3-16768 on Flame Retardant Polyphosphazenes. The investigations were carried out by K. L. Paciorek, D. W. Karle, and R. H. Kratzer, project manager, with assistance from J. H. Nakahara. This contract was administered by the NASA Lewis Research Center with Dr. Tito T. Serafini as the project manager.

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1. SUMMARY

This is the final report describing work performed by Ultrasystems, Inc. for the National Aeronautics and Space Administration, Lewis Research Center, under Contract NAS3-16768.

The objective of the program was to prepare a series of polymeric compositions intended for use as laminating resins which would be flame retardant and would not afford toxic products on oxidative thermal degradation. The polymerization process was the reaction of a suitable diazide with a tertiary diphosphine resulting in the formation of P=N linkages.

To attain the objectives of subject contract (1) two monomers were purchased and four synthesized; all were subjected to appropriate characterizations, (2) selected model compounds were prepared and studied to provide insight into the polymerization processes and thermal behavior, (3) polymerizations were carried out under a variety of conditions and all products were characterized by appropriate methods, and (4) the oxidative thermal behavior and the flammability of four of the polymeric compositions prepared were investigated; these studies included smoke density measurements and the quantitative determination of all decomposition products formed.

The first phase of the work involved the synthesis of the monomers which were unavailable commercially, namely 2,4-diazido-6-phenyl-s-triazine, 2,4-bis(azidodiphenylphosphazo)-6-phenyl-s-triazine, 2,4-bis(diphenylphosphino)-6-phenyl-s-triazine, and 2,4-bis(phenyl-p-diphenylphosphino)-6-phenyl-s-triazine. All the monomers were fully characterized, including differential scanning calorimetry. Concurrently three model compounds representing the

projected polymer systems were prepared, characterized, and subjected to thermogravimetric analyses. Their thermal behavior corresponded fairly closely to that of the analogous polymeric systems.

The polymerizations were conducted using three bisphosphines and two diazides. Both diazides contained a phenyl-s-triazine moiety, as did one of the bisphosphines studied. The other two bisphosphines were of an aliphatic nature. Six polymer systems were prepared. Most of the polymerizations were performed in dilute solutions; however in view of the low reactivity of 2,4-bis(azidodiphenylphosphazo)-6-phenyl-s-triazine the reactions involving this comonomer had to be carried out practically in the absence of solvent. High molecular weight polymers were not obtained. Based on elemental analyses and molecular weight determinations it would seem that cyclic materials were predominantly, if not exclusively, formed. The thermal stability as determined by thermogravimetric analysis was in agreement with that which could be projected for the monomers employed. The data obtained indicate that the thermal stability of the model compounds and polymeric materials prepared was almost exclusively dictated by the nature of the bisphosphine employed, thus making the bisphosphines the thermal stability limiting factor. Use of truly aromatic bisphosphines should increase the thermal stability of the projected polymer systems significantly above 350°C, which is the thermal stability limit if aliphatic linkages are present.

Isothermal gravimetric analyses in air revealed that the two materials containing 1,4-bis(diphenylphosphino) butane do not lose any weight at 200°C during 96 hr periods, but decompose at 250°C leaving after the same periods residues amounting to 25 and 55%, respectively, of the original sample weight. The material producing the higher char

yield was prepared using 2,4-diazido-6-phenyl-s-triazine as co-monomer, the material leaving a 25% residue was synthesized using 2,4-bis(azidodiphenylphosphazo)-6-phenyl-s-triazine. Two other compositions based on 1,2-bis(diphenylphosphino) ethane and 2,4-bis(diphenylphosphino)-6-phenyl-s-triazine degraded already at 200°C, the former after 70 hr (85% residue after 118 hr), the latter began to decompose immediately yielding 42% char after 118 hr.

These same four materials failed to sustain a flame when horizontally mounted specimens were exposed to a Bunsen burner flame for 15 sec. Self extinguishment occurred as soon as there was no contact between resin and flame. During thermal oxidative degradation testing in a stagnation burner in air, with heating block and air temperatures of 500°C, all but one of the four compositions studied autoignited. The material which failed to autoignite under these conditions was obtained from the reaction of 1,4-bis(diphenylphosphino) butane and 2,4-bis(azidodiphenyl-phosphazo)-6-phenyl-s-triazine. The main toxic substances found among the decomposition products were hydrogen cyanide (0.01 - 0.74%) and benzene (5.6 - 10.5% of the original sample weight); the material which did not autoignite producing the smaller of the quantities listed within brackets. The accepted threshold limit values for hydrogen cyanide and benzene are 11 and 80 mg/m^3, respectively.

2. INTRODUCTION

Many factors influence the flame retardance of high polymers. High thermal stability, molecular weight, and char yield and the chemical nature of the repeating unit of the polymer backbone, contribute to flame resistance. One important method to flameproof a material is to incorporate elements or components containing elements which are known to impart flame resistance.

The elements known to impart flame resistance are members of the third, fifth, and seventh main groups of the periodic table, specifically boron, nitrogen, phosphorus, antimony, fluorine, chlorine, and bromine. Of these boron (ref. 1) and antimony (ref. 2,3) are in all cases used as additives only, whereas nitrogen, phosphorus, and the halogens are incorporated both as additives and as constituents of the base polymer. For a flame retardant to be most effective at fire temperature it is considered mandatory that it is of the reactive type. This means that the element imparting flame resistance must be bonded within or to the polymer backbone. The flame retarding element, furthermore, should contribute to increased thermal stability and char yield, which requires that it remains in the char and not be eliminated in the early stages of the oxidative thermal decomposition process.

This latter aspect is one of the reasons why the halogens are not very effective flame retardants for thermally stable polymers. Because halogens are monovalent it may be expected that they are more readily evolved during decomposition than multiply bonded elements. Thus, polyvinyl chloride (ref. 4) was found to lose practically all its chlorine via dehydrohalogenation at temperatures up to 280°C leaving a residue which was oxidized by air in a strongly exothermic reaction.

The same was found to be true for nylon reinforced polyvinyl chloride (ref. 5,6), except that decomposition onset temperatures were as low as 150°C. Another drawback of the halogens is that they are evolved during decomposition in form of highly toxic substances. If hydrogen is present in the materia: he halogens are evolved mainly as hydrogen halides, the recommended threshold limit values (TLV) (ref. 7) for which are, e.g., 3 and 5 ppm, respectively, for HF and HCl. If hydrogen is not present in the material, as is the case with polytetrafluoroethylene fluorine is liberated as carbonyl fluoride which is subsequently hydrolyzed to hydrogen fluoride by reaction with atmosphermic moisture (ref. 8, 9). Presumably, a perchlorinated analogue to polytetrafluoroethylene would thus form phosgene (TLV = 0.1 ppm), which again would be hydrolyzed by atmospheric moisture to carbon dioxide and hydrogen chloride.

In view of the shortcomings of halogen containing polymers (relatively ready elimination and formation of toxic decomposition products), the incorporation of nitrogen and phosphorus for the purposes of flameproofing appears to be the preferred safe procedure. The flame retarding capability of nitrogen in the form of triazine derivatives (ref. 10, 11) and in particular of phosphorus-nitrogen combinations (ref. 12-15) has been amply demonstrated. In addition, both elements have been found to contribute to char formation and phosphorus has been reported (ref. 16) to produce particularly strong chars when contained in an aromatic structure or when substituted by aromatic moieties such as phenyl groups. Of considerable importance is the finding (ref. 17, 18) that phosphorus-nitrogen combinations, so-called phosphazenes, do not form toxic or otherwise hazardous products upon oxidative thermal decomposition.

The ultimate objective of this work was to develop flame retardant polymers containing triazine and phosphazene (P=N) moieties and to establish that flame resistant polymers could be produced which did not form toxic products originating from the flame retarding groups. The specific approach taken to introduce the phosphazene linkage was based on the finding by Staudinger (ref. 19) that this linkage is formed readily with concurrent nitrogen evolution in the interaction between tertiary phosphines and azides. Accordingly, two diazides containing the triazine nucleus and three bis-tertiary phosphines, one of which was also triazine derived, were employed as the monomers for the synthesis of six novel compositions.

Overall the program thus consisted of (1) preparation of monomers, (2) synthesis of selected model compounds to evaluate reactivities and thermal stabilities, (3) polymerizations of monomers, and (4) oxidative thermal degradation of the polymers formed to determine their flame retarding characteristics and to establish the absence of toxic or corrosive substances among the decomposition products.

3. EXPERIMENTAL DETAILS AND PROCEDURES

All solvents used were reagent grade and were dried and distilled prior to use. Operations involving moisture or air sensitive materials were carried out either in an inert atmosphere enclosure (Vacuum Atmospheres Model HE-93B) or under nitrogen by-pass. The commercially available starting materials were usually purified by distillation, crystallization, or other appropriate means.

Molecular weights (MW) were determined in chloroform solutions using a Mechrolab Osmometer Model 302 at concentrations of 4-6 mg/ml. Infrared (IR) spectra were recorded on double mulls (Kel-F oil No. 10 and Nujol) using a Perkin-Elmer Corporation Infrared Spectrophotometer Model 21. Differential scanning calorimetry (DSC), thermogravimetric (TGA), and isothermal gravimetric analyses (ITGA) were performed on a duPont 951/990 Thermal Analyzer.

All materials synthesized were dried at 100°C or higher in vacuo before physical and chemical characterization unless their melting point was lower than this temperature. The melting points of the monomers were determined in nitrogen filled or evacuated sealed capillaries, the softening and melting points of the polymers were obtained using a Fisher-Johns apparatus. The elemental analyses were performed by Schwarzkopf Microanalytical Laboratory, Woodside, New York.

Since both the structural formulae and the appropriate chemical nomenclature for the five monomers used during this program are complex and cumbersome these five compounds have been coded to aid in clarity of presentation throughout this report. The codes used are as follows:

TDA $N_3-C_3N_3\Phi-N_3$

2,4-diazido-6-phenyl-s-triazine

TDPA $N_3-P\Phi_2=N-C_3N_3\Phi-N=P\Phi_2-N_3$

2,4-bis(azidodiphenylphosphazo)-6-phenyl-s-triazine

DPPE $\Phi_2P-(CH_2)_2-P\Phi_2$

1,2-bis(diphenylphosphino) ethane

DPPB $\Phi_2P-(CH_2)_4-P\Phi_2$

1,4-bis(diphenylphosphino) butane

DPPT $\Phi_2P-C_3N_3\Phi-P\Phi_2$

2,4-bis(diphenylphosphino)-6-phenyl-s-triazine

3.1 MONOMER SYNTHESES

1,2-Bis(diphenylphosphino)ethane, DPPE

This monomer was purchased from Alfa Inorganics, Beverly, Massachusetts and was used without further purification, mp 140-141°C, reported in literature mp 142-143°C (ref. 20), 143-144°C (ref. 21). The infrared spectrum is given in Figure 1, whereas the DSC curve is presented in Figure 19.

1,4-Bis(diphenylphosphino)butane, DPPB

This monomer was purchased from Strem Chemicals, Inc., Danvers, Massachusetts and was used without further purification, mp 132-133°C, reported in literature mp 135-136°C (ref. 22). The infrared spectrum is given in Figure 2, the DSC curve in Figure 20.

Preparation of 2,4-Dichloro-6-phenyl-s-triazine

(a) Via Grignard reaction from cyanuric chloride. The procedure used was a slight modification of the method of Jones, et al. (ref. 23). Under nitrogen atmosphere a solution of bromobenzene (70 g, 0.445 mol) in ether (100 ml) was added dropwise with stirring over a period of 2 hr to a mixture of magnesium turnings (10.71 g, 0.445 mol), ether (150 ml), and iodine (one crystal). The rate of addition was such as to maintain a gentle reflux. After the addition was complete, the reaction mixture was refluxed for 1 hr following which it was allowed to cool with stirring to room temperature.

Subsequently the Grignard solution was added dropwise with stirring over a period of 1.5 hr to a solution of purified cyanuric chloride (50 g, 0.271 mol) in benzene (500 ml) at ice-water bath temperature. After the addition was complete, the reaction mixture was stirred for an additional 0.5 hr and allowed to stand overnight in an ice-water bath. Next day the reaction mixture was refluxed for 2 hr. After cooling to room temperature, the reaction mixture was filtered; the solids were washed with ether (2 x 200 ml). Evaporation of the combined filtrates, using a rotary evaporator, resulted in a solid which was then distilled at 198-205°C at 0.7 mm affording 26.8 g (43.7% yield) of product, bp 125-132°C, which was crystallized from heptane to give 22.8 g (37.2% yield) of 2,4-dichloro-6-phenyl-s-triazine, mp 114-115°C. Another crystallization from heptane raised the mp to 117-118°C; lit. (ref. 24) mp 121°C, lit. (ref. 23) mp 120-120.5°C.

(b) Via 2,4-dihydroxy-6-phenyl-s-triazine from 2,4-diamino-6-phenyl-s-triazine. 2,4-Dihydroxy-6-phenyl-s-triazine was prepared using a slight modification of a literature procedure (ref. 25). Thus, a

mixture of 2,4-diamino-6-phenyl-s-triazine (150 g, 0.802 mol) and 90% sulfuric acid (600 ml) was heated with stirring in an oil bath maintained at 106-124°C for 20.5 hr. Subsequently the reaction mixture was cooled to room temperature and poured into an ice-water mixture (5000 ml). Upon standing overnight in the refrigerator, the solution deposited a white solid which was collected, washed with water (3000 ml) and dried to give 126.6 g (83% yield) of 2,4-dihydroxy-6-phenyl-s-triazine, mp 292-296°C (dec), lit. (ref. 25) 289-290°C (dec).

In the next step a somewhat modified procedure of Albers, Oster, and Schroeder (ref. 24) was utilized. Thus, dimethylformamide (50 ml) was added dropwise with stirring under anhydrous conditions to a mixture of 2,4-dihydroxy-6-phenyl-s-triazine (45 g, 0.239 mole) and thionyl chloride (250 ml) over a period of 1.25 hr at ambient conditions. After the addition was complete, the reaction mixture was heated with stirring in an oil bath maintained at 70-75°C for 4.5 hr. After cooling to room temperature the crystals which formed in the reaction mixture were filtered off and washed with heptane. The crystals were then suspended in ice-water (600 ml) and stirred for 1 hr. This was followed by filtration, washing with additional ice-water, and drying. The amount of reaction medium insoluble crude product was 25.5 g. The original filtrate was evaporated in vacuo and the residue was stirred with ice-water (1000 ml). The water insoluble material was filtered off washed with water and dried affording 24.[illegible] g of the reaction medium soluble crude product. Both the reaction medium soluble and insoluble portions were extracted with boiling heptane which gave on cooling 41.7 g (77.2% yield) of 2,4-dichloro-6-phenyl-s-triazine, mp 118.5-119.5 °C.

Preparation of 2,4-Diazido-6-phenyl-s-triazine, TDA

A mixture (prepared in an inert atmosphere enclosure) of sodium azide (19.57 g, 0.3 mol), lithium azide (1.0 g, 0.0204 mol), 2,4-dichloro-6-phenyl-s-triazine (23.0 g, 0.102 mol) and acetonitrile (400 ml) was stirred at ambient conditions under nitrogen atmosphere for 160 hr. Filtration gave 37.0 g of insoluble materials, whereas evaporation of the filtrate using a rotary evaporator afforded 6.5 g of material, which was crystallized from heptane yielding 5.8 g of 2,4-diazido-6-phenyl-s-triazine, mp 130-131°C. The insoluble material was extracted with boiling heptane which upon partial evaporation and cooling, afforded 16.9 g of material, mp 130-131°C. Total yield of 2,4-diazido-6-phenyl-s-triazine was 22.7 g, (93% yield), mp 130-131°C; found to be identical with an authentic sample by infrared spectroscopy and mixed melting point (ref. 6). The infrared spectrum is given in Figure 3, whereas the DSC curve is presented in Figure 21.

Preparation of 2,4-Bis(azidodiphenylphosphazo)-6-phenyl-s-triazine, TDPA

Interaction of 2,4-diazido-6-phenyl-s-triazine (4.54 g, 1.898 mmol) and diphenylchlorophosphine (8.38 g, 3.798 mmol) in benzene (180 ml) at room temperature over a period of 72 hr gave the desired product bis(chlorodiphenylphosphazo)-6-phenyl-s-triazine (11.20 g, 94.5% yield) in the form of an insoluble precipitate. Subsequently an aliquot of this material (5.00 g, 8.007 mmol) was treated at room temperature in chloroform (100 ml) with lithium azide (970 mg, 19.01 mmol) over a period of 70 hr. After filtration of the insoluble precipitate (2.93 g; lithium salts plus products) the chloroform solution (on evaporation in vacuo) yielded 2.96 g of product. Both these materials were found by infrared spectral analysis to contain some unreacted bis(chlorodiphenylphosphazo)-6-phenyl-s-triazine.

Accordingly the solids were stirred in acetonitrile (100 ml) with additional lithium azide (100 mg) for 154 hr. The insoluble material was extracted with hot chloroform; evaporation of chloroform gave (4.65 g (91 .1% yield) of the pure diazide mp 237.5 - 238.5°C. Its infrared spectrum is presented in Figure 4 , the DSC curve in Figure 22. Anal. Calcd. for $C_{33}H_{25}N_{11}P_2$: C, 62.17%; H, 3.95%; N, 24.17%; P, 9.71%. Found: C, 62.14%; H, 4.25%; N, 24.90%; P, 9.40%.

Preparation of Diphenylphosphine

Diphenylphosphine was prepared from diphenylchlorophosphine following the procedure of W. Kuchen and H. Buchwald (ref. 26). In an inert atmosphere enclosure into a 2-liter 3-neck flask was introduced lithium aluminum hydride (16 g, 0.422 mol) and ether (450 ml). Under nitrogen by-pass into this stirred mixture with ice cooling was added via an additional funnel a solution of diphenylchlorophosphine (289.5 g, 1.313 mol) in ether (450 ml) (this solution was prepared in the inert atmosphere enclosure) over a period of 3 hr. This was followed by 1 hr reflux. Subsequently, the mixture was cooled and water (40 ml) was added over a 30 min period. The resulting mixture was then refluxed for 2.75 hr, cooled and transferred into an inert atmosphere enclosure where it was filtered through glass wool. The ethereal washings (300 ml) and the original filtrate were dried over $CaCl_2$. The majority of ether was removed at atmospheric pressure under nitrogen by-pass. The last traces were removed at reduced pressure. The fraction distilling at 130.8 - 131.8°C/ 4.2 mm produced 188.6 g (77% yield) of pure diphenylphosphine.

Preparation of Potassium Diphenylphosphide

Potassium diphenylphosphide was prepared following basically the procedure of K. Issleib and D. Jakob (ref. 27). In the inert atmosphere enclosure into a solution containing diphenylphosphine (21.9 g, 0.118 mol) in benzene (120 ml) was added freshly cut potassium metal (3.95 g, 0.101 mol). Subsequently, the mixture was heated with stirring under nitrogen

by-pass (oil bath 93°C) for 5 hr. The solution turned originally brown, at the conclusion an orange solution with an orange precipitate resulted. The precipitate was filtered off in an inert atmosphere enclosure affording after drying 21.30 g (94% yield) of pure potassium diphenylphosphide.

Preparation of 2,4-Diphenoxy-6-phenyl-s-triazine

To a stirred solution of 2,4-dichloro-6-phenyl-s-triazine (8.08 g, 35.30 mmol) in acetone (150 ml) cooled in an ice bath was added dropwise a solution of sodium phenoxide (prepared from 6.72 g (71.40 mmol) of phenol and 3.19 g (79.8 mmol) of sodium hydroxide) in water (150 ml) over a period of 1 hr. This was followed by stirring overnight at room temperature. Some of the product precipitated out (8.9 g), the rest was obtained on solvent evaporation (7.7 g). Crystallization from hexane gave 2,4-diphenoxy-6-phenyl-s-triazine 11.3 g (93.5% yield) mp 115 - 116°C (reported mp 110 (ref. 28) and 116°C (ref. 29)).

Preparation of 2,4-Bis(diphenylphosphino)-6-phenyl-s-triazine, DPPT

(a) Via reaction of 2,4-dichloro-6-phenyl-s-triazine with potassium diphenylphosphide. Potassium diphenylphosphide (1.5 g, 6.7 mmol) was added in 0.1 - 0.3 gram portions to a stirred solution of 2,4-dichloro-6-phenyl-s-triazine (0.76 g, 3.35 mmol) in ether (40 ml) at ambient conditions in the inert atmosphere enclosure. Subsequently, the red brown reaction mixture was stirred for an additional 52 hr. The solid collected on filtration was washed with anhydrous ether (20 ml) and dried to give 0.64 g of red brown solid, which contained 69.8% of potassium chloride. The filtrate was evaporated in vacuo to give an unidentifiable dark red oil, which was discarded. Conducting the reaction in benzene resulted also in the formation of the unidentified red oil.

(b) Via reaction of diphenylphosphine with 2,4-dichloro-6-phenyl-s-triazine. In the inert atmosphere enclosure to diphenylphosphine (13.0 g, 70.0 mmol) was added 2,4-dichloro-6-phenyl-s-triazine (3.96 g, 17.5 mmol), instantaneous reaction took place as indicated by a temperature rise and gas evolution. The mixture was subsequently heated under nitrogen by-pass at 100°C for 4.5 hr; although an excess of diphenylphosphine over that required for phosphonium salt formation was employed, evolution of hydrogen chloride was observed. On cooling the mixture solidified. Treatment of the yellow solid with heptane followed by benzene extraction left an insoluble residue of $\Phi_2PH{\cdot}HCl$, 3.42 g (44% yield, based on the chlorine available), calcd. for $C_{12}H_{12}PCl$:Cl, 15.92%, found, Cl, 15.2%. The benzene soluble material on removal of solvent gave 8.9 g of a solid. Two crystallizations from acetonitrile afforded 2.74 g (21.14% yield, based on chlorine available), mp 125 - 126°C, of $\Phi_2P\text{-}P\Phi_2$ which was identified by comparison of an infrared spectrum with that of an authentic sample and by elemental analysis.

Anal. Calcd. for $C_{24}H_{20}P_2$: C, 77.83%; H, 5.44%; P, 16.72%.
Found: C, 78.13%; H, 4.92%; P, 17.07%.

Fractional crystallization of the mother liquors from acetonitrile and ethanol afforded the desired product 1.34 g (15% yield), 2,4-bis(diphenylphosphino)-6-phenyl-s-triazine, mp 133 - 134°C (reported by Hardy (ref. 30) mp 134 - 135°C). Its infrared spectrum is given in Figure 5; the DSC curve in Figure 23. Anal. Calcd. for $C_{33}H_{25}N_3P_2$:
C, 75.42%, H, 4.79%; N, 8.00%; P, 11.79%; MW, 525.54.

Found: C, 75.90%; H, 5.17%; N, 8.54%; P, 11.76%; MW, 523.

Conducting this reaction at 150°C afforded diphenylphosphine-hydrochloride in 43% yield, tetraphenyldiphosphine in 60% yield (based on chlorine available), and the desired product 2,4-bis(diphenylphosphine)-6-phenyl-s-triazine in 11.8% yield.

(c) Via reaction 2,4-diphenoxy-6-phenyl-s-triazine with diphenylphosphine. In the inert atmosphere enclosure a mixture of diphenylphosphine (11.52 g, 61.87 mmol), 2,4-diphenoxy-6-phenyl-s-triazine (8.58 g, 25.13 mmol) and zinc acetate (2.31 g)was prepared in a 100 ml round bottom flask equipped with a stirring bar to which a distillation head and condenser were attached. The mixture was heated at 220°C, under nitrogen by-pass, with stirring for a period of 4.5 hr; this was followed by distillation at reduced pressure (< 0.01 mm) at 130°C to remove phenol. The solid residue was extracted, in inert atmosphere enclosure with boiling heptane (300 ml) and the solution was filtered hot. The crystalline material which formed on cooling (7.73 g) was recrystallized from acetonitrile giving 7.10 g (53.8 % yield) mp 132 - 133°C, of 2,4-bis(diphenylphosphino)-6-phenyl-s-triazine.

Preparation of p-Bromophenyldiphenylphosphine

Under nitrogen by-pass to a stirred solution of n-butyl lithium (22 g, 0.344 mol) in heptane (180 ml) at -76°C was added a solution of p-dibromobenzene (81.2 g, 0.334 mol) in tetrahydrofuran (200 ml) over a period of 2 hr. This was followed by addition (also at -76°C) of diphenylchlorophosphine (76.1 g, 0.344 mol) in tetrahydrofuran (35 ml) over a period of 1 hr. Subsequently, the solution was warmed gradually to room temperature over a period of 2.5 hr and allowed to stand overnight. Filtration afforded LiCl (11.80 g, 80.3% yield), the filtrate was evaporated in vacuo giving a yellow oil. Crystallization from methanol afforded crystals of p-bromophenyldiphenylphosphine (67.9 g, 58% yield) mp 76.5 - 77.5°C, lit. (ref. 31) mp 78.5 - 79.5°C.

Preparation of 2,4-Dimethoxy-6-phenyl-s-triazine

Following the procedure of Thurston et al (ref. 32) a mixture of 2,4-dichloro-6-phenyl-s-triazine (4.047 g, 17.903 mmol) and sodium carbonate (5.0 g) in methanol (50 ml) was refluxed for 3 hr. Subsequently the insoluble material was filtered off and the filtrate was evaporated to dryness in vacuo. Extraction of the residue with heptane followed by crystallization from this solvent gave (3.53 g, 90.8% yield) of 2,4-dimethoxy-6-phenyl-s-triazine mp 65 - 67°C; reported in literature mp 69°C (ref. 33) and 64°C (ref. 34).

Preparation of Triphenylphosphine via Hydrolysis of the Grignard of p-Bromophenyldiphenylphosphine

To a stirred mixture of tetrahydrofuran (5 ml), magnesium turnings (100 mg, 4.15 mmol), and a crystal of iodine was added under nitrogen by-pass a solution of p-bromophenyldiphenylphosphine (1.23 g, 3.60 mmol) in tetrahydrofuran (8 ml) over a period of 0.5 hr at room temperature. No reaction took place. Subsequently the mixture was refluxed for 2.5 hr, then cooled to 0°C and to it with stirring was added dilute (20%) sulfuric acid (25 ml) over a period of 20 min. The product was then extracted with ether. After evaporation of ether triphenylphosphine (954 mg, 100% yield) admixed with a small quantity of the oxide was obtained. Treatment with concentrated hydrochloric acid failed to remove the oxide. Based on the high yield of triphenylphosphine it can be deduced that the Grignard Φ_2P-Φ-MgBr is formed fairly readily.

Preparation of 2,4-Diphenyl-6-(phenyl-p-diphenylphosphino)-s-triazine

(a) Adding the chlorotriazine to the Grignard solution. Under nitrogen by-pass to a stirred mixture of tetrahydrofuran (20 ml), magnesium turnings (350 mg, 14.38 mmol), and a crystal of iodine was added a solution of

p-bromophenyldiphenylphosphine (4.91 g, 14.38 mmol) in tetrahydrofuran (20 ml) over a period of 3 hr at 44°C. This was followed by stirring at 44°C for 2.25 hr. Subsequently the reaction mixture was cooled in an ice bath and to it was added a solution of 2,4-diphenyl-6-chloro-s-triazine (3.50 g, 13.07 mmol) over a period of 30 min. After standing overnight at room temperature the reaction mixture was stirred at 36°C for 3 hr. Filtration in an inert atmosphere enclosure failed to afford any precipitate. Evaporation in vacuo yielded a tar-like material from which on extraction with hot heptane a mixture of 2,4-diphenyl-6-chloro-s-triazine, 4,4'-bis(diphenylphosphino)biphenyl and what appeared to be the desired product 6-(phenyl-p-diphenylphosphino)-2,4-diphenyl-s-triazine was obtained.

(b) Adding the Grignard to the chlorotriazine solution. Under nitrogen by-pass to a stirred mixture of tetrahydrofuran (25 ml), magnesium turnings (380 mg, 15.60 mmol), and a crystal of iodine was added a solution of p-bromophenyldiphenylphosphine (4.91 g, 14.38 mmol) in tetrahydrofuran (25 ml) over a period of 1.5 hr at 35 - 37°C. No apparent reaction was observed. Subsequently the mixture was refluxed at 65 - 70°C for 2 hr; the magnesium dissolved and the solution turned dark. To a stirred solution of 2,4-diphenyl-6-chloro-s-triazine (3.50 g, 13.07 mmol) in benzene (30 ml) at 0°C was added the Grignard prepared above over a period of 35 min. Subsequently the mixture was allowed to stand overnight at room temperature. Next day air-free distilled water (50 ml) was added at 0°C. The organic layer after addition of ether (200 ml) was separated off, dried, and evaporated. The black, tar-like residue (5.74 g) was stirred with concentrated hydrochloric acid (300 ml) over a period of 2 hr. The filtered solution was poured onto ice water giving 3.05 g of a tan precipitate. Extraction with hot heptane afforded on cooling of the heptane solution 1.15 g of crystals, mp = 137 - 151°C, which were found to be a mixture of what appeared to be the desired

product, 2,4-diphenyl-6-(phenyl-p-diphenylphosphino)-s-triazine and 4,4'-bis-(diphenylphosphino)biphenyl. The 4,4'-bis(diphenylphosphino)-biphenyl was separated by crystallization from benzene-heptane; whereas the mother liquors yielded the desired product, mp 164 - 167°C, in ca 9% yield. The original heptane insoluble material consisted mainly of 2,4-diphenyl-6-hydroxy-s-triazine.

Preparation of 2,4-Bis(phenyl-p-diphenylphosphino)-6-phenyl-s-triazine

(a) Via reaction of p-bromophenyldiphenylphosphine Grignard with 2,4-dichloro-6-phenyl-s-triazine. Under nitrogen by-pass to a stirred mixture of tetrahydrofuran (30 ml), magnesium turnings (700 mg, 28.75 mmol), and a crystal of iodine was added a solution of p-bromophenyldiphenylphosphine (9.81 g, 28.75 mmol) in tetrahydrofuran over a period of 1 hr at room temperature. No apparent reaction was observed. Subsequently the mixture was heated to 67°C over a period of 2 hr; again no reaction took place. Refluxing at 70 - 73°C for 2 hr resulted in reaction (disappearance of magnesium; solution became burgundy in color). Under nitrogen by-pass to a stirred solution of 2,4-dichloro-6-phenyl-s-triazine (2.97 g, 13.07 mmol) in tetrahydrofuran (30 ml) at 0°C was added the Grignard prepared above over a period of 1 hr. After standing overnight at room temperature to the stirred greenish-black reaction mixture at 0°C was added air-free water (50 ml) over a period of 15 min. The organic layer, after addition of ether (200 ml) was separated off, dried and evaporated. The dark colored residue (9.24 g) was stirred under nitrogen by-pass with concentrated hydrochloric acid (200 ml) at room temperature for 2 hr. The filtered solution was poured onto ice-water (ca 600 ml) giving after drying at 37 - 50°C 6.3 g of yellow precipitate. Based on the infrared spectrum the hydrochloric acid treatment removed some of the oxidized material, but it also resulted in hydrolysis

as shown by absorption in the vicinity of 6.0μ. The hydrolyzed product formed was not 2-phenyl-4,6-dihydroxy-s-triazine. It should be mentioned that identical hydrochloric acid treatment of pure 2,4-diphenyl 6-chloro-s-triazine left the starting material unchanged. Since 2,4-diphenyl-6-hydroxy-s-triazine has been isolated from the attempted preparation of 2,4-diphenyl-6-(phenyl-p-diphenylphosphino)-s-triazine a Grignard exchange process could be operative.

Crystallization of the hydrochloric acid treated material from heptane yielded a small quantity of what appeared to be 4,4'-bis(diphenylphosphino)biphenyl and an impure fraction of the desired product 2,4-bis-(phenyl-p-diphenylphosphino)-6-phenyl-s-triazine mp 161 - 171°C.

(b) Via reaction of p-bromophenyldiphenylphosphine Grignard with 2,4-dimethoxy-6-phenyl-s-triazine. To prepare the Grignard $\Phi_2P\text{-}C_6H_4\text{-}MgBr$, a mixture of p-bromophenyldiphenylphosphine (6.92 g, 20.28 mmol), magnesium turnings (540 mg, 22.38 mmol), and a crystal of iodine in tetrahydrofuran (20 ml) were refluxed for 1 hr at 70°C. Subsequently the cool Grignard solution was added (under nitrogen bypass) over a period of 0.5 hr at room temperature into a stirred solution of 2,4-dimethoxy-6-phenyl-s-triazine (2.17 g, 9.99 mmol) in tetrahydrofuran (30 ml). After the addition was completed the solution was refluxed at 78°C for 3 hr. Cooling in an ice bath was followed by addition of a solution of ammonium chloride (5.0 g) in water (50 ml) over a period of 15 min. The resulting mixture was extracted with ether (two 50-ml portions). The dried ethereal extract was evaporated in vacuo giving 7.30 g of a brown solid. This material was dissolved in boiling acetonitrile affording on slight cooling a crystalline precipitate of 2,4-bis(phenyl-p-diphenylphosphino)-6-phenyl-s-triazine (1.73 g, 25.6%), mp 202 - 204°C.

Additional purification was effected by boiling in acetonitrile, in which the bulk of the sample appeared to be insoluble, giving material mp 209 - 210°C. Its infrared spectrum is given in Figure 6, whereas the DSC scan is presented in Figure 24.

Anal. Calcd.for $C_{45}H_{33}N_3P_2$: C, 79.75%; H, 4.91%; N, 6.20%; P, 9.14%; MW,677.73.

Found: C, 79.48%; H, 5.46%; N, 6.38%; P, 8.97%; MW, 693.

It should be mentioned that one of the products obtained from the interaction of the Grignard $\Phi_2P\text{-}C_6H_4\text{-}MgBr$, with 2,4-dichloro-6-phenyl-s-triazine exhibited the same infrared spectrum.

The acetonitrile soluble portion was crystallized from heptane affording 2-(phenyl-p-diphenylphosphino)-4-methoxy-6-phenyl-s-triazine (1.55 g, 34.7% yield) mp 149.5 - 150.5°C. Its infrared spectrum is given in Figure 7, whereas the DSC scan is presented in Figure 25.

Anal. Calcd. for $C_{28}H_{22}N_3OP$: C, 75.16%; H, 4.96%; N, 9.39%; P, 6.92%; O, 3.58%; MW, 447.48.

Found: C, 75.70%; H, 5.30%; N, 9.38%; P, 6.91%; MW, 470.

3.2 MODEL COMPOUND SYNTHESES

Preparation of $\Phi_2C_3N_3\text{-}N{=}P\Phi_2\text{-}(CH_2)_4\text{-}P\Phi_2{=}N\text{-}C_3N_3\Phi_2$

To a stirred solution of 1,4-bis(diphenylphosphino)butane (1.00 g, 2.36 mmol) in benzene (20 ml) was added via an addition funnel a solution of 2,4-diphenyl-6-azido-s-triazine (1.29 g, 4.69 mmol) in benzene (25 ml) over a period of 15 min. Instantaneous reaction took place as evidenced by gas evolution. Stirring at room temperature was continued overnight; subsequently, approximately half of the solvent was removed in vacuo affording a precipitate 1.70 g (39% yield) mp 139 - 141°C. Crystallization

from benzene resulted in mp 144 - 145°C. The infrared spectrum of this material is given in Figure 8, whereas the TGA curves in nitrogen and air are presented in Figures 26 and 27, respectively.

Anal. Calcd. for $C_{58}H_{48}N_8P_2$: C, 75.80%; H, 5.26%; N, 12.19%; P, 6.74%; MW, 919.

Found: C, 75.11%; H, 5.31%; N, 11.88%; P, 6.78%; MW, 1040.

Preparation of $\Phi_2C_3N_3$-N=PΦ_2-$C_3N_3(\Phi)$-PΦ_2=N-$C_3N_3\Phi_2$

In an inert atmosphere enclosure to a stirred solution of 2,4-diphenylphosphino-6-phenyl-s-triazine (260 mg, 0.495 mmol) in benzene (10 ml) was added 2,4-diphenyl-6-azido-s-triazine (270 mg, 0.988 mmol) in benzene (10 ml) over a period of 11 min. On stirring overnight a white precipitate formed (0.26 g, 52% yield). This was crystallized from benzene, mp >250°C. The spectrum is given in Figure 9, whereas the TGA in air is presented in Figure 28.

Anal. Calcd. for $C_{63}H_{45}N_{11}P_2$: C, 74.33%; H, 4.46%; N, 15.13%; P, 6.08%; MW, 1018.09.

Found: C, 74.22%; H, 4.49%; N, 15.24 . P, 6.14%; MW, 1018.

Preparation of Φ_3P=N-PΦ_2=N-$C_3N_3(\Phi)$-N=PΦ_2-N=PΦ_3

In an inert atmosphere enclosure a mixture of triphenylphosphine (1.24 g, 4.73 mmol), 2,4-bis(azidodiphenylphosphazo)-6-phenyl-s-triazine (750 mg, 1.18 mmol) and benzene (2 ml) was heated at 79°C for 9 hr. Evolution of nitrogen was noted. Subsequently the excess triphenylphosphine was removed by vacuum sublimation at 85 - 100°C for 11 hr. The residue was extracted with hot heptane and acetonitrile. The insoluble material (0.75 g, 67% yield) was crystallized from benzene-heptane, mp 233.5 - 235°C. The infrared spectrum is presented in Figure 10, whereas the TGA curves in nitrogen and air are given in Figures 29 and 30, respectively.

Anal. Calcd. for $C_{69}H_{55}N_7P_4$: C, 74.92%; H, 5.01%; N, 8.86%; P, 11.20%; MW, 1106.09.

Found: C, 74.19%; H, 5.33%; N, 8.40%; P, 10.62%; MW, 1200.

3.3 POLYMER SYNTHESES AND CHARACTERIZATION

The majority of polymerizations were conducted in a solvent and a nitrogen atmosphere, either in the inert atmosphere enclosure or under nitrogen by-pass. The experimental details of the individual runs together with certain physical characteristics of the products are summarized in Table I (contained in Section 4). Other details which are not covered in this table are delineated below.

In runs 1 to 8 the azide solution was added dropwise to the phosphine solution at room temperature. The addition was accompanied by nitrogen evolution. Subsequently the solution was stirred at room temperature for at least 12 hr and in certain instances (runs 5,6, and 7) this was followed by refluxing for 3 - 5 hr. In runs 1-7 both reaction medium soluble and insoluble products were obtained. The insoluble polymer was filtered off, washed, and then dried in vacuo at 100 - 110°C, whereas the medium soluble material was precipitated with heptane which was followed again by drying. The runs 1-8 involved the 2,4-diazido-6-phenyl-s-triazine (TDA) which is much more reactive than 2,4-bis(azido-diphenylphosphazo)-6-phenyl-s-triazine (TDPA). Thus even at room temperature the reaction was completed as shown by the absence of azido absorption in the infrared and by the quantitative nitrogen evolution, which was measured in run 1.

The runs 9-13 involved the TDPA azide. Due to the relative unreactivity of this azide the majority of the tests 9, 11-13, were conducted more or less in the semi-solid state. In runs 9, 11, 12 the two components were ground together,moistened with benzene and then heated at the specified temperature for the denoted period of time (see Table I). In

runs 10 and 12 traces of unreacted azide were recovered. In run 13 the reaction in chloroform was incomplete as shown by IR absorption of the azido group in the reaction mixture; thus heating at 78 - 96°C for 11 hr was required to complete the process. The only test conducted truly in solvent was run 10. Here the bisphosphine was added to the diazide at room temperature and the resulting solution was then refluxed. All the products obtained in runs 9 - 13 were dissolved in chloroform and then precipitated with heptane.

The infrared spectra, thermogravimetric, isothermal gravimetric analysis, elemental analysis, molecular weights, thermal oxidative tests, softening, and melting points were performed on materials dried in vacuo at 100 - 110°C for at least 6 hr.

In Table II (contained in Section 4) are summarized the physical characteristics of the particular polymers. The data given, with the exception of elemental analyses, are the ranges found for a particular polymer system prepared in different experiments which are listed in Table I. Also given in Table II are the references to figures depicting the infrared and thermogravimetric curves of representative materials. For each polymer system only one set of TGA data (nitrogen and air) is given since these were found to be independent of the method of preparation. In some instances more than one infrared spectrum is listed for a given polymer system, since these were found to vary depending on the type of solvent employed.

3.4 DECOMPOSITION AND BURN TESTS

Oxidative thermal decomposition testing was performed using a modified stagnation burner the operation of which has been previously described (ref. 8,9). The modifications consisted of sealing the system

and attaching it to three traps, one cooled to -78°C and two held at -196°C, for quantitative collection of all decomposition products formed. Provisions were also made to determine smoke density changes during the entire decomposition period. The light emission and detection system was constructed and installed using the specifications of ASTM method D-2843-70 as a guideline (ref. 35). The light source was a Universal Illuminator, Model 359, manufactured by American Optical Company, Buffalo, New York, containing a reflector, focusing lens, and a General Electric No. 1493 lamp. The light detection system was Solar Systems A-1, Stock No. 945-1411 selenium photovoltaic cell with 90 microamps minimum output and a peak spectral response at 5650 Å, which is equivalent to the Weston Photronic cell, 594 RRV, specified by ASTM method D-2843-70. The output of the photocell was continuously recorded with a Varian Associates Model G-14A-1 strip chart recorder. The optical path length of this system was 390 mm, that of the referenced ASTM test is 300 mm. The volume of the burner system is ~ 1.5 l, the volume of the ASTM smoke test chamber is ~ 71 l.

The test samples were prepared from finely ground polymer powder by compression at room temperature under ~ 7.8×10^8 N/m^2 pressure in a Pasadena Hydraulic, Inc. Model Q-2400 press. These pressed samples were 12 mm in diameter, 5 mm thick and weighed 0.5 ± 0.01 g. The oxidative thermal degradations were carried out in a stagnation burner at 500 ± 5°C using air at atmospheric pressure with a flow rate at that temperature of 144 cc/sec. After the block and gas temperatures and the air flow rate (ref. 8,9) had been equilibrated, the three sampling traps were cooled to the appropriate temperatures. The sample was then placed in a platinum dish onto the heating block, and the stagnation burner port,

through which the sample was inserted, was sealed with a glass window and Teflon seal. Timing and the measurement of optical transmittance were started at the time the sample was placed on the heating block and the thermal decomposition was allowed to proceed for a period of 15 min. After completion of the test the platinum dish was retrieved from the stagnation burner and the amount of residue was determined. The three cooling traps were sealed and attached to a high vacuum system for removal of the condensed air and for separation of the liquid nitrogen condensible decomposition products into fractions condensing at -23, -78, and -196°C and a fraction not volatile at room temperature. For each fraction the weights and IR spectra were determined and each fraction was analyzed for cyanide ion using Liebig's method (ref. 36). The fractions condensing at -23, -78, and -196°C furthermore were quantitatively analyzed by mass spectrometry and gas chromatography. The mass spectrometric analyses were performed with a CEC Model 21-620 mass spectrometer using materials of known purity for calibrations. For gas chromatography a Loenco Model 70 dual column, dual thermal conductivity detector instrument was employed with 1/8" x 8' Porapak Q filled stainless steel columns, a helium flow rate of 38 ml/min, and a column temperature from 50 to 220°C programmed at 8°C/min.

Flammability testing was performed in accordance with Federal Motor Vehicle Safety Standard No. 302, Flammability of Interior Materials in Passenger Cars (ref. 37). This test was selected because the instrumentation was available. It consists of exposing a horizontally mounted specimen, 10.16 mm wide by 35.56 mm long, to a natural gas flame for 15 sec inside a cabinet. The specimens for these tests were prepared by impregnating glass cloth (70.3 g/m^2) with a chloroform

solution of the polymer, drying at 110°C for 1 hr and pressing at ~ 390°F for 4 min under an applied load of about 10 tons. The resin contents of all specimens were approximately 30%.

4. TECHNICAL DISCUSSION

The flame resistance of a solid material is a function of numerous physical and chemical properties, some of which are material derived whereas others are due to external factors. For a material to burn, it must initially decompose forming combustible volatiles at a rate and in quantities that the surrounding atmosphere of the decomposing specimen has a composition which lies within the ignition limits of this particular system. If the fuel concentration, that is the concentration of combustile decomposition products in this surrounding atmosphere is either above or below these limits, the mixture cannot be ignited and cannot sustain combustion. Accordingly, the smaller the amount of combustible decomposition products and the lower the rate of their formation, the more flame resistant the composition will be.

Based on this reasoning a flame resistant material should have high thermal stability, should produce a high char yield, and should have a low rate of decomposition. To have a low rate of decomposition the material also should be of high molecular weight since fragments of sufficient volatility to escape into the gas phase are more readily produced from low molecular weight polymers (ref. 42). Furthermore, the original decomposition products should not be toxic, corrosive, or otherwise hazardous for safety reasons, especially in the case of enclosed locations such as aircraft and spacecraft.

All these considerations led to the selection of the particular polymer system investigated under this program. It has been reported by a number of investigators that triazine derivatives (ref. 10, 11) and phosphorus-nitrogen combinations (ref. 12-15) have pronounced flame

retarding properties and good thermal stability (ref. 38), that these elements contribute to char formation, particularly if phosphorus is substituted by aromatic moieties, (ref. 16) and that phosphazene derivatives apparently do not form toxic or corrosive decomposition or combustion products (ref. 17, 18). The synthetic approach to produce flame retardant polyphosphazenes was based on the reaction of tertiary bisphosphines with diazides in analogy to the reaction of triphenylphosphine with phenyl azide reported by Staudinger (ref. 19). In a generalized form the expected polymerization process can be represented by the following equation:

$$R_2P\text{-}X\text{-}PR_2 + N_3\text{-}Y\text{-}N_3 \longrightarrow 1/x\left[PR_2\text{-}X\text{-}PR_2\text{=}N\text{-}Y\text{-}N\right]_x + 2N_2$$

During the course of the program three biphosphines and two diazides were subjected to this reaction producing six different compositions. The individual "monomers" were selected on the basis of availability and accessibility, since proof of feasibility of forming polymers by the above process was considered to be more important than extensive synthesis of unavailable and hard to prepare, yet potentially more promising candidates.

The overall program thus consisted of (1) monomer synthesis, (2) preparation of some model compounds to evaluate reactivities and thermal stabilities, (3) polymerization reactions, and (4) oxidative thermal decomposition testing to determine flame retarding characteristics and to establish the absence of toxic or otherwise hazardous decomposition products.

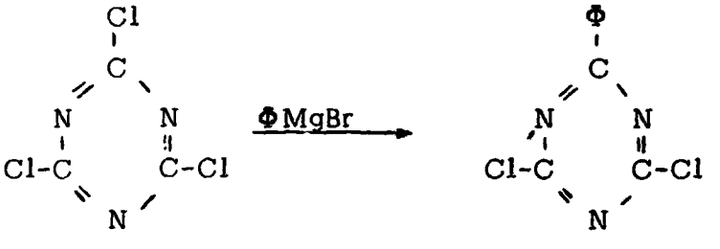
4.1 MONOMER SYNTHESES

The polymerization process as delineated above is based on the interaction of a diazido compound with a diphosphine. A total of four diphosphines and two diazides were thus investigated under this program

in addition to several "monofunctional" compounds which were needed for model studies. Of all the monomers involved only two diphosphines were commercially available, two materials had previously been described in the literature, and two substances were produced for the first time under this program.

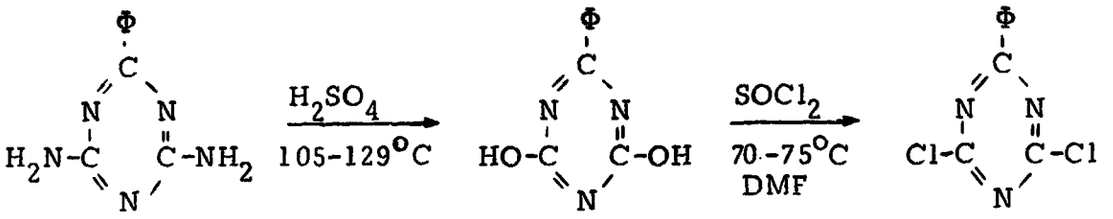
All four compounds which had to be synthesized under this program are s-triazine derivatives. They were chosen in view of the known flame retardant characteristics of this system and the high thermal stability of the aromatic substituted derivatives as exemplified by s-triphenyltriazine. Thus of over 100 organic compounds tested of vastly differing composition and structure, the two most stable materials were p-quaterphenyl and s-triphenyltriazine (ref. 38). The common starting material for all these monomers was 2,4-dichloro-6-phenyl-s-triazine. Consequently, the development of an economical and relatively easy synthetic route for its preparation was of utmost importance.

Two different approaches were employed for the preparation of 2,4-dichloro-6-phenyl-s-triazine. The first process involved the interaction of the bromobenzene Grignard with cyanuric chloride following the procedure of Jones et al (ref. 23), i.e.:



I II

The purification process was tedious and the pure product yield was 37%. The second approach was based on the relatively recently reported (ref. 24, 25) two-step process starting with the diamino-s-triazin III via the dihydroxy-s-triazine IV, which produced compound II

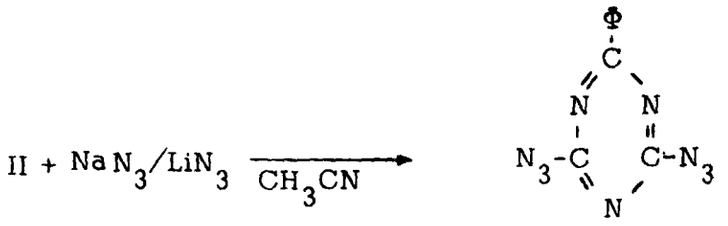


III IV II

in a 64% overall yield. This procedure is considerably less complicated than the Grignard approach, starting materials are significantly cheaper, and it lends itself more readily to large scale production. Compound II was the starting material for all monomers synthesized.

Two triazine diazides were investigated under this program, as the comonomers to the bisphosphines mentioned above. One was 2,4-diazido-6-phenyl-s-triazine (compound V), in which the azido groups are directly attached to the triazine nucleus. In the second diazide employed, 2,4-bis(azidodiphenylphosphazo)-6-phenyl-s-triazine, compound VII, a N=P linkage was interposed between each azido group and the triazine ring. It was believed that in addition to increasing flame resistance this linkage would provide a greater flexibility in the resultant polymer chain by increasing the number of P=N units between the rigid heteroaromatic rings.

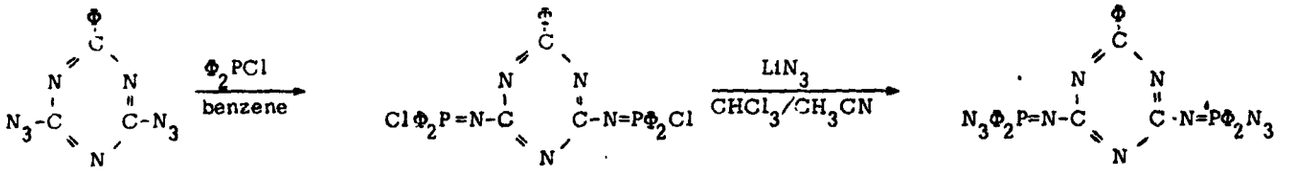
The first of these azides was prepared by treating 2,4-dichloro-6-phenyl-s-triazine (II) with a sodium azide-lithium azide mixture in acetonitrile:



V, TDA

The desired 2,4-diazido-6-phenyl-s-triazine V was produced in 93% yield. Lithium azide (which is commercially not available) was used in catalytic quantities only. The melting point and infrared spectrum of the product was identical with that of compound V (ref. 6).

Compound VII, 2,4-bis(azidodiphenylphosphazo)-6-phenyl-s-triazine was synthesized in 91% overall yield by reacting diazide V with diphenylchlorophosphine and subsequent chloride-azide exchange as shown in the following equation:



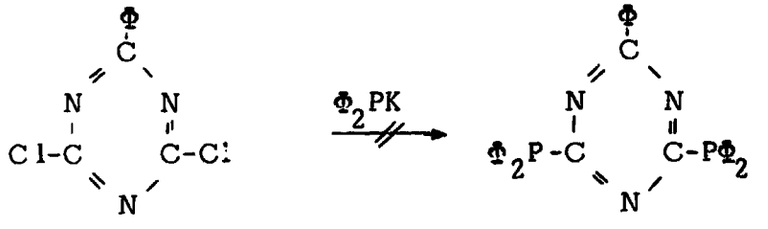
V VI VII

The dichloro intermediate VI was characterized by comparison of its IR spectrum with that of an authentic sample. This material, once it precipitated out of solution (benzene) could not be redissolved in this solvent. However, this material as well as the diazide VII, was soluble in chloroform. Yet, to effect complete exchange of chloro for azido moieties the process had to be carried out in acetonitrile in which both the chloro compound VI and the azido derivative VII were only slightly soluble. It would appear that for the exchange to occur the polarity of

the solvent and its interaction with lithium azide is of great importance, thus the necessity of having acetonitrile present in the exchange reaction. It should be noted that the DSC scan of the diazide VII (Figure 22) does not exhibit a very sharp melting endotherm due to the decomposition which occurs simultaneously, the latter was also observed during conventional melting point determination.

Two of the bisphosphines, 1,4-bis(diphenylphosphino)butane (DPPB) and 1,2-bis(diphenylphosphino)ethane (DPPE) were obtained commercially. Based on their respective melting points and DSC scans (Figures 19, 20) these materials were of acceptable purity.

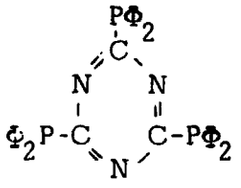
An attempt was made to prepare 2,4-bis(diphenylphosphino)-6-phenyl-s-triazine (DPPT, compound VIII) using the reaction of potassium diphenylphosphide and 2,4-dichloro-6-phenyl-s-triazine, in analogy with the successful preparation of ? 4-diphenyl-6-diphenylphosphino-s-triazine, which was previously accomplished in this laboratory (ref. 6):



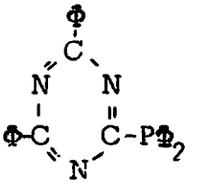
II VIII, DPPT

Unfortunately, interaction of the potassium salts with the dichloro triazine II both in ether and benzene resulted only in a red oil. Similar results were reported by **Hewertson et al (ref. 39). Thus** it is quite possible that more than one chlorine on the triazine ring cannot be substituted using a metal phosphide without rearrangement.

These authors (ref. 39), however, were successful in preparing tris(diphenylphosphino)-s-triazine (IX) and 2-diphenylphosphino-4,6-diphenyl-s-triazine (X) from cyanuric chloride and 2-chloro-4,6-diphenyl-s-



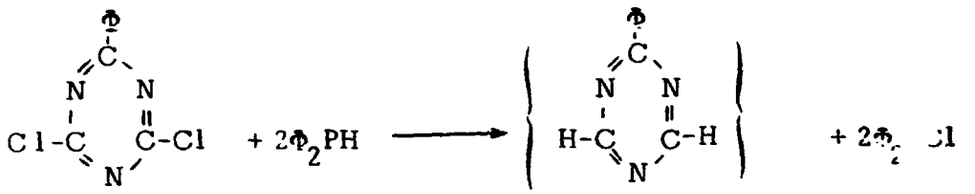
IX



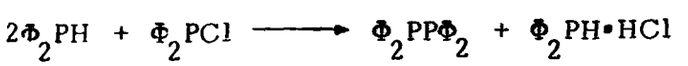
X

triazine, respectively, via interaction with diphenylphosphine. Yet, under the conditions which produced compound X in ca 75% yield only a 12% yield of the desired substance VIII was realized. The major product (21% yield) isolated from this reaction was tetraphenyldiphosphine, $\Phi_2P\text{-}P\Phi_2$. Conducting the reaction at higher temperatures (150°C versus 100°C) for a longer period of time resulted in an increased yield of tetraphenyldiphosphine (60% based on the available chlorine) and just a trace of the desired diphosphinotriazine VIII. It would appear that the main process occurring is exchange of chlorine on the triazine nucleus with the hydrogen atom of diphenylphosphine followed by the known interaction of the thus produced Φ_2PCl with Φ_2PH to produce tetraphenyldiphosphine as shown in the following scheme I:

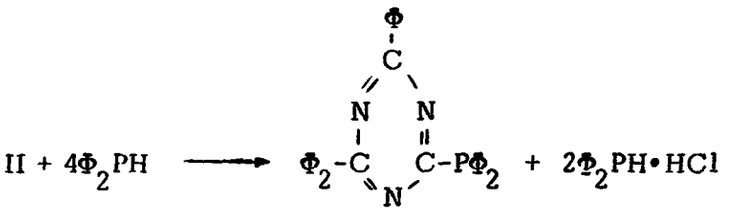
Scheme I:



V

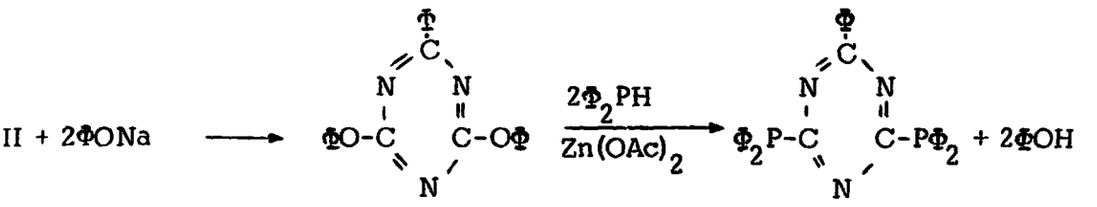


The desired substitution reaction depicted below apparently takes place to only a limited extent.



VIII

Finally, compound VIII was produced in reasonable yield employing the procedure disclosed by Hardy (ref. 30):



XI VIII

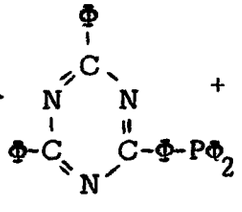
Thus, 2-4-diphenoxy-6-phenyl-s-triazine XI was prepared from the 2,4-dichloro-6-phenyl-s-triazine (compound II) and sodium phenoxide in 94% yield following the procedure of Jones et al (ref. 23). Heating XI with diphenylphosphine gave the desired diphosphinotriazine VIII in 54% yield.

To synthesize a more stable polymer system than could be prepared from either of the two purchased aliphatic diphosphines, $\Phi_2P\text{-}(CH_2)_2\text{-}P\Phi_2$ (DPPE) and $\Phi_2P\text{-}(CH_2)_4\text{-}P\Phi_2$ (DPPB) or from the triazine diphosphine VIII, the synthesis of 2,4-bis(phenyl-p-diphenylphosphino)-6-phenyl-s-triazine was pursued. This compound appeared particularly attractive since it embodies the triphenyl triazine nucleus known to be one of the most stable organic moieties (ref. 32) and the thermally stable triphenylphosphine arrangement.

It appeared advantageous first to synthesize the monosubstituted compound, namely 2,4-diphenyl-6-(phenyl-p-diphenylphosphino)-s-triazine to determine the optimum reaction conditions. The following reaction sequence was visualized:

Scheme II

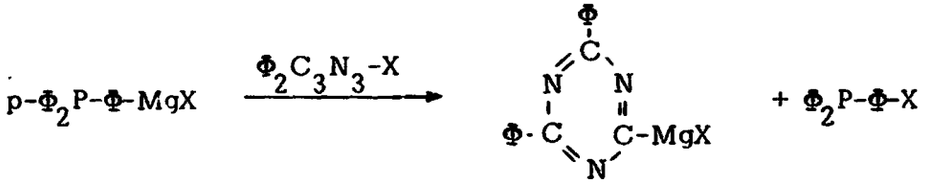
(1) $n\text{-}C_4H_9Li + p\text{-}Br\text{-}\Phi Br \longrightarrow p\text{-}Br\text{-}\Phi\text{-}Li \xrightarrow{\Phi_2PCl} p\text{-}Br\text{-}\Phi\text{-}P\Phi_2$

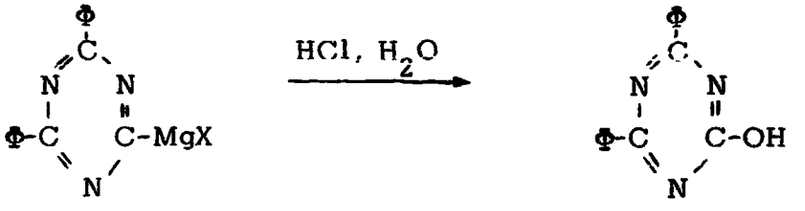
(2) $p\text{-}\Phi_2P\text{-}\Phi\text{-}Br \xrightarrow{Mg} p\text{-}\Phi_2P\text{-}\Phi\text{-}MgBr \xrightarrow{\Phi_2C_3N_3Cl}$  + MgClBr

XIII

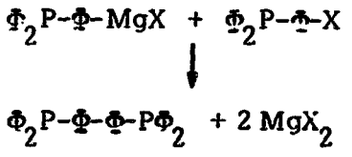
The first step, namely the preparation of p-bromophenyldiphenylphosphine proceeded readily using the basic procedure of Baldwin and Cheng (ref. 31).

The Grignard p-Φ_2P-Φ-MgBr was apparently also readily formed since on hydrolysis triphenylphosphine was afforded in quantitative yield. The next step however posed difficulties since a coupling reaction giving Φ_2P-Φ-Φ-PΦ_2 occurred also. Furthermore on hydrolysis of the reaction mixture 2-hydroxy-4,6-diphenyl-s-triazine was isolated. Acidic hydrolysis of 2-chloro-4,6-diphenyl-s-triazine failed to yield the hydroxy derivative indicating that the chloro compound is not the hydroxy triazine precursor. Based on the above findings it can be deduced that the predominant process is the Grignard exchange resulting the side reactions as shown below:



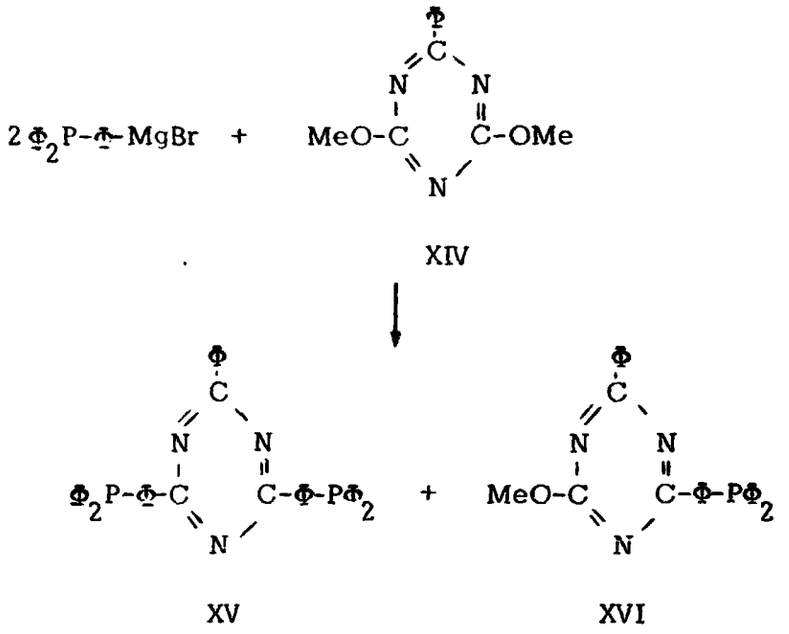


XII



The desired process depicted in scheme II above appears to take place only to a very limited degree as shown by the very low yield of the product XIII. Under these conditions the 2,4-dichloro-6-phenyl-s-triazine was found to behave in a similar fashion as the monochloro-compound.

To avoid the Grignard exchange instead of 2,4-dichloro-6-phenyl-s-triazine the dimethoxy derivative XIV was employed using the Bader and Ruckel approach (ref. 40), i.e.:

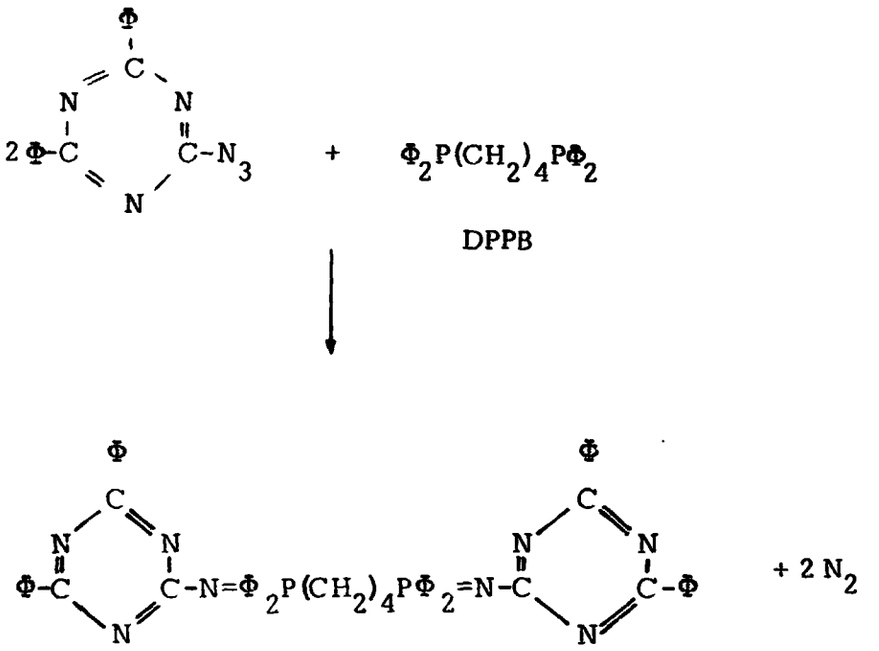


Using this reaction the desired 2,4-bis(phenyl-p-diphenylphosphino)-6-phenyl-s-triazine (compound XV) was obtained in 26% yield whereas the mono-methoxy intermediate XVI was isolated in 35% yield. It is believed that by modifying somewhat the reaction conditions the yield of the diphosphine XV can be significantly improved.

4.2 MODEL COMPOUND STUDIES

To gain better insight into the thermal oxidative behavior of the polymers and to determine reaction conditions for polymerizations three representative model systems were prepared. Structures and methods of synthesis are depicted below:

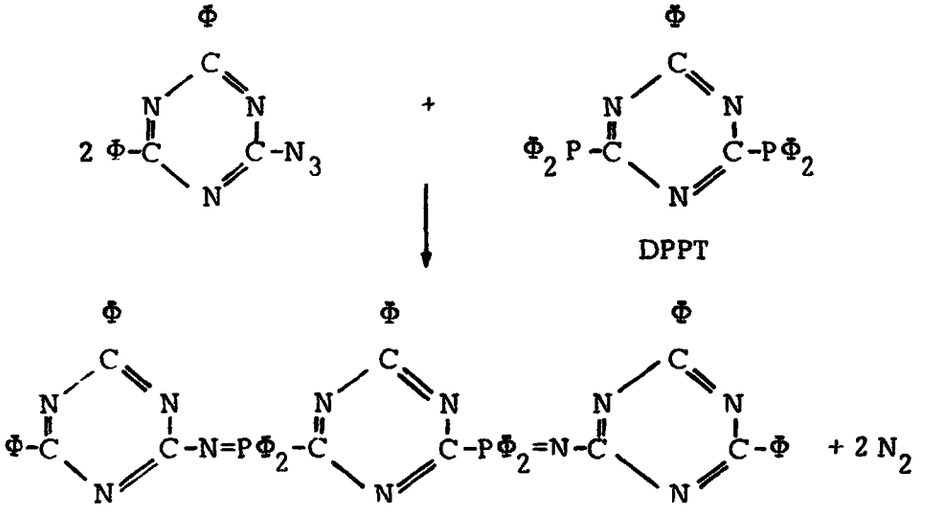
a)



DPPB

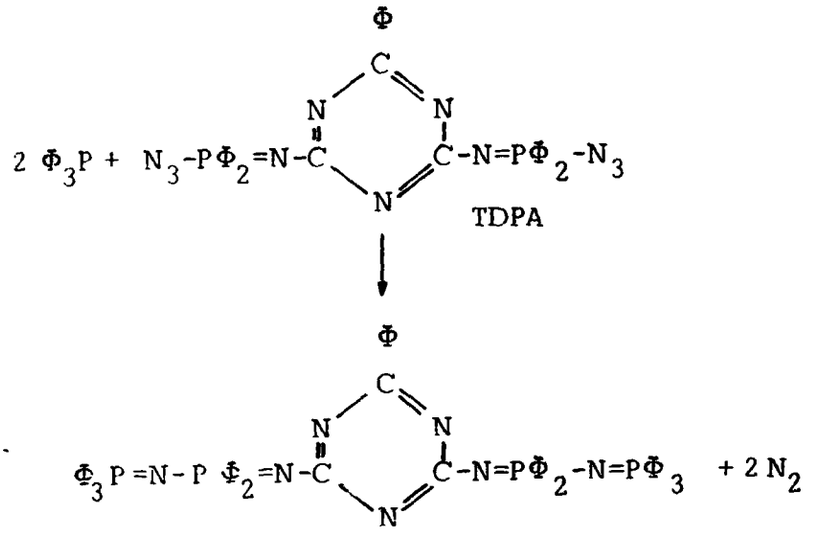
XVII

b)



DPPT

XVIII



XIX

The model compound XVII was prepared to portray a system similar to the polymer formed from 1,4-bis(diphenylphosphino)butane (DPPB) and 2,4-diazido-6-phenyl-s-triazine (TDA), but substituting the diazide TDA by the monoazide 2-azido-4,6-diphenyl-s-triazine, which had been prepared previously (ref. 48). Since in the model only one of the carbons of the triazine ring is nitrogen substituted one would expect, in view of the high thermal stability (ref. 38) of triphenyl-s-triazine, this compound to be possibly more thermally stable than the polymer system itself. The TGA curves (Figures 26, 27) indicate decomposition onset in nitrogen at 360°C and in air near 330°C. In the case of the corresponding polymer (TDA-DPPB) $\left[P\Phi_2-(CH_2)_4-P\Phi_2=N-C_3N_3(\Phi)-N\right]$ the data are roughly comparable (see Figures 31, 32) with the exception that the model compound XVII seems to be somewhat more stable in nitrogen than the polymer (compare Figures 26 and 32). The onset of decomposition around 350°C is to be expected due to the presence of an aliphatic chain, $-(CH_2)_4-$

(ref.41). However, as was delineated in the beginning of Section 4, the aliphatic chain containing diphosphines were included in the current study mainly in view of their commercial availability to test the feasibility of the polymerization concepts.

The second model compound XVIII embodied the triazine derived diphosphine, 2,4-bis(diphenylphosphino)-6-phenyl-s-triazine, DPPT. The only TGA determined was that in air (see Figure 28). The decomposition onset is evident here at 300°C which is significantly higher than that observed for the corresponding polymer system TDA-DPPT (see Figures 35, 36) wherein the decomposition commenced around 200°C. The gross difference in thermal stability between that of the model compound XVIII and the corresponding polymer $\left[P\Phi_2-C_3N_3(\Phi)-P\Phi_2=N-C_3N_3(\Phi)-N\right]_x$, TDA-DPPT may be due to the high concentration of end groups in the polymer. Yet, it is noteworthy that even in this system the rate of decomposition was found to be lower and the char or residue yield higher than found for those materials wherein aliphatic linkages were present, e.g., compare Figures 36 and 32.

The last model compound XIX was synthesized to evaluate the thermal behavior of an arrangement containing 2,4-bis(azidodiphenylphosphazo)-6-phenyl-s-triazine, TDPA, as a structural component. The TGA data (see Figures 29, 30) indicate decomposition onset for this compound in the vicinity of 330°C, whereas a polymer system containing TDPA, e.g., TDPA-DPPB,

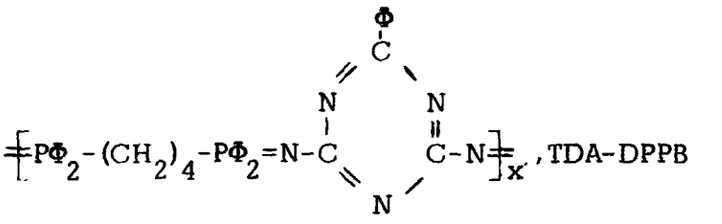
$$\left[P\Phi_2-(CH_2)_4-P\Phi_2=N-P\Phi_2=N-C_3N_3(\Phi)-N=P\Phi_2-N\right]_x ,$$

which contains aliphatic linkages, shows decomposition onset at 345°C (see Figures 37, 38). The lower thermal stability of the model compound, which contains only aromatic and heterocyclic moieties

would tend to indicate that the weight loss being observed is a sublimation. The zero residue at 490°C supports this hypothesis.

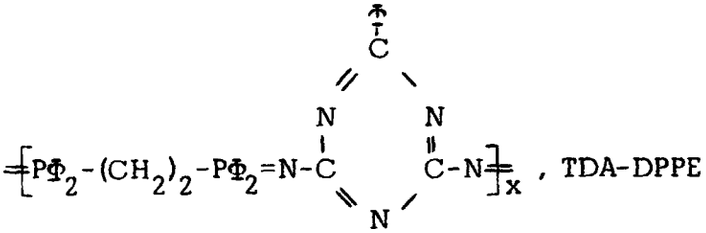
4.3 POLYMERIZATION STUDIES

Six potential polymer systems were investigated under this program. For ease of discussion their structural composition is given below:



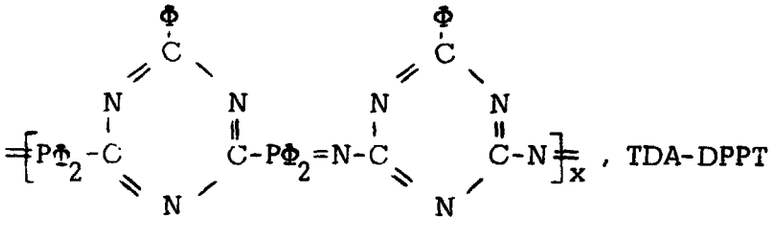
, TDA-DPPB

XX



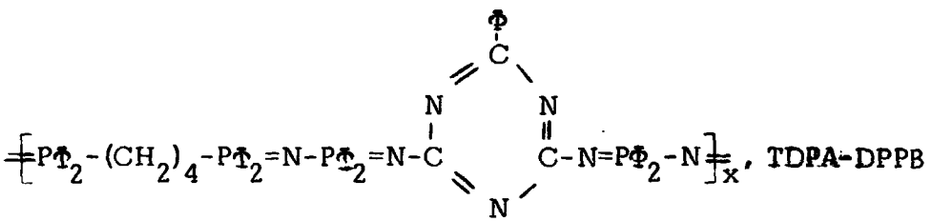
, TDA-DPPE

XXI

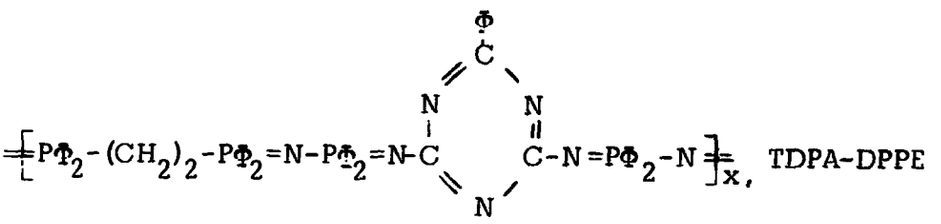


, TDA-DPPT

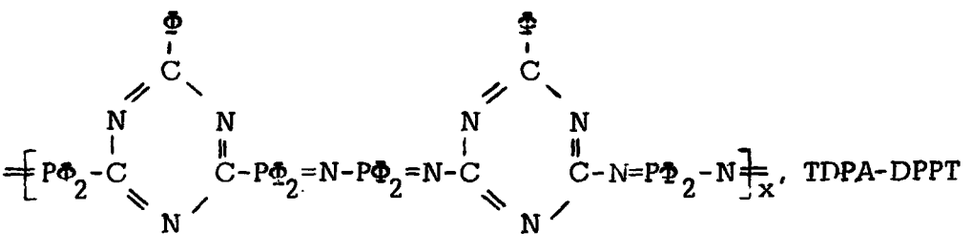
XXII



XXIII

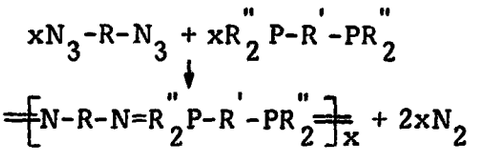


XXIV



XXV

These systems are derived from five monomers, namely, two diazido compounds and three bisphosphines which were described adequately in the previous sections. As was delineated briefly above the polymerization itself is the oxidation of a tertiary trivalent phosphorus moiety by an azido group:



The actual process could be visualized as an addition reaction if one considers the phosphine monomer; it can be also viewed as a condensation reaction since N_2 is eliminated from the azido moiety.

The experimental details of the performed investigations are summarized in Table I. These data are presented in greater details in the experimental section 3.3. The physical characteristics, including elemental analyses results, together with references to TGA and IR figures are listed in Table II.

Examining Tables I and II it is apparent that in the instances where molecular weights could be determined only short chain oligomers were isolated. The chain length varied from two to ten units. Based on the results of the elemental analyses, which are fairly close to the theoretical composition of the repeating segments, no end-groups appear to be present. The end-group effects in high molecular weight polymers are negligible, and are normally not reflected in their elemental analyses. However, since here we appear to be dealing with low molecular weight species one is forced to conclude that these are cyclic in nature. Cyclic compounds involving triazine rings joined by sulfur linkages have been reported by Laughran et al (ref. 43) which would support the feasibility of such an occurrence in this case. Furthermore in certain instances the azide oxidation reaction to form a P-N link was found to give almost exclusively ring compounds (ref. 44). On the other hand when a blocking end group was deliberately introduced the azido-process yielded predominantly linear materials (ref. 45). It was assumed that the introduction of either rings or chains such as these present in the diphosphines and diazides studied under this program will prevent cyclization. Based on the current work to avoid cyclization it might be necessary to employ a certain fraction of monofunctional monomers as inherent end group formers. Another approach would be to use a true condensation process as polymer forming reaction. The latter procedure based on reported data (ref. 46, 47) appears to yield mainly polymeric materials.

TABLE I

SUMMARY OF POLYMERIZATIONS

Run No.	Monomers A	Monomers B	T °C	Reaction Conditions Time hr	Reaction Conditions Solv.	Reactant Quantities A g	Reactant Quantities B g	Reactant Quantities Solv. ml	Medium Soluble Polymer Yield %	Medium Soluble Polymer SP[a] °C	Medium Soluble Polymer MP[b] °C	Medium Soluble Polymer MW	Medium Insoluble Polymer Yield %	Medium Insoluble Polymer SP °C	Medium Insoluble Polymer MP °C	Medium Insoluble Polymer MW
1	TDA	DPPB	RT[d]	16	C_6H_6	0.17	0.30	40	14	162	166-176	2070	41	170	176-186	6130
2	TDA	DPPB	RT	16	C_6H_6	0.57	1.00	40	28	nd[c]	nd	nd	62	182	187-192	nd
3	TDA	DPPB	RT	16	C_5H_5N	0.57	1.00	50	35	177	182-185	2910	42	187	190-195	5180
4	TDA	DPPB	RT	168	$CHCl_3$	0.57	1.00	40	88	190	195-205	4010	trace	-	-	-
5	TDA	DPPB	Reflux	73	C_6H_6	3.92	7.00	280	37	175	184-194	nd	63	181	186-203	2080
6	TDA	DPPE	Reflux	48	C_6H_6	0.59	0.98	24	4	169	180-192	nd	91	208	216-223	nd
7	TDA	DPPE	Reflux	76	C_6H_6	4.11	6.85	230	11	201	208-216	2780	88	214	217-230	nd
8	TDA	DPPT	RT	24	$CHCl_3$	0.46	1.01	30	78	186	191-195	4330	-	-	-	-
9	TDPA	DPPB	74	11	C_6H_6	0.64	0.43	1	65	158	163-171	2840	-	-	-	-
10	TDPA	DPPB	Reflux	150	$CHCl_3$	0.64	0.43	70	89	174	182-205	2065	-	-	-	-
11	TDPA	DPPB	74	8	C_6H_6	2.00	1.34	3	79	155	158-172	2160	-	-	-	-
12	TDPA	DPPE	74	11	C_6H_6	0.64	0.40	1	82	155	165-170	3520	-	-	-	-
13	TDPA	DPPT	Reflux	38	$CHCl_3$	2.12	1.75	100	81	159	165-180	1770	-	-	-	-

a SP = softening point b MP = melting point c nd = not determined d RT = room temperature

TABLE II

SUMMARY
POLYMER CHARACTERIZATION

Polymer Identification	Run No.	IR Fig. No.	TGA N_2 Fig. No.	TGA Air Fig. No.	SP °C	MP °C	MW Found	MW Seq.	Analyses %				
										C	H	N	P
TDA-DPPB	1-5	11,12	31	32	162-190	166-203	2070-6180	609.66	Calcd	72.90	5.46	11.43	10.16
									Found	72.45	5.75	12.04	10.01
TDA-DPPE	6,7	13	33	34	165-214	180-230	2780	681.60	Calcd	72.28	5.03	12.04	10.65
									Found	72.65	5.05	11.90	10.79
TDA-DPPT	8	14	35	36	186	191-195	4330	708.71	Calcd	71.18	4.27	15.81	8.74
									Found	70.74	4.41	15.96	8.54
TDPA-DPPB	9-11	15,16	37	38	158-174	158-205	2065-2840	1008.05	Calcd	72.68	5.30	9.73	12.29
									Found	71.47	5.75	9.88	12.38
TDPA-DPPE	12	17	39	40	155	165-170	3520	979.99	Calcd	72.31	5.04	10.00	12.64
									Found	71.89	5.27	9.66	13.16
TDPA-DPPT	13	18	41	42	159	165-180	1770	1107.11	Calcd	71.60	4.55	12.65	11.19
									Found	70.96	4.98	12.93	11.21

As noted above the results of the present investigation would tend to indicate that the cyclization process is favored in the particular system studied although this conclusion could be premature since the number of polymerization conditions investigated was limited. The relatively dilute solution in the polymerizations 1-8 (see Table I) could be considered conducive to cyclization. Yet in runs 9, 11, 12, and to a certain degree in run 13, (here solvent had to be removed to carry the reaction to completion), where the polymerization was carried out practically in the absence of solvent, cyclization apparently occurred also. Surprisingly, solvent does not appear to affect this process at least insofar as the molecular weight is concerned. It should be noted, however, that different products, as shown by their infrared spectra, were obtained using chloroform and benzene as the reaction media (compare IRs 11 and 12; also IRs 15 and 16). It furthermore should be noted that the material obtained from a reaction carried out in pyridine (see Table I, run 3) was identical with those formed using benzene as a solvent. No detailed study, including elemental analyses of the various preparations, was performed to elucidate whether the observed infrared spectral differences stem from the formation of cyclics and linear species. Since it was found that a given polymer system exhibited superimposable TGA curves regardless of the method of preparation it would seem safe to deduce that in each instance basically identical compounds or mixtures of compounds were obtained and that the spectral differences noted are probably associated with crystalline forms or orientation effects. It is believed that the thermal behavior of linear species would differ significantly from that of the cyclic compounds.

In the section dealing with the model compounds (Section 4.2) some of the TGA data of the polymeric systems were discussed. A point which was not emphasized there and which is of major interest is that these compositions seemed to exhibit very similar if not identical TGA curves in air and nitrogen up to 400°C. In most cases, however, the

char yield at 600°C (at a constant heating rate of 5°C/min) was higher in air than in a nitrogen atmosphere. In Table III are listed the decomposition onset temperatures and the char yields at 400°C for the six polymer systems investigated:

TABLE III
TGA DECOMPOSITION ONSET TEMPERATURES
AND CHAR YIELDS IN AIR

Material	Dec. Onset Temp. °C	Char Yield, % at 400°C	TGA Fig. No.
TDA-DPPB (XX)	340	75	31, 32
TDA-DPPE (XXI)	295	25	33, 34
TDA-DPPT (XXII)	220	58	35, 36
TDPA-DPPB (XXIII)	340	78	37, 38
TDPA-DPPE (XXIV)	295	34	39, 40
TDPA-DPPT (XXV)	230	35	41, 42

Examining these figures it is apparent that the system based on 1,4-bis(diphenylphosphino)butane, DPPB, is the most stable of those prepared under the current program. It would thus seem that the nature of the diazide, N_3-Φ_2P=N-C_3N_3(Φ)N=PΦ_2-N_3 versus N_3-C_3N_3(Φ)-N_3, TDPA and TDA, respectively has no apparent effect on the decomposition onset temperature, although the rate of decomposition is somewhat lower and the char yield at 400°C somewhat higher in the polymer derived from TDPA (material XXIII) as compared with the product containing TDA (material XX). The same observation can be made for the two polymers containing bis-diphenylphosphino ethane, DPPE (polymers XXI and XXIV) and for the two materials based on bis(diphenylphosphino)-s-triazine, DPPT, (polymers XXII and XXV) with the exception that here in contrast to the other two comparable polymer pairs the material containing TDPA (XXV) produces a significantly lower char yield at 400°C (35%) than the material containing TDA (XXII, 58%). This discrepancy, however, may be explained by the exceptionally lower molecular weight of material XXV, (see Table I) which shows an average degree of polymerization of 1.6 whereas that for material XXII is 6.1.

This finding implies that the limiting factor which determines the thermal stability of the materials investigated here is the bisphosphine moiety. This hypothesis is also supported by the studies with model compounds (Section 4.2). Of the three bisphosphines employed bis(diphenylphosphino) butane, DPPB, appears to impart the highest thermal stability followed by bis-(diphenylphosphino) ethane, DPPE and the bis-phosphino triazine, DPPT. There is no obvious reason for this order of decreasing thermal stability, although the lower stability of the materials based on DPPE (XXI and XXIV) may be traced to the thermal behavior of DPPE itself, which was found by DSC (see Figure 19) to undergo exothermic decomposition at 275°C. The exceptionally low stability of the materials containing DPPT (XXII and XXV), on the other hand, may be attributed to the low oxidative and hydrolytic stability of phosphinotriazines as described in Section 4.2.

As previously mentioned the maximum thermal stability of aliphatic materials lies around 350-400°C, whereas aromatic systems are stable to above 550°C (ref. 41).

Accordingly one could conclude that employing a thermally and oxidatively stable diphosphine unit the thermal stability of the polymer can be significantly increased. Since no aromatic diphosphines were available and since the synthesis of an aromatic diphosphine was beyond the original scope of the program, this hypothesis unfortunately could not be proven. However, based on the DSC curve for the bisphosphine XV (see Figure 24), which shows aside from melting practically no endothermic or exothermic reaction up to 400°C and based on the high thermal stability of triphenyl-s-triazine and triphenylphosphine (ref. 38) it can be concluded that a polymer containing 2,4-bis(phenyl-p-diphenylphosphino)-6-phenyl-s-triazine (XV) prepared for the first time under this program should exhibit very good thermal stability.

To study further the thermal behavior of the compositions prepared four of these namely TDA-DPPB (XX), TDA-DPPE (XXI), TDPA-DPPB (XXIII), and TDPA-DPPT (XXV) were subjected to isothermal gravimetric analysis, (ITGA) at 200°C (see Figure 43). The two 1,4-bis(diphenylphosphino) butane derived systems, TDA-DPPB and TDPA-DPPB, failed to show any weight loss under these conditions for up to 96 hr, whereas the other two materials, TDA-DPPE and TDPA-DPPT were degraded. Both of the bis(diphenylphosphino) butane derived polymers, TDA-DPPB and TDPA-DPPB were, however, degraded at 250°C as shown in Figure 44. From this plot of retained weight versus time it can be concluded that polymer XX is the thermally and oxidatively most stable of the six polymers prepared under this contract.

4.4 FLAMMABILITY AND DECOMPOSITION STUDIES

The same four polymers characterized by isothermal gravimetric analysis, TDA-DPPB (XX), TDA-DPPE (XXI), TDPA-DPPB (XXIII), and TDPA-DPPT (XXV) were also subjected to flammability and oxidative thermal degradation testing.

For the flammability tests the procedure specified for car interior materials (ref. 37) was employed. In essence the method consists of exposing the edge of a horizontally mounted specimen to the flame of a Bunsen burner for 15 sec, shutting off the supply of natural gas to the burner, and measuring the time it takes the flame to travel a 10"distance starting from the point 1.5" from the ignited edge of the sample. According to this test all four specimens, which were prepared as described in Section 3.4, failed to burn since all four samples self extinguished as soon as there was no contact between resin and the Bunsen burner flame.

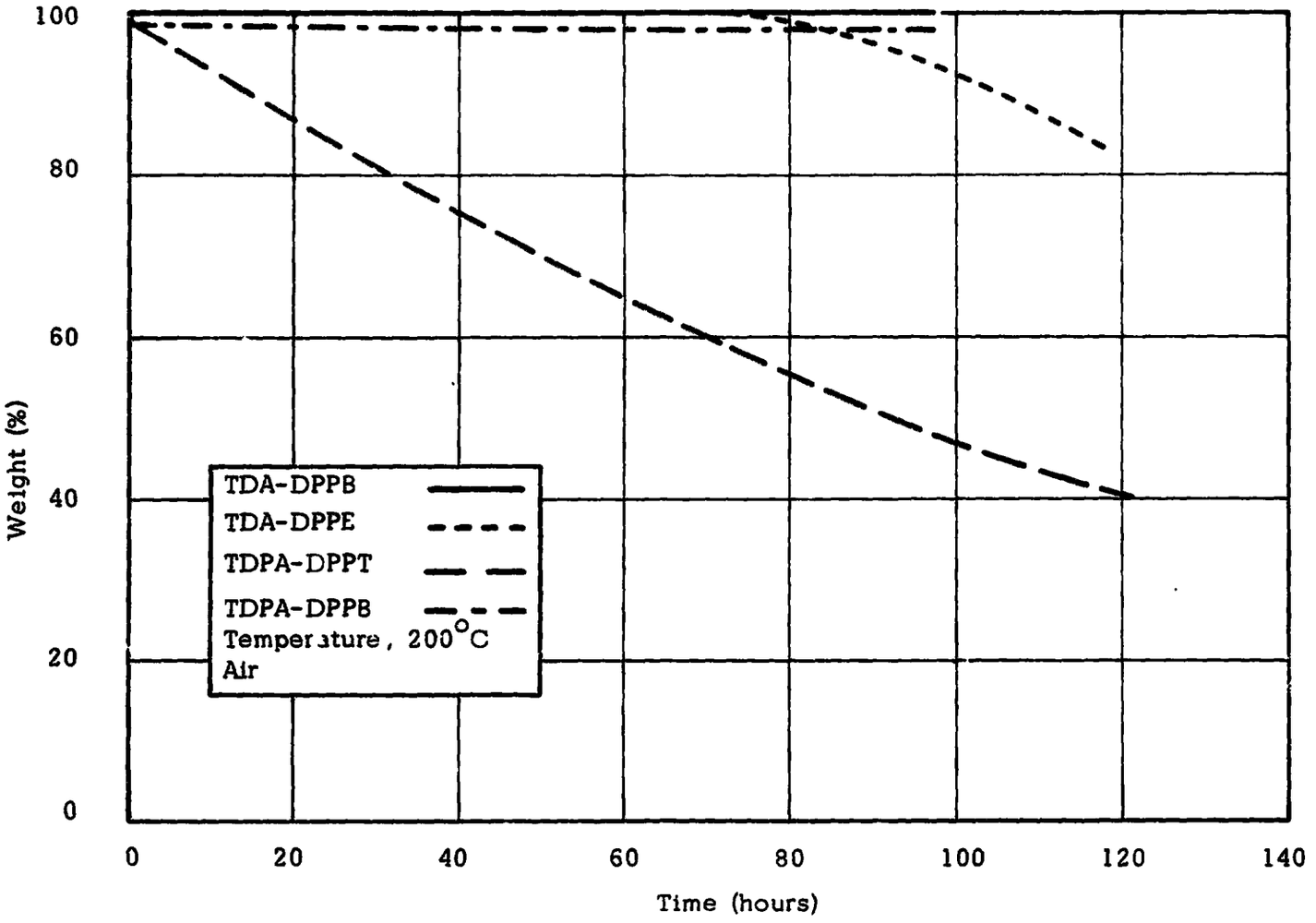


Fig. 43: Isothermal Gravimetric Analyses at 200°C in air.

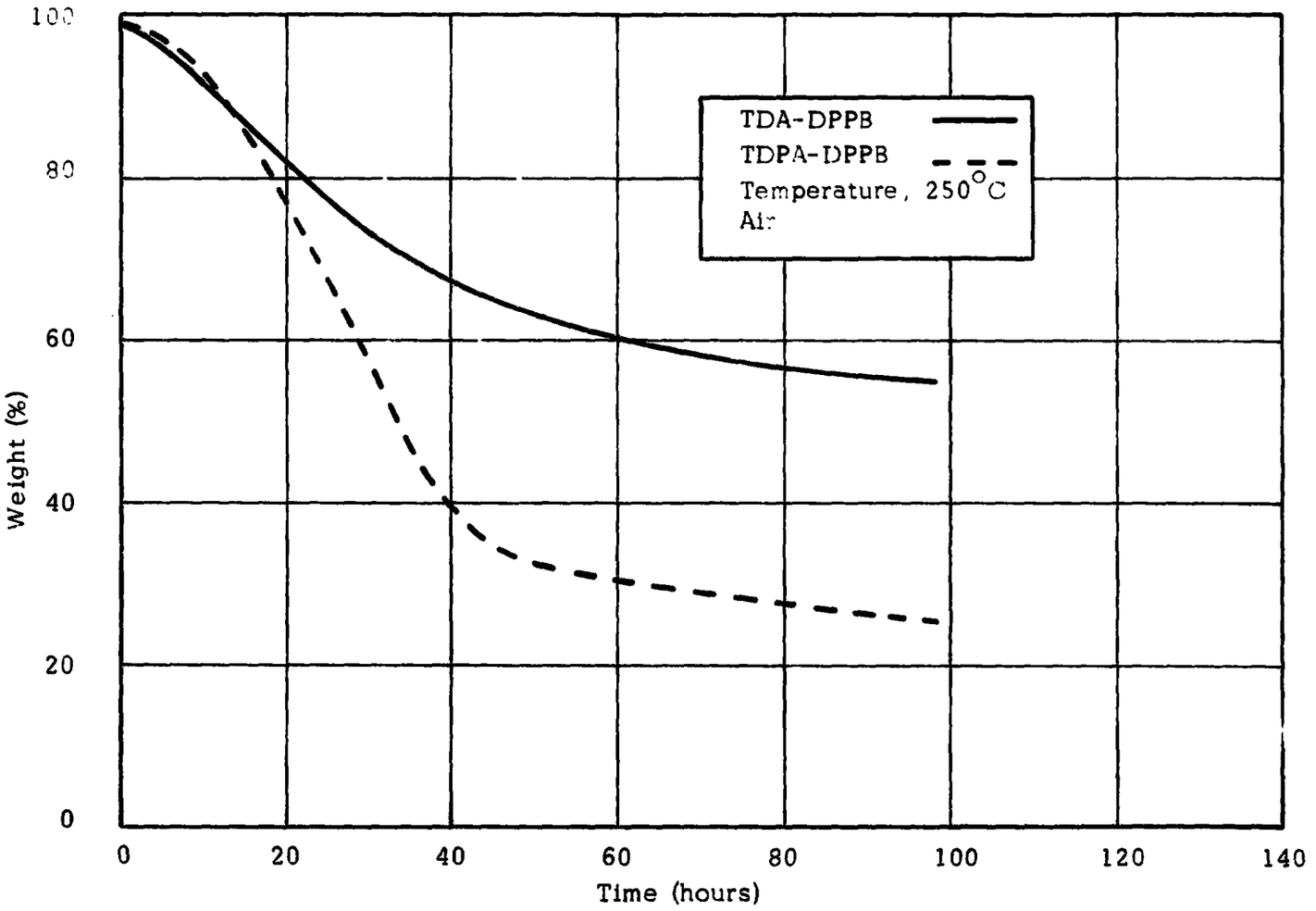


Fig. 44: Isothermal Gravimetric Analyses at 250°C in air.

Smoke and ignition testing and the quantative analysis for all oxidative thermal decomposition products were carried out with the aid of a stagnation burner using ~ 0.5 g pellets prepared from finely ground polymer powder as described in Section 3.4. The four specimens tested were made of the same stock as those subjected to flammability and ITGA testing as described above. Under the conditions of the test (air flow of 144 cc/sec, air and heating block at 500 ± 5°C) polymers, XX (TDA-DPPB), XXI (TDA-DPPE), and XXV (TDPA-DPPT) autoignited whereas material XXIII (TDPA-DPPB) failed to autoignite. As can be seen from Figure 45 ignition was accompanied by heavy smoke formation pointing to evolution of large quantities of optically opaque substances from the polymers. It will be shown later that this smoke consisted, aside from soot, of materials the infrared spectra of which resembles strongly those of the polymers tested. The amount of these oligomers corresponded to 12-40% of the original sample weight which, in agreement with the conclusions presented in Section 4.3, would indicate that part of the loss of optical transmission must be attributed to evaporation of lower molecular weight substances such as e.g., cyclics and not to "polymer" degradation. The presence of these low molecular weight compounds in the test samples also explains the occurrence of ignition since it is well established (ref. 49) that flammability increases strongly with decreasing molecular weight of a polymer. From Figure 45 it can furthermore be seen that smoke formation begins approximately one minute after the samples are placed into the stagnation burner and is completed, under the conditions of the experiment, within four to nine minutes. The fact that after this time the optical transmission in no case returned to 100% (see Figure 45) is due to deposition of smoke constituents on the windows of the optical system and is not due to continued smoke formation.

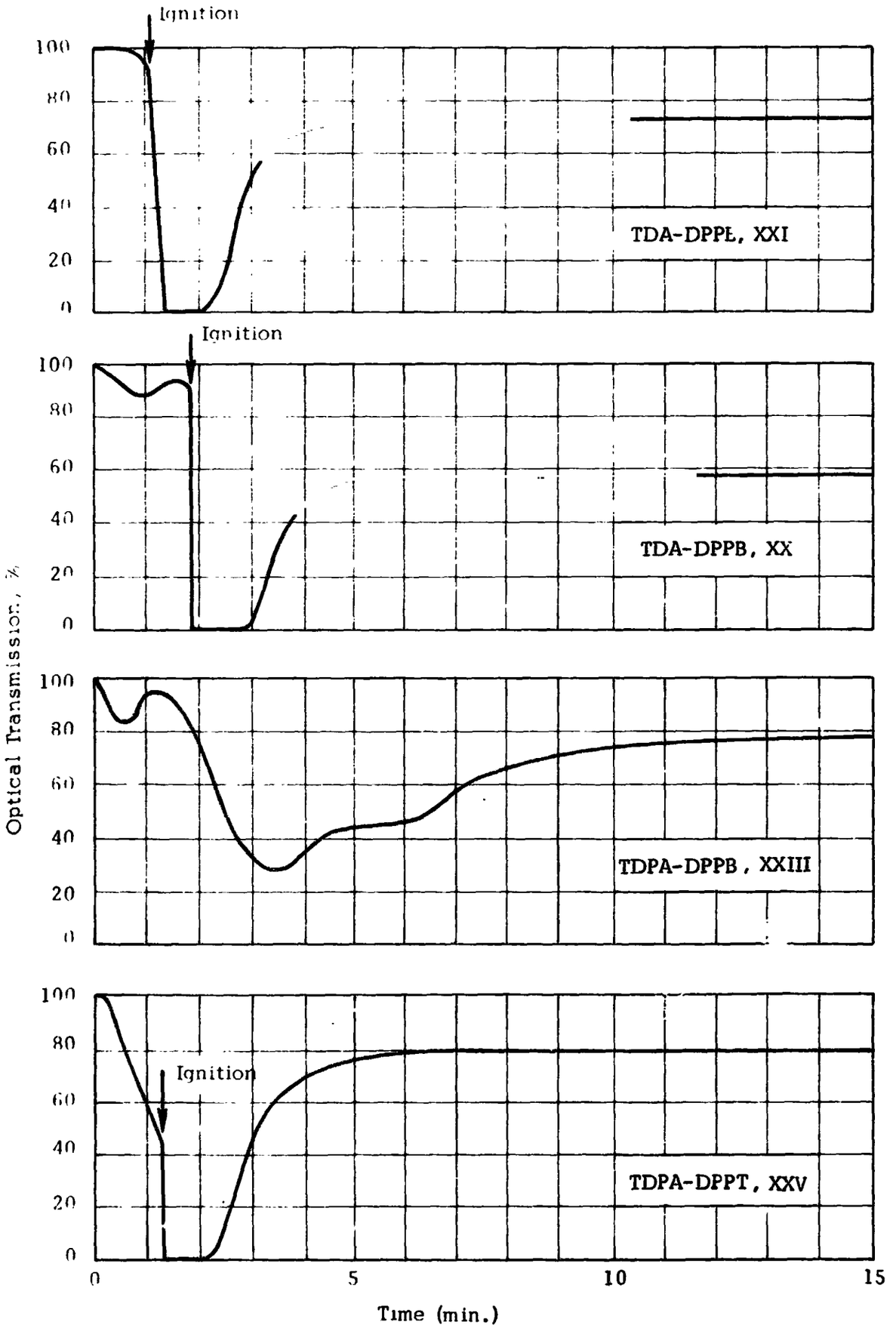


Fig. 45: Stagnation Burner Smoke Density Changes

The results of the quantitative analysis of oxidative thermal decomposition products formed in the above described stagnation burner tests are summarized in Table IV. As can be seen 64-77% of the test sample can be accounted for assuming that only negligible oxidation of the involatile residues took place. This mass balance is surprisingly good when one considers that materials of low volatility were deposited on the walls of the stagnation burner and on the windows. Furthermore relatively large quantities of soot collected in the sampling traps, in the case of polymers XX, XXI, and XXV, which could be removed from the traps only by washing with hydrofluoric acid and thus could not be determined quantitatively. Only polymer XXIII (TDPA-DPPB), which did not ignite, did not form any soot; at the same time this material produced the highest char yield (25% after 15 min at 500°C) and formed the largest quantity (40%) of room temperature involatile products. These involatiles, which were swept by the stream of hot air into the sampling traps and which could be recovered from the traps only by rinsing with acetone, consisted in all four experiments of low molecular weight oligomers, some diphenylphosphinic acid, and possibly traces of biphenyl; among the involatiles from TDPA-DPPB (XXIII) there was possibly also some 2,4-diamino-6-phenyl-s-triazine present.

The formation of all the products listed in Table IV with the exception of heptane (C_7H_{16}) detected in material XXIII (TDPA-DPPB) can be expected based on the polymers' composition. Although the sample of TDPA-DPPB (XXIII) had been dried under vacuum at 110°C for 6 hr it would seem that the 1.3% heptane found amongst the decomposition products is actually retained solvent. The production of small amounts of dinitrogen oxide, N_2O, can be rationalized in view of the finding (ref. 6) that polystyrene substituted in the p-position by a

TABLE IV

OXIDATIVE THERMAL DECOMPOSITION PRODUCTS

Product	Quantity, mg/g			
	TDA-DPPE XXI	TDA-DPPB XX	TDPA-DPPB XXIII	TDPA-DPPT XXV
CO_2	(497.9)	(524.8)	(59.1)	(500.3)
C in CO_2	135.7	143.1	16.1	136.4
HCN	7.7	1.2	0.1	2.7
C_2H_2	11.4	4.1	trace	4.4
C_2H_4	2.0	1.9	0.2	1.2
C_2H_6	1.5	0.8	trace	trace
C_3H_6	1.2	1.3	0.6	1.0
C_4H_6	trace	3.2	1.4	trace
C_6H_6	85.4	104.7	56.7	56.5
C_7H_{16}	0	0	12.7	0
C_6H_5-CH_3	0.7	3.2	1.2	0.3
C_6H_5-CN	37.1	40.9	20.1	51.3
H_2O	(74.2)	(195.8)	(67.6)	(49.1)
H in H_2O	8.2	21.8	7.5	5.5
N_2O	2.0	1.3	0.7	5.5
Char	203.0	190.7	251.3	195.0
Involatiles [a]	164.5	120.3	400.1	207.1
Total	660.4	638.5	768.7	666.9

a Residues not volatile at room temperature, recovered from sampling traps by washing with acetone.

$-P\Phi_2=N-P(O)\Phi_2$ group (ref. 48) also produced some N_2O. The explanation used for its formation in this case was that possibly some unreacted azide was present in the test sample. The formation of benzene is also not surprising since it is the major decomposition product of phenyl substituted polyphosphazenes (ref. 18). The production of hydrogen cyanide, HCN, during combustion of an organic material in air can occur even if this material does not contain nitrogen. However, in view of the detection of relatively large amounts (2-5% of the original sample weight) of benzonitrile, C_6H_5CN, it may be concluded that HCN as well as C_6H_5CN originate from the decomposition of the 6-phenyl-s-triazine moieties present in all materials prepared under this program and not from phosphazene units or reactions with air. Based on this reasoning it may be concluded that the s-triazine unit, despite its high thermal stability and good flame retardation and char forming characteristics, may not be as desirable a component of a polymer in regard to toxic product formation as it would seem to be. Thus the elimination of the s-triazinee based polymer components (or at least the use of only fully aromatically substituted s-triazine units) can be assumed to reduce or completely prevent the formation of those two products.

In regard to HCN formation it is interesting to compare the data of Table IV with the autoignition behavior and smoke production depicted in Figure 45. As can be seen, the material which did not ignite (XXIII, TDPA-DPPB), formed the smallest amounts of both HCN and C_6H_5CN of the four samples tested, whereas the material XXI, TDA-DPPE, which ignited the soonest after insertion into the stagnation burner, produced the largest quantity of HCN. It is known (ref. 50) that the amount of HCN produced increases with the heating rate. Although for the four samples tested here the heating rates were the same (approximately $500^{\circ}C$/min) it may be said that the material, which ignited first XXI, TDA-DPPE,

was the one which decomposed the fastest and thus produced the conditions most conducive to HCN formation. The low molecular weights of all materials prepared indicate the possible presence of cyclic substances and/or many chain ends and these are further factors which can be assumed to favor HCN production. Thus the data obtained are really not representative of high molecular weight polyphosphazenes and the low HCN yields, e.g., 0.1 mg/g for material XXIII (see Table IV) are even encouraging, if extrapolated to high molecular weight polymers, when one considers that high molecular weight polyimides were found to form 19-30 mg/g of HCN at much lower heating rates (5-50^{o}C/min) (ref. 50). In this context it therefore may be deduced that a material of higher molecular weight will exhibit a lower rate of decomposition, which may also result in a reduction of the quantity of HCN formed.

According to published threshold limit values (TLV's) (ref. 7), of all substances detected among the decomposition products of the four test samples HCN is the most dangerous product with a TLV of 11 mg/m^{3}. It is closely followed by benzene (TLV = 80 mg/m^{3}), then by toluene, $C_6H_5-CH_3$ (TLV = 375 mg/m^{3}). Heptane, C_7H_{16}, (TLV - 1,800 mg/m^{3}) and carbon dioxide (TLV = 9,000 mg/m^{3}) are the only other products formed for which the American Conference of Governmental Industrial Hygienists has published TLV values. Acetylene, ethylene, ethane, and dinitrogen oxide are listed as asphyxiants, all other decomposition products are not listed at all. On this basis it then can be concluded that HCN and benzene are the most toxic products formed during the oxidative thermal decomposition of the polyphosphazenes prepared and tested under this program.

5. CONCLUSIONS AND RECOMMENDATIONS

Summarized below are the conclusions reached during this experimental study to prepare flame retardant polyphosphazanes. Based on the findings, recommendations are presented for material improvements insofar as higher molecular weights and increased thermal stability are concerned, which in view of the observations made during this program should increase flame resistance and lower the amounts of toxic decomposition products formed during oxidative thermal degradation.

1) The molecular weights together with the elemental analyses of all materials prepared under this program indicate the presence of (low molecular weight) cyclic compounds. Further studies need to be performed to establish the validity of this finding. To obtain linear, high molecular weight polyphosphazenes the thermal rearrangement of the cyclic phosphazenes into linear polymers should be attempted. Another approach considered promising is blocking the reactivity of one end of the growing polymer chain. A promising approach for the synthesis of high molecular weight linear polymers, however, is believed to be the condensation of selected diamines with bis(dichlorophosphoranes).

2) In view of TGA and DSC data obtained for all monomers, model compounds, and polymers prepared under this program it is evident that the thermal stability of the polymer systems investigated is largely limited by the nature of the bisphosphine unit. For the preparation of thermally stable and flame retardant polyphosphazenes only fully aromatic bisphosphines or bisphosphoranes should be employed.

3) Based on the thermal oxidative degradation studies performed and on the nature and relative concentration of the decomposition products it can be concluded that triazine rings, (unless fully aromatically substituted), tend to decompose into benzonitrile and/or HCN. To prevent the formation of these substances monomers containing triazine rings should not be used or only fully aromatically substituted triazines as exemplified by 2,4-bis(phenyl-p-diphenyl-phosphino)-6-phenyl-s-triazine, should be employed.

4) The flammability and autoignition behavior as well as the smoke formation observed can be attributed to the low molecular weight and associated volatility of the compositions prepared under this program. The preparation of high molecular weight materials employing monomers of high thermal stability should alleviate this problem.

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APPENDIX

IR, DSC, AND TGA SCANS

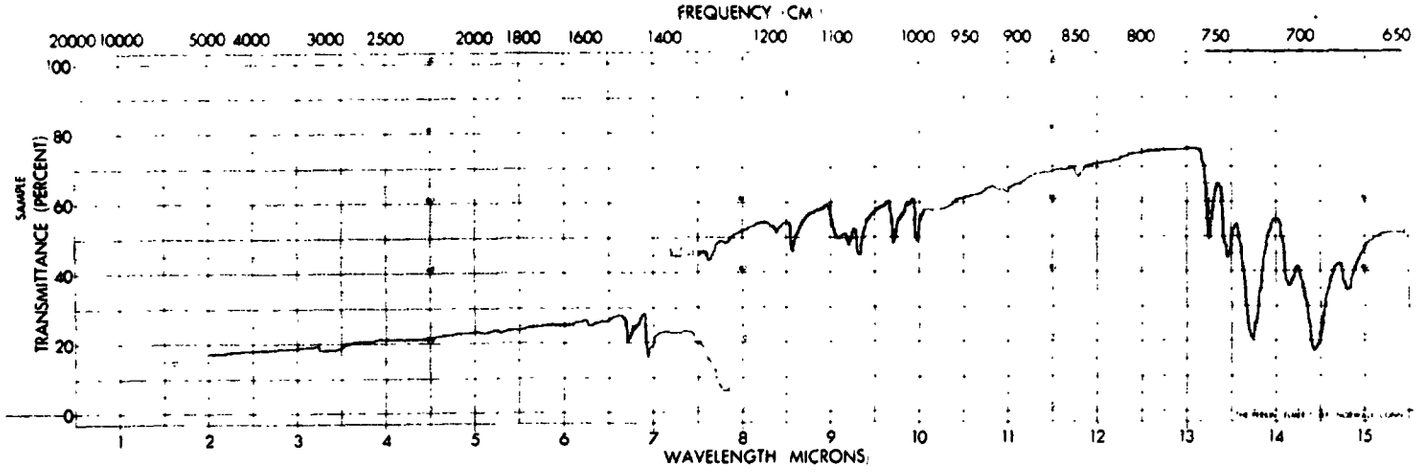

Fig. 1: Infrared Spectrum of $\Phi_2P\text{-}(CH_2)_2\text{-}P\Phi_2$, DPPE

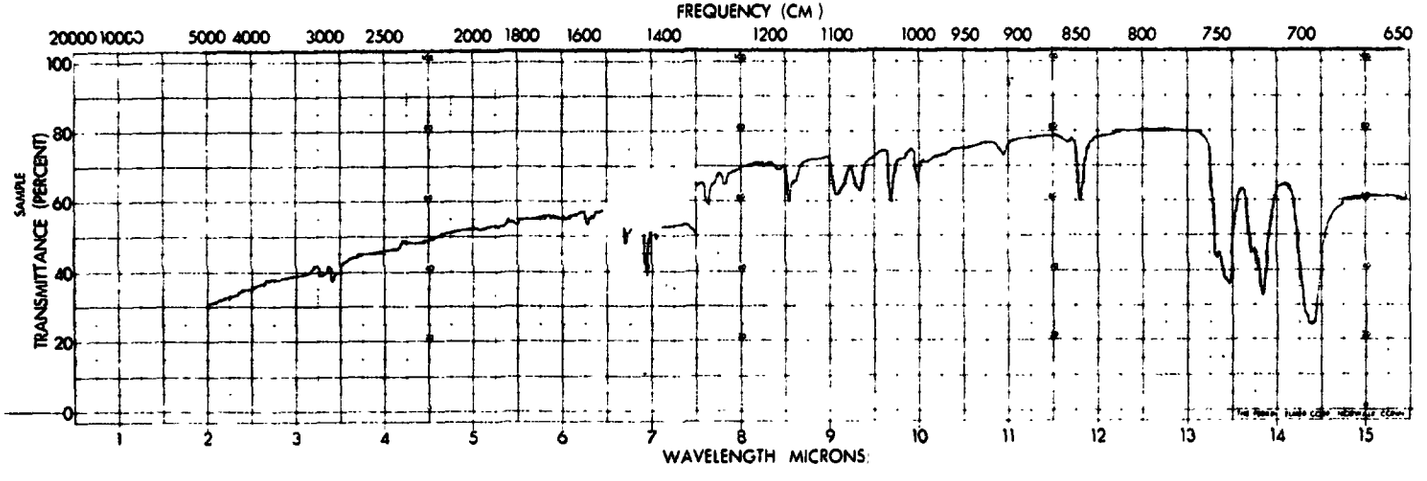

Fig. 2: Infrared Spectrum of $\Phi_2P\text{-}(CH_2)_4\text{-}P\Phi_2$, DPPB

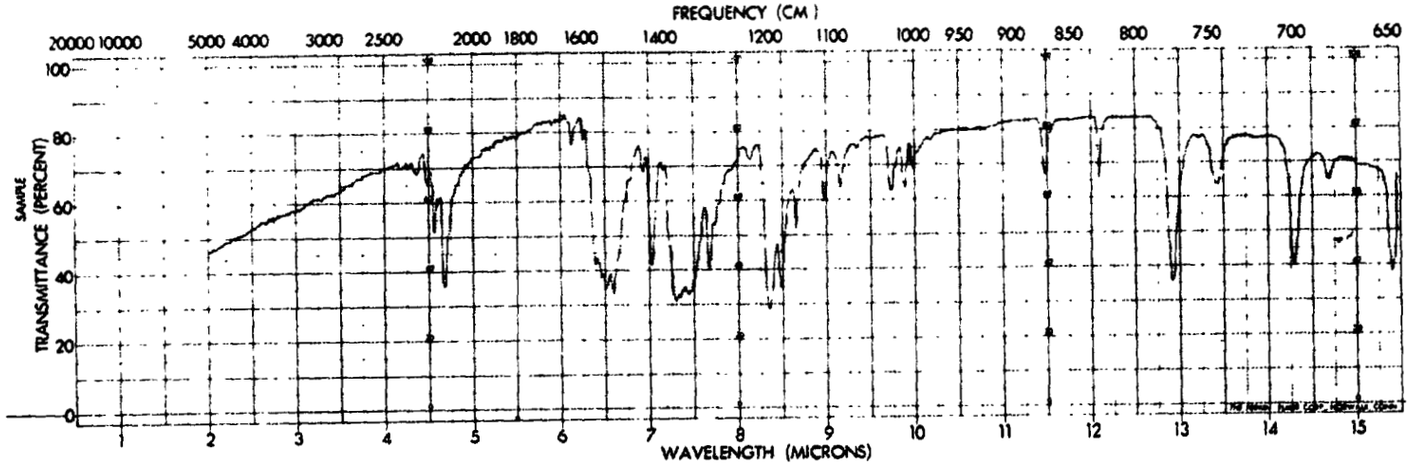

Fig. 3: Infrared Spectrum of N_3-$C_3N_3(\Phi)$-N_3, TDA

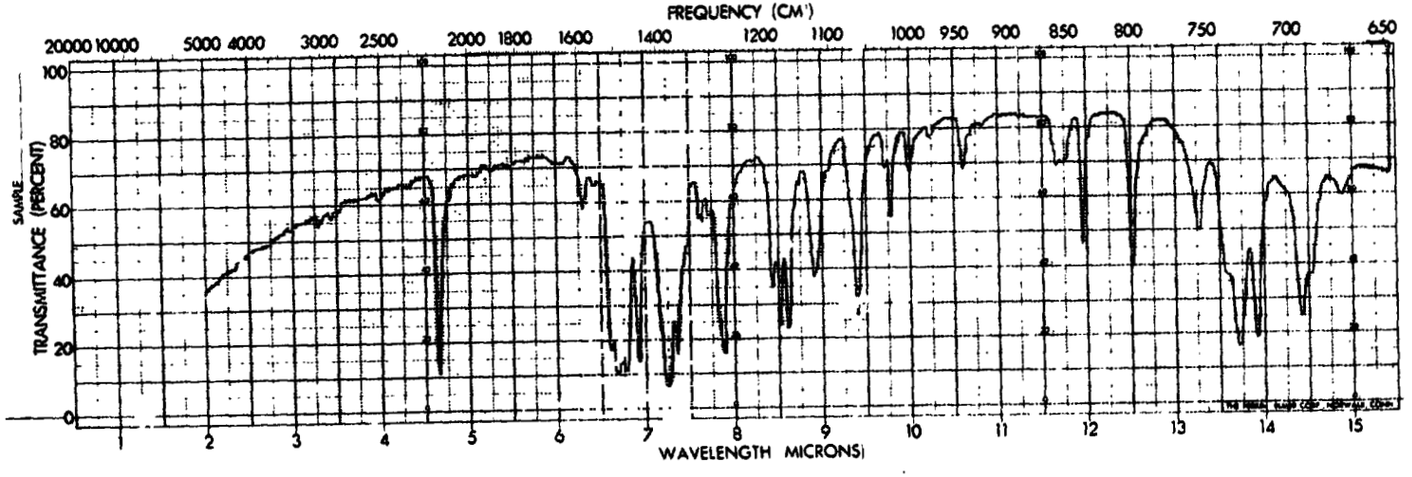

Fig. 4: Infrared Spectrum of N_3-$P\Phi_2$=N-$C_3N_3(\Phi)$-N=$P\Phi_2$-N_3, TDPA

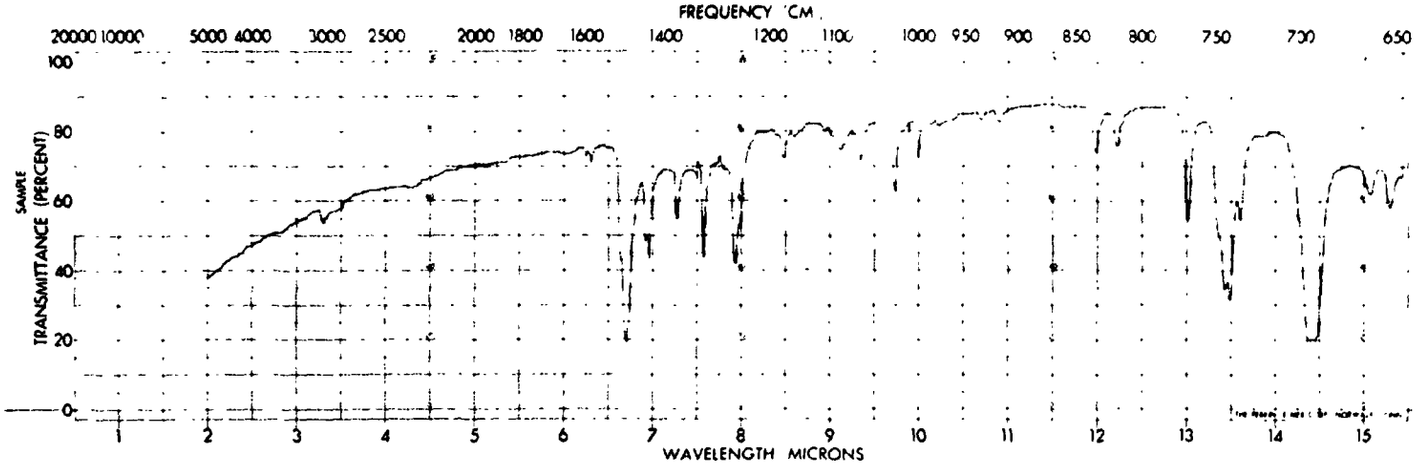

Fig. 5: Infrared Spectrum of $\Phi_2P\text{-}C_3N_3(\Phi)\text{-}P\Phi_2$, DPPT

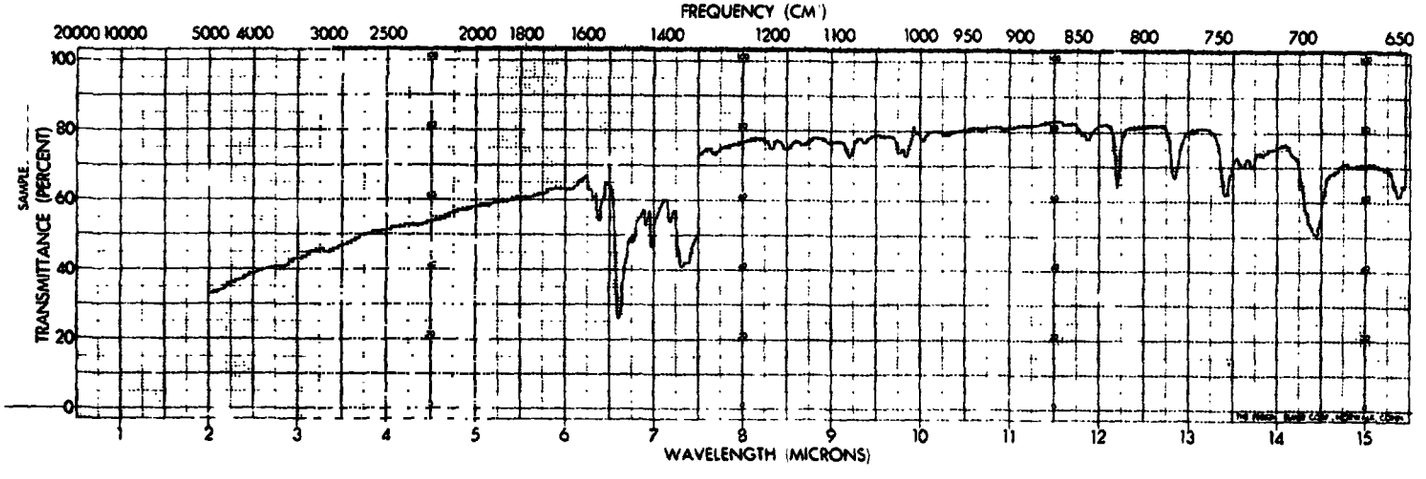

Fig. 6: Infrared Spectrum of $\Phi_2P\text{-}\Phi\text{-}C_3N_3(\Phi)\text{-}\Phi\text{-}P\Phi_2$

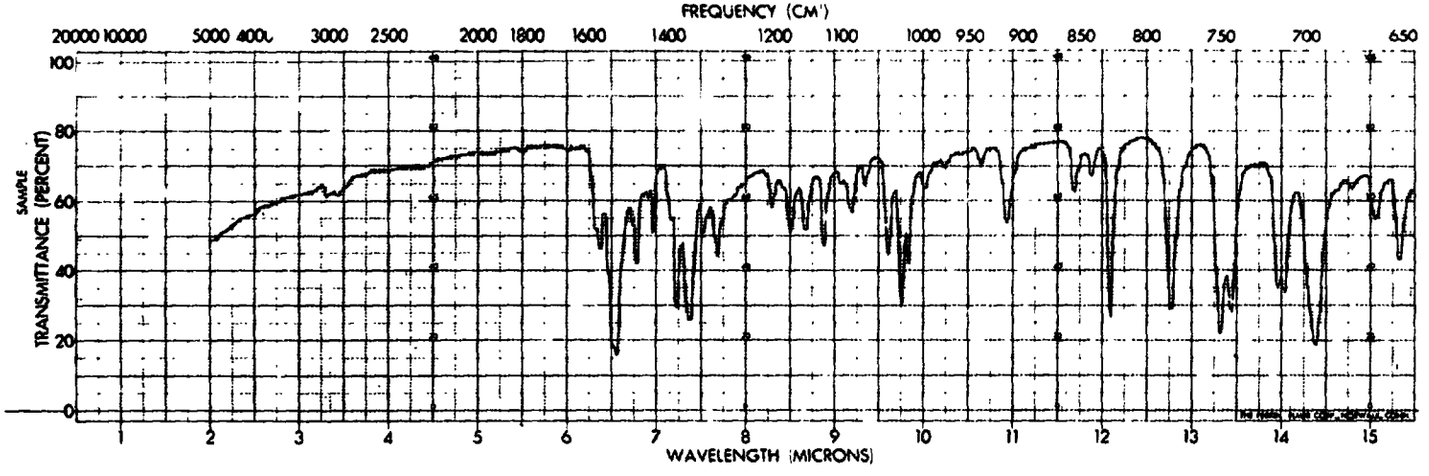

Fig. 7: Infrared Spectrum of $\Phi_2P\text{-}\Phi\text{-}C_3N_3(\Phi)\text{-}OCH_3$

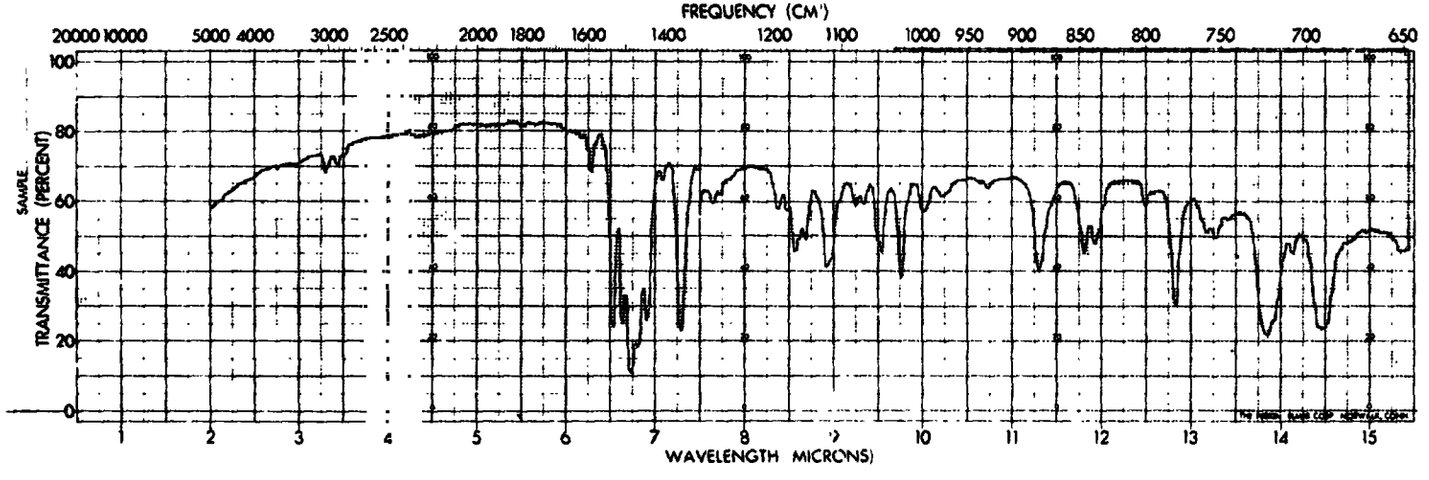

Fig. 8: Infrared Spectrum of $\Phi_2C_3N_3\text{-}N\text{:}P\Phi_2\text{-}(CH_2)_4\text{-}P\Phi_2\text{=}N\text{-}C_3N_3\Phi_2$

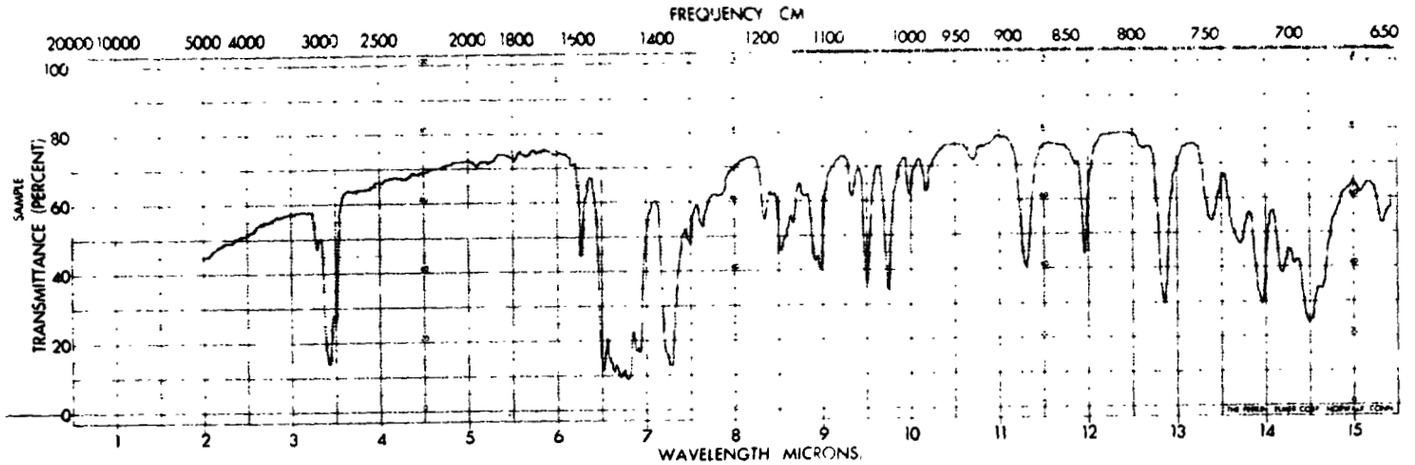

Fig. 9: Infrared Spectrum of $\Phi_2C_3N_3$-N=PΦ_2-$C_3N_3(\Phi)$-PΦ_2=N-$C_3N_3\Phi_2$

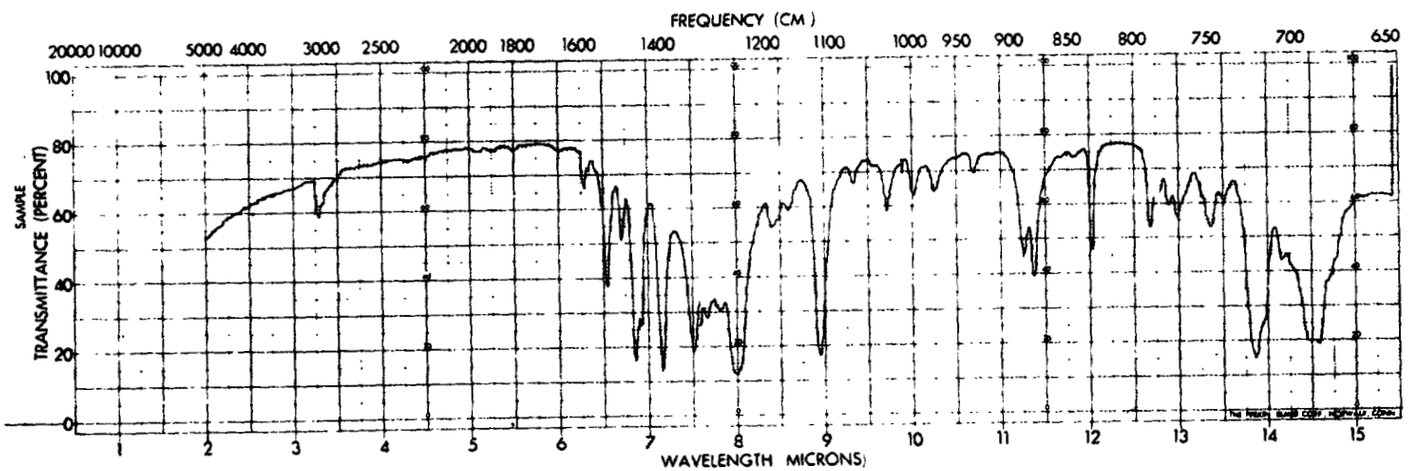

Fig. 10: Infrared Spectrum of Φ_3P=N-PΦ_2=N-$C_3N_3(\Phi)$-N=PΦ_2-N=PΦ_3

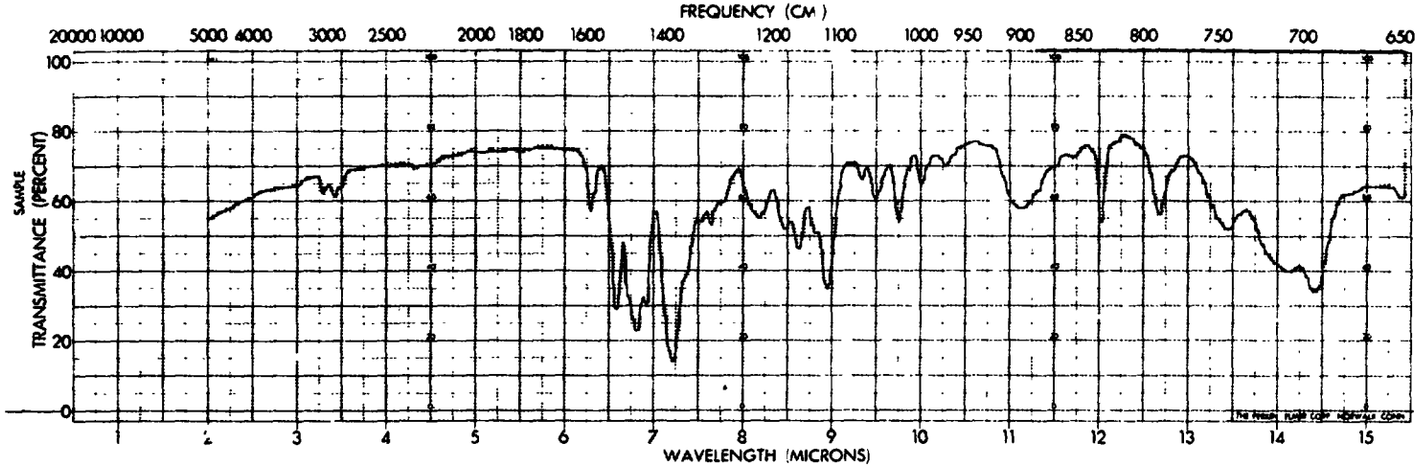

Fig. 11: Infrared Spectrum of $\left[P\Phi_2-(CH_2)_4-P\Phi_2=N-C_3N_3(\Phi)-N\right]_x$, TDA-DPPB, from benzene

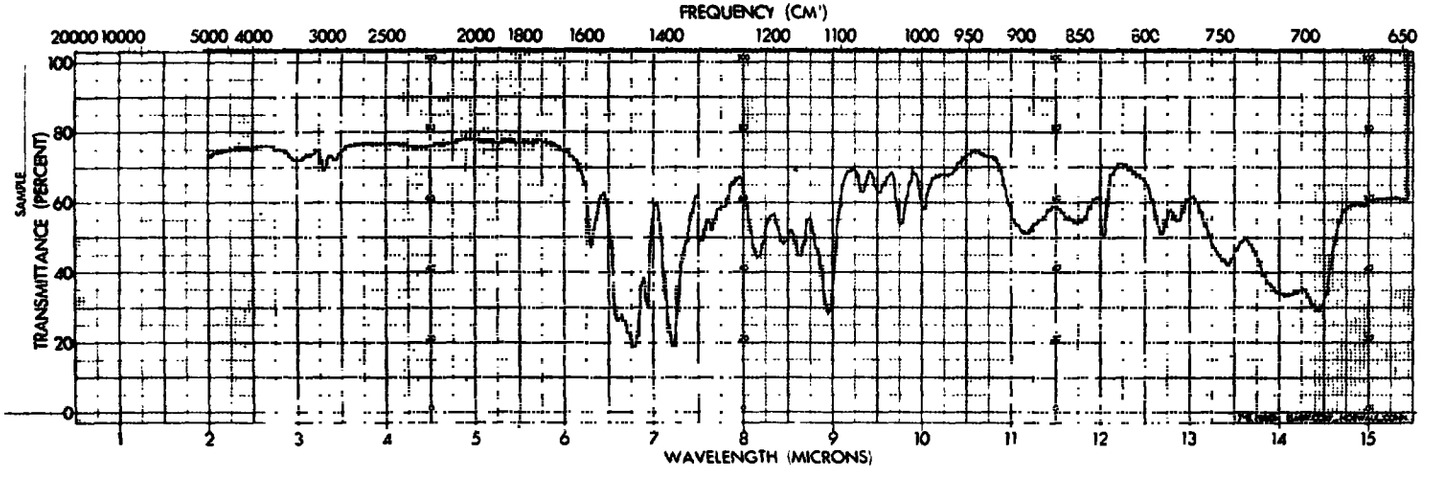

Fig. 12: Infrared Spectrum of $\left[P\Phi_2-(CH_2)_4-P\Phi_2=N-C_3N_3(\Phi)-N\right]_x$, TDA-DPPB, from chloroform

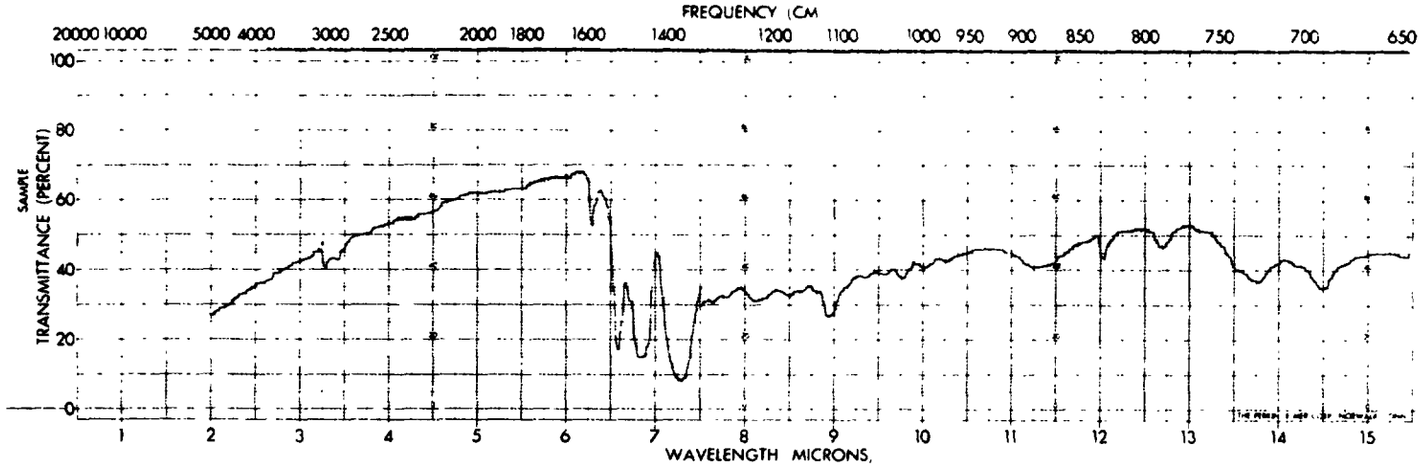

Fig. 13: Infrared Spectrum of $\left[P\Phi_2\text{-}(CH_2)_2\text{-}P\Phi_2\text{=}N\text{-}C_3N_3(\Phi)\text{-}N \right]_x$, TDA-DPPE

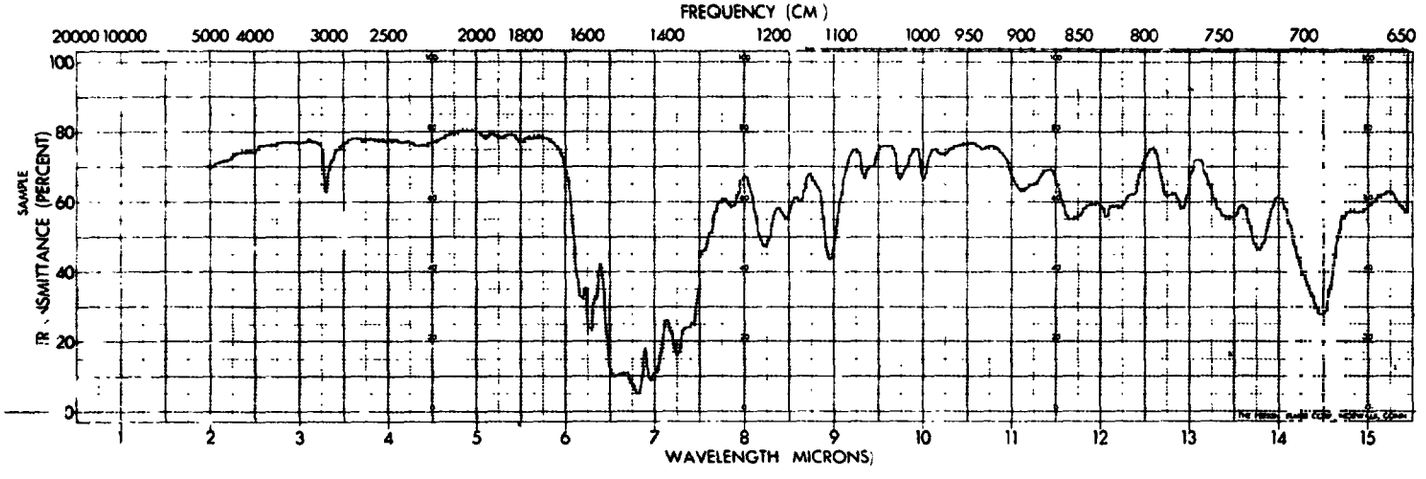

Fig. 14: Infrared Spectrum of $\left[P\Phi_2\text{-}C_3N_3(\Phi)\text{-}P\Phi_2\text{=}N\text{-}C_3N_3(\Phi)\text{-}N \right]_x$, TDA-DPPT

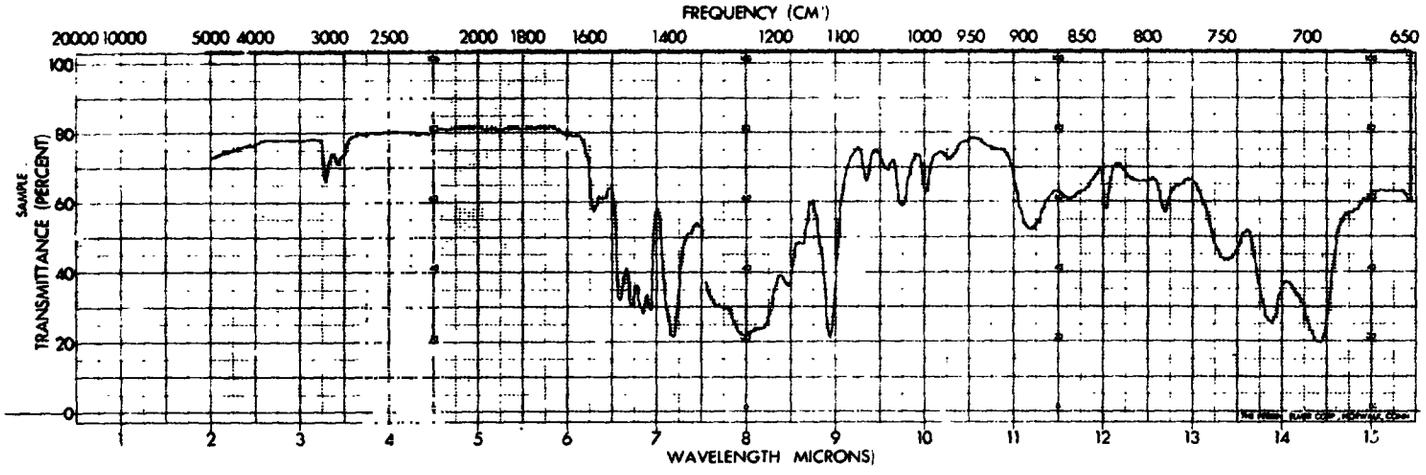

Fig. 15: Infrared Spectrum of $\left[P\Phi_2-(CH_2)_4-P\Phi_2=N-P\Phi_2=N-C_3N_3(\Phi)-N=P\Phi_2-N=\right]_x$, TDPA-DPPB, from benzene

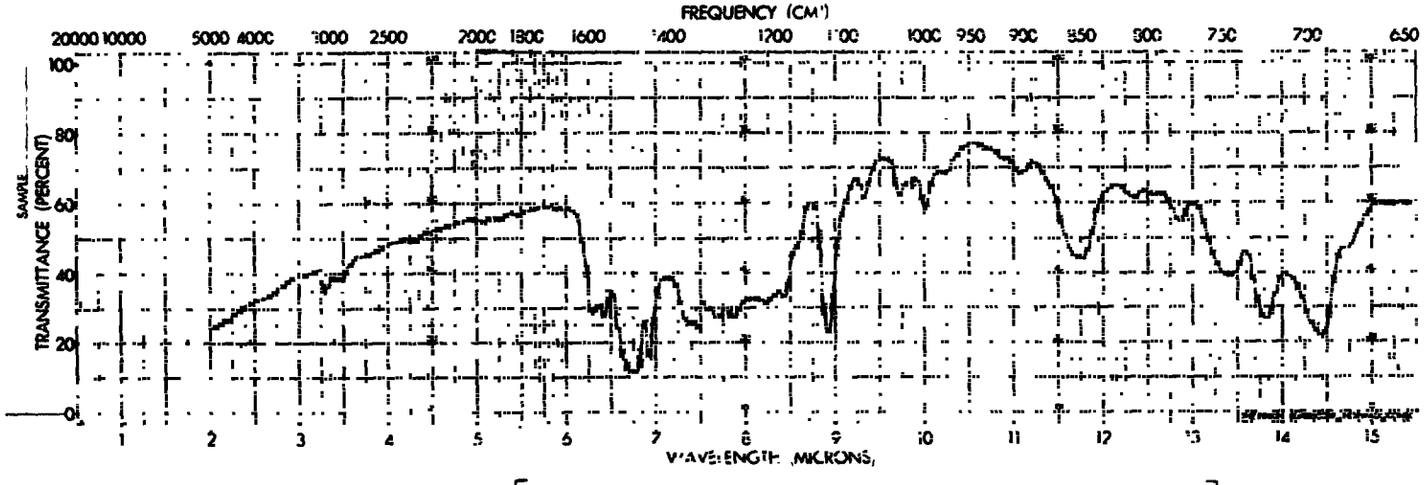

Fig. 16: Infrared Spectrum of $\left[P\Phi_2-(CH_2)_4-P\Phi_2=N-P\Phi_2=N-C_3N_3(\Phi)-N=P\Phi_2-N=\right]_x$, TDPA-DPPB, from chloroform

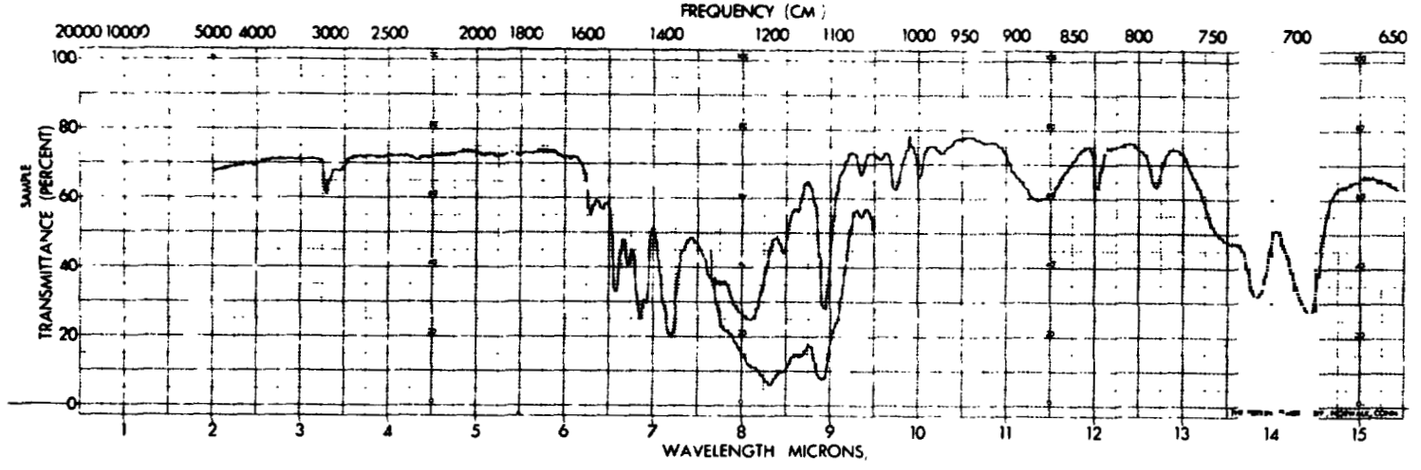

Fig. 17: Infrared Spectrum of $\left[P\Phi_2-(CH_2)_2-P\Phi_2=N-P\Phi_2=N-C_3N_3(\Phi)-N=P\Phi_2-N\right]_x$, TDPA-DPPE

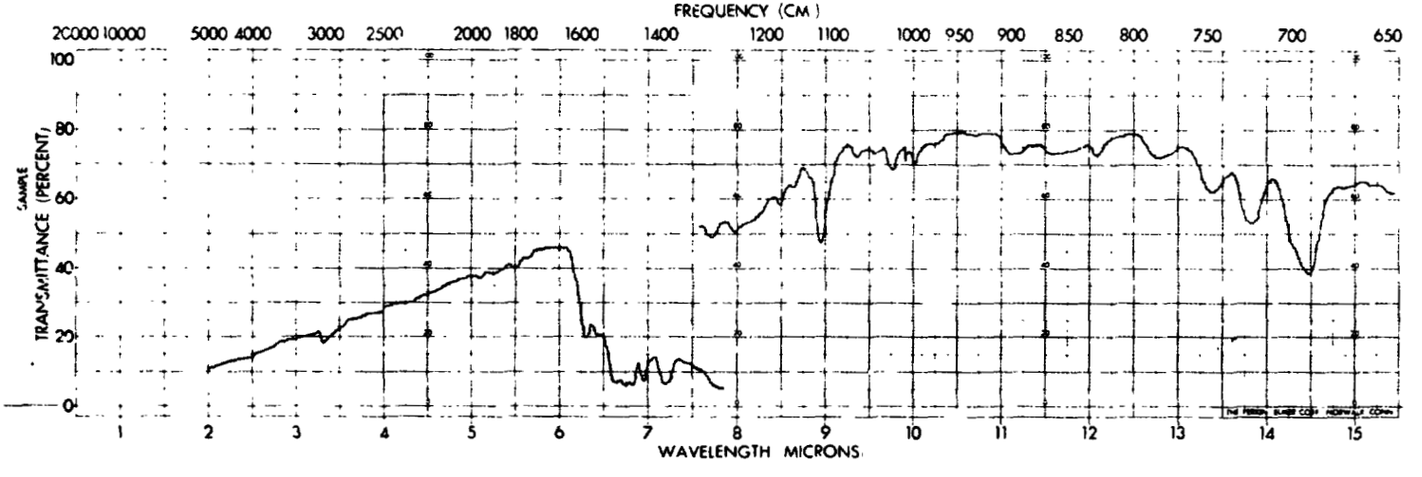

Fig. 18: Infrared Spectrum of $\left[P\Phi_2-C_3N_3(\Phi)-P\Phi_2=N-P\Phi_2=N-C_3N_3(\Phi)-N=P\Phi_2-N\right]_x$, TDPA-DPPT

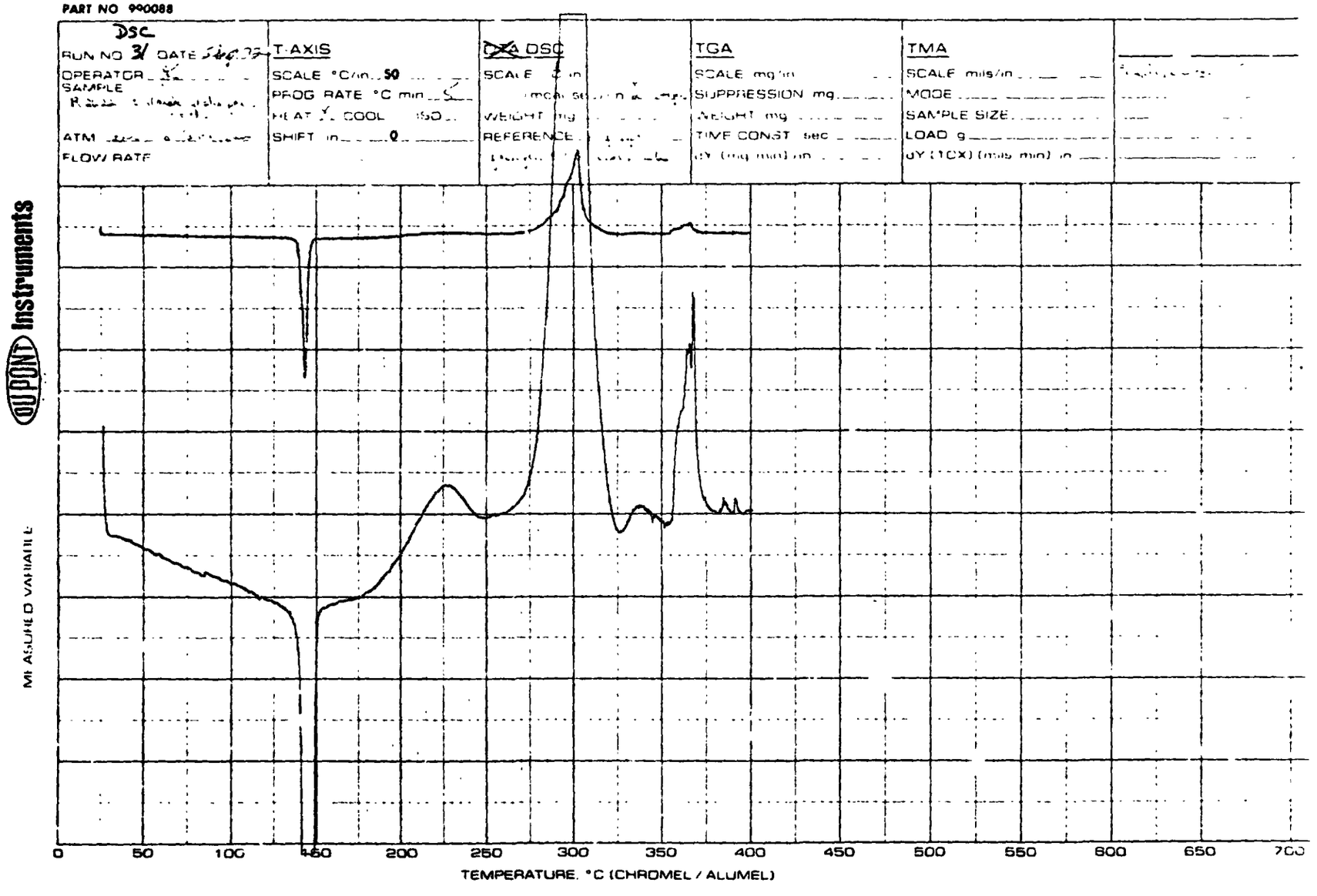

Fig. 19: DSC of $\Phi_2P\text{-}(CH_2)_2\text{-}P\Phi_2$, DPPE

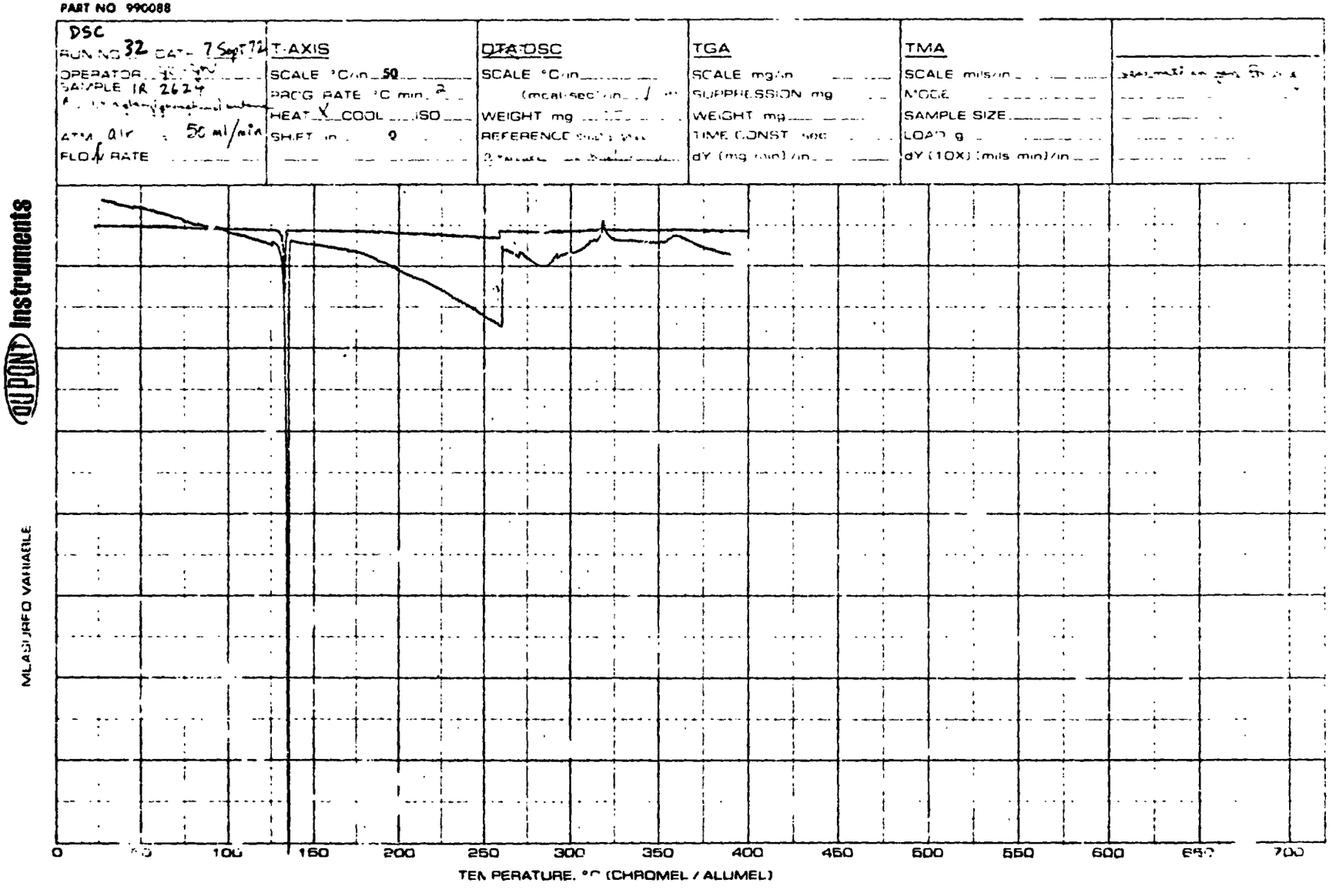

Fig. 20: DSC of $\Phi_2P\text{-}(CH_2)_4\text{-}P\Phi_2$, DPPB

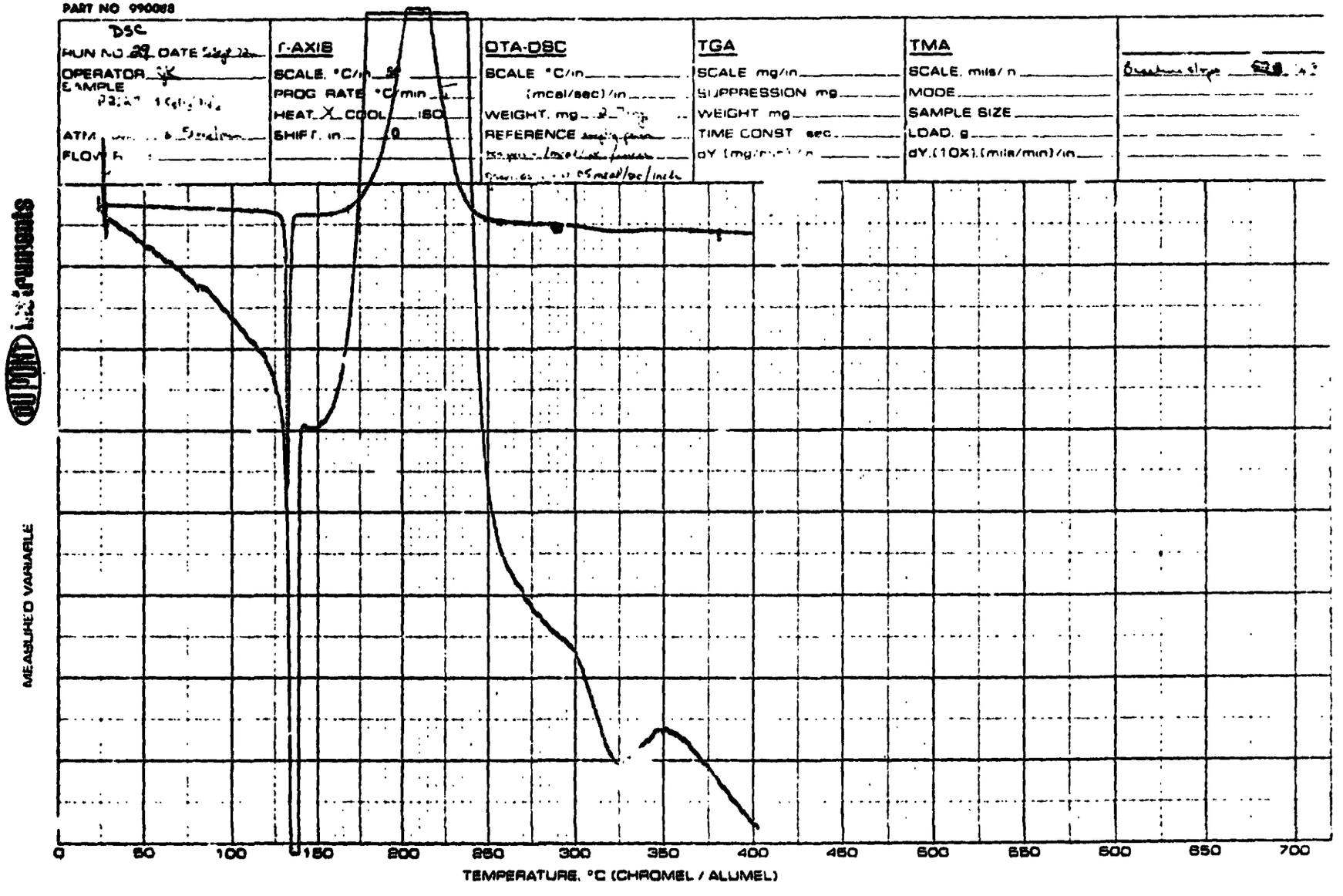

Fig. 21: DSC of N_3-$C_3N_3(\Phi)$-N_3, TDA

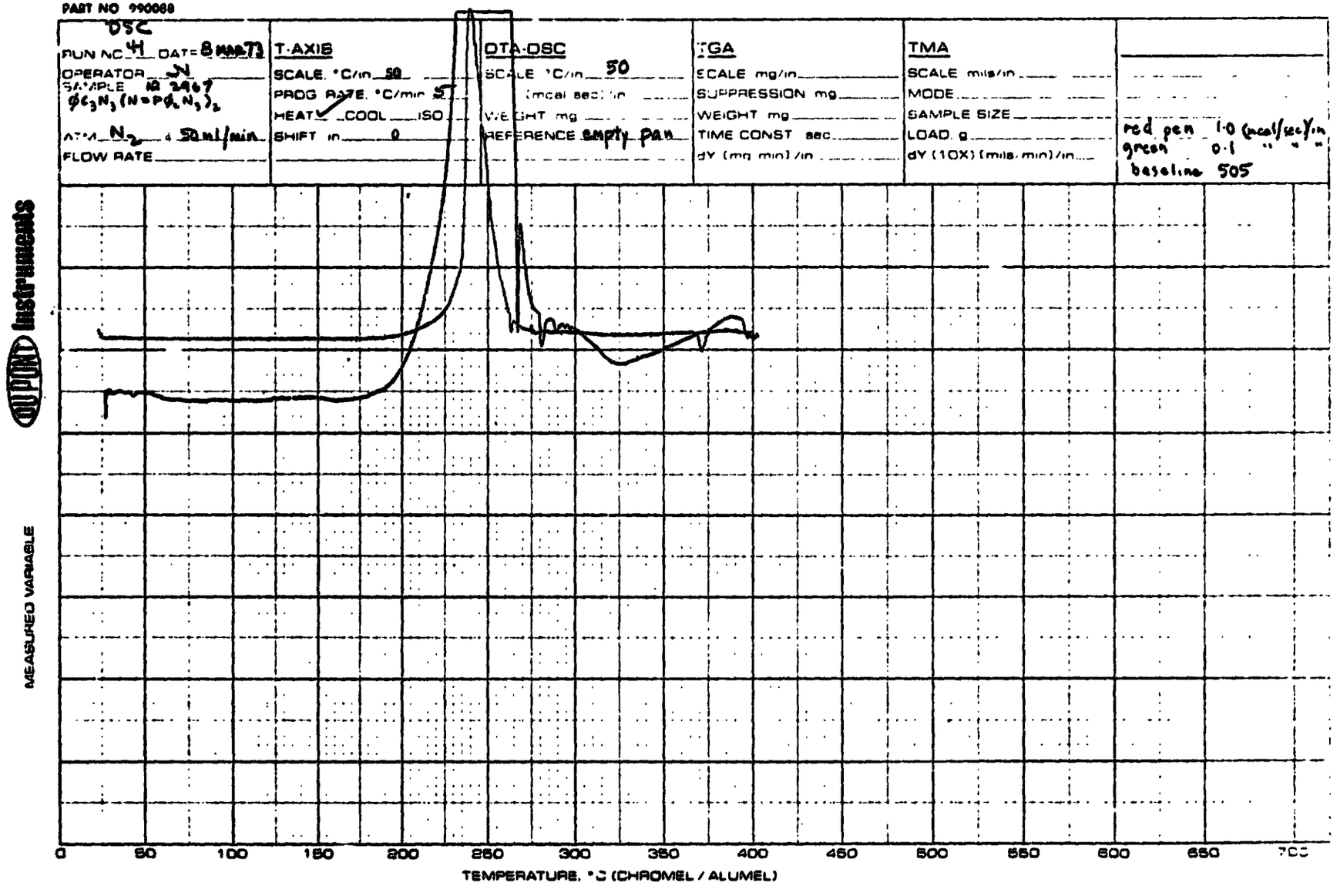

Fig. 22: DSC of $N_3-P\Phi_2=N-C_3N_3(\Phi)-N=P\Phi_2-N_3$, TDPA

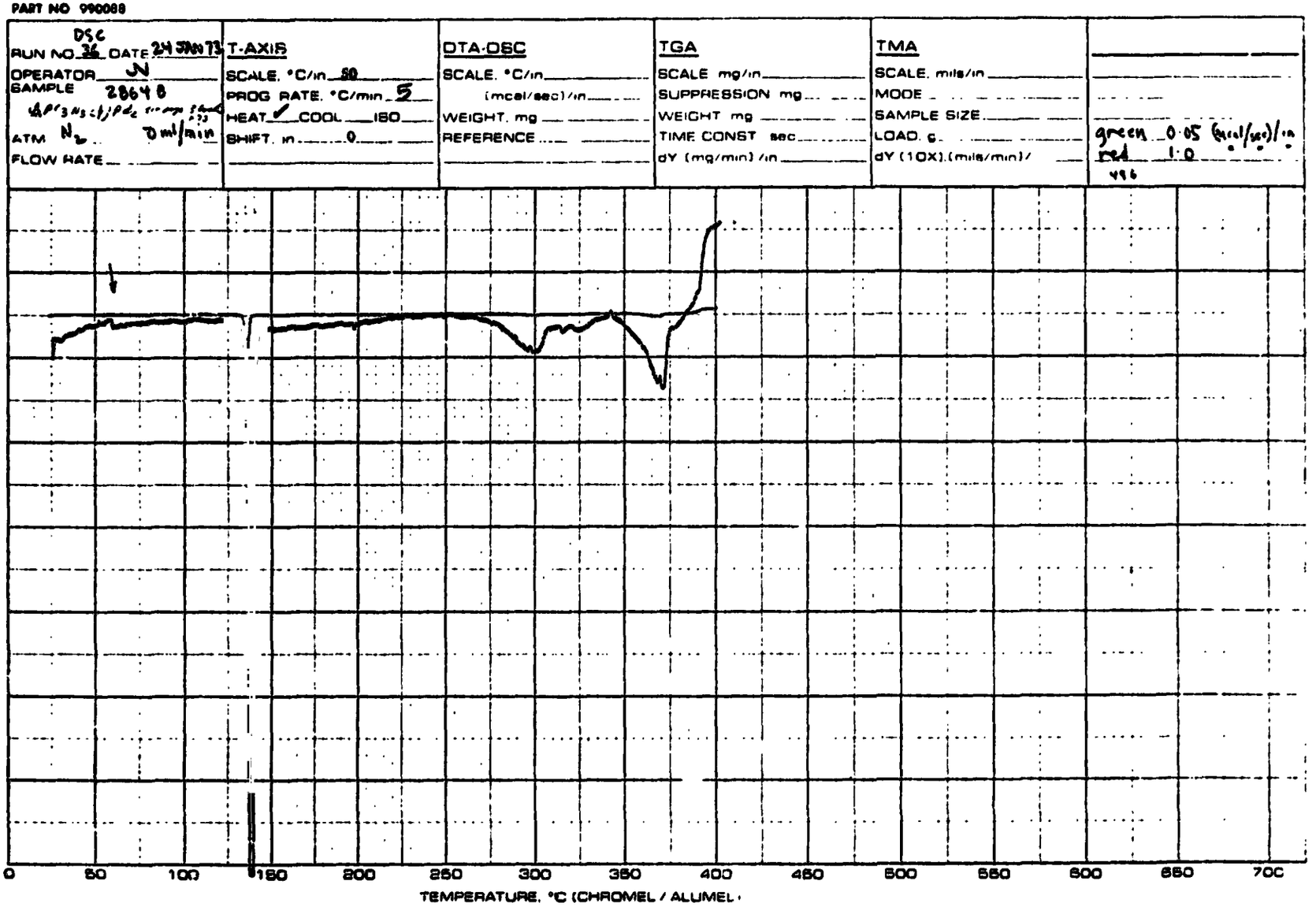

Fig. 23: DSC of $\Phi_2P\text{-}C_3N_3(\Phi)\text{-}P\Phi_2$, DPPT

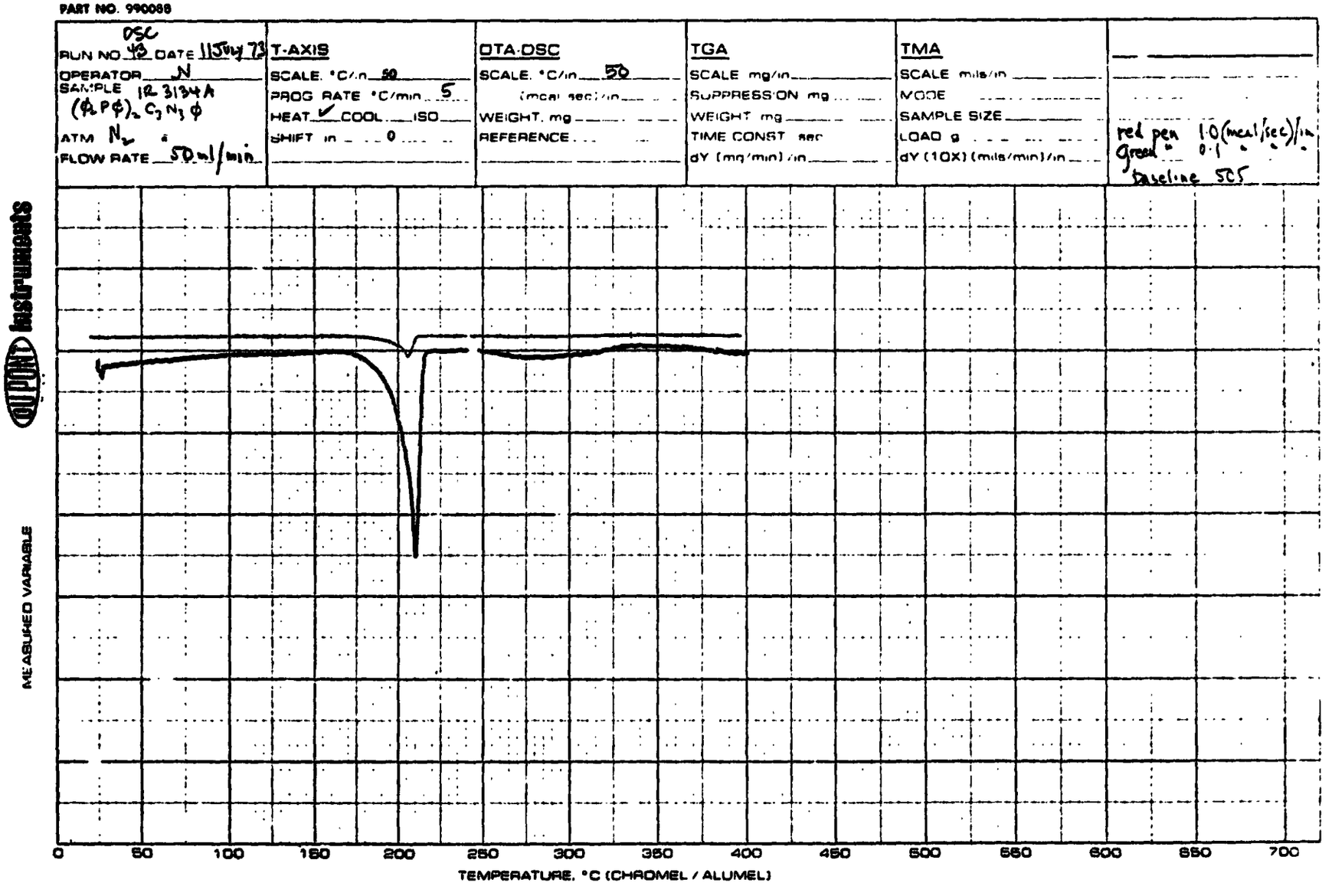

Fig. 24: DSC of $\Phi_2P\text{-}\Phi\text{-}C_3N_3(\Phi)\text{-}\Phi\text{-}P\Phi_2$

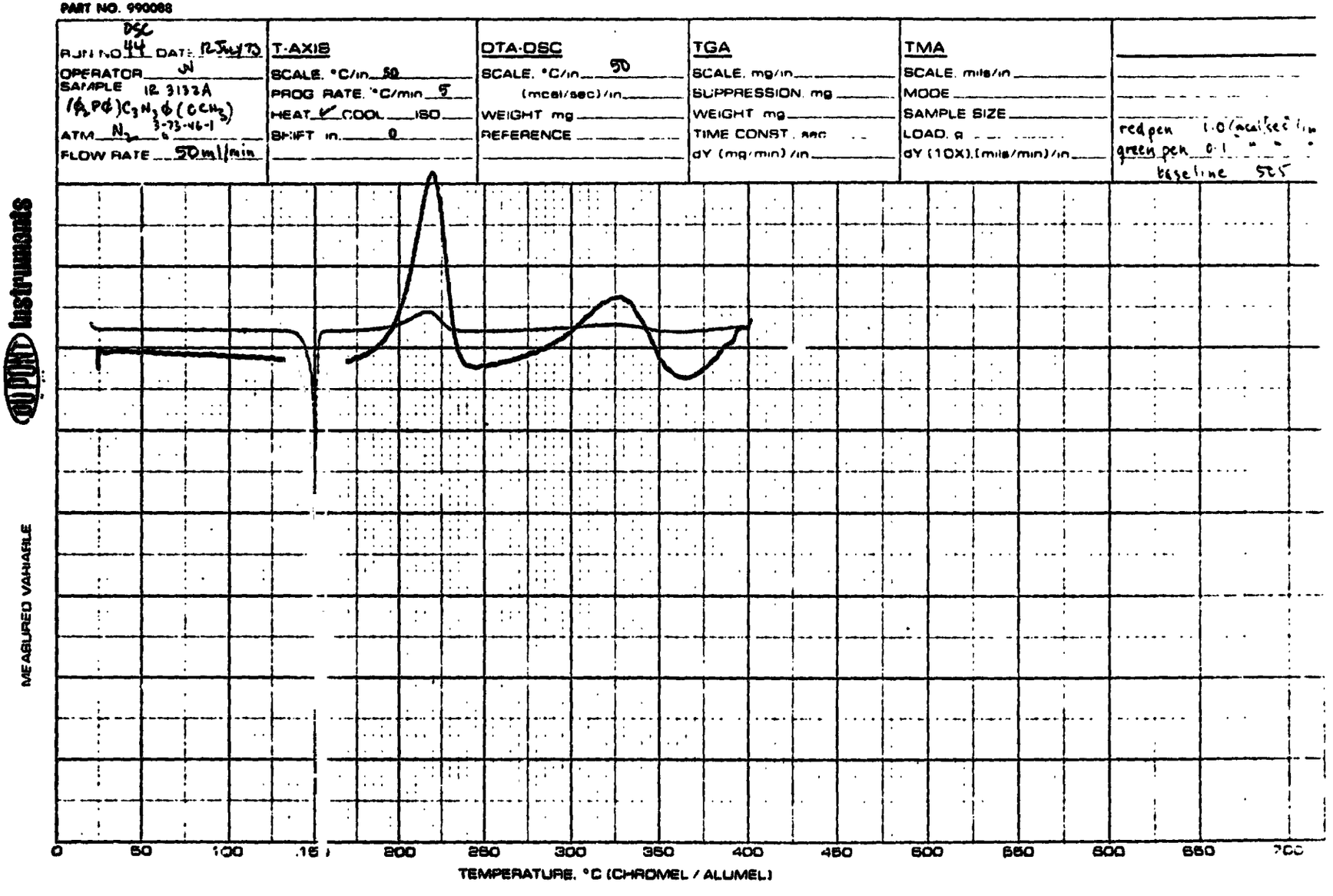

Fig. 25: DSC of $\Phi_2P\text{-}\Phi\text{-}C_3N_3(\Phi)\text{-}OCH_3$

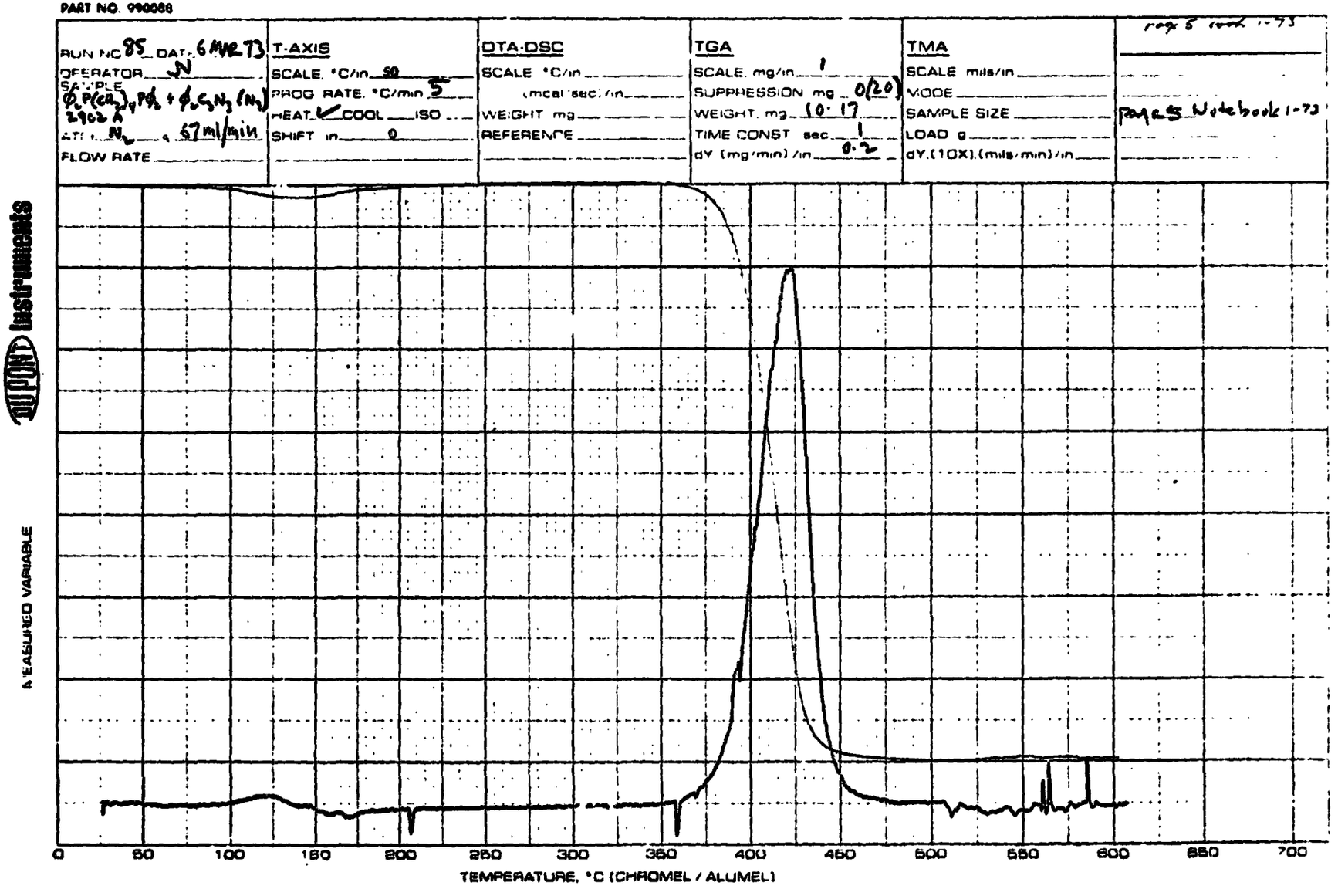

Fig. 26: TGA of $\Phi_2C_3N_3$-N=PΦ_2-$(CH_2)_4$-PΦ_2=N-$C_3N_3\Phi_2$ (in N_2)

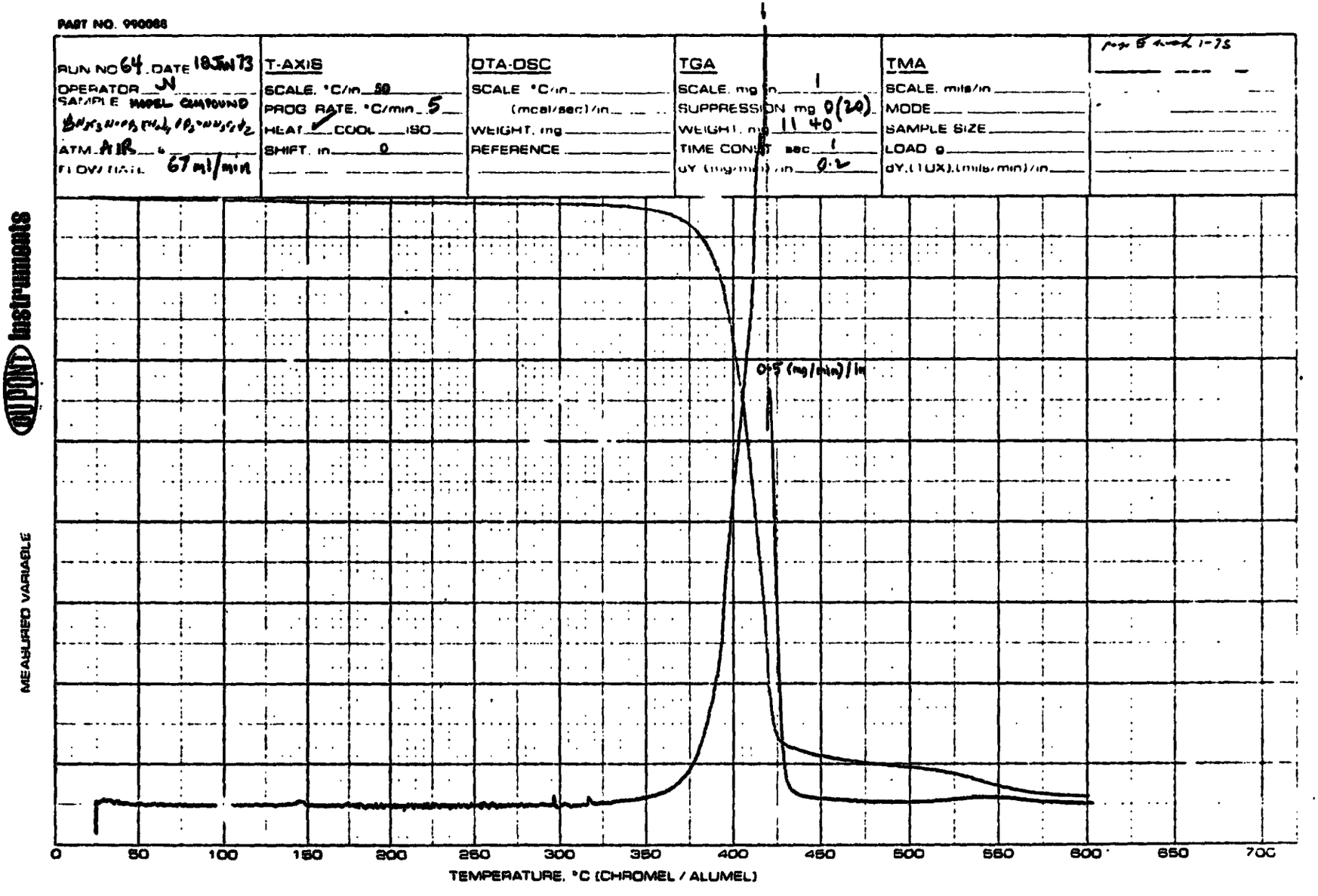

Fig. 27: TGA of $\Phi_2C_3N_3$-N=PΦ_2-$(CH_2)_4$-PΦ_2=N-$C_3N_3\Phi_2$ (in air)

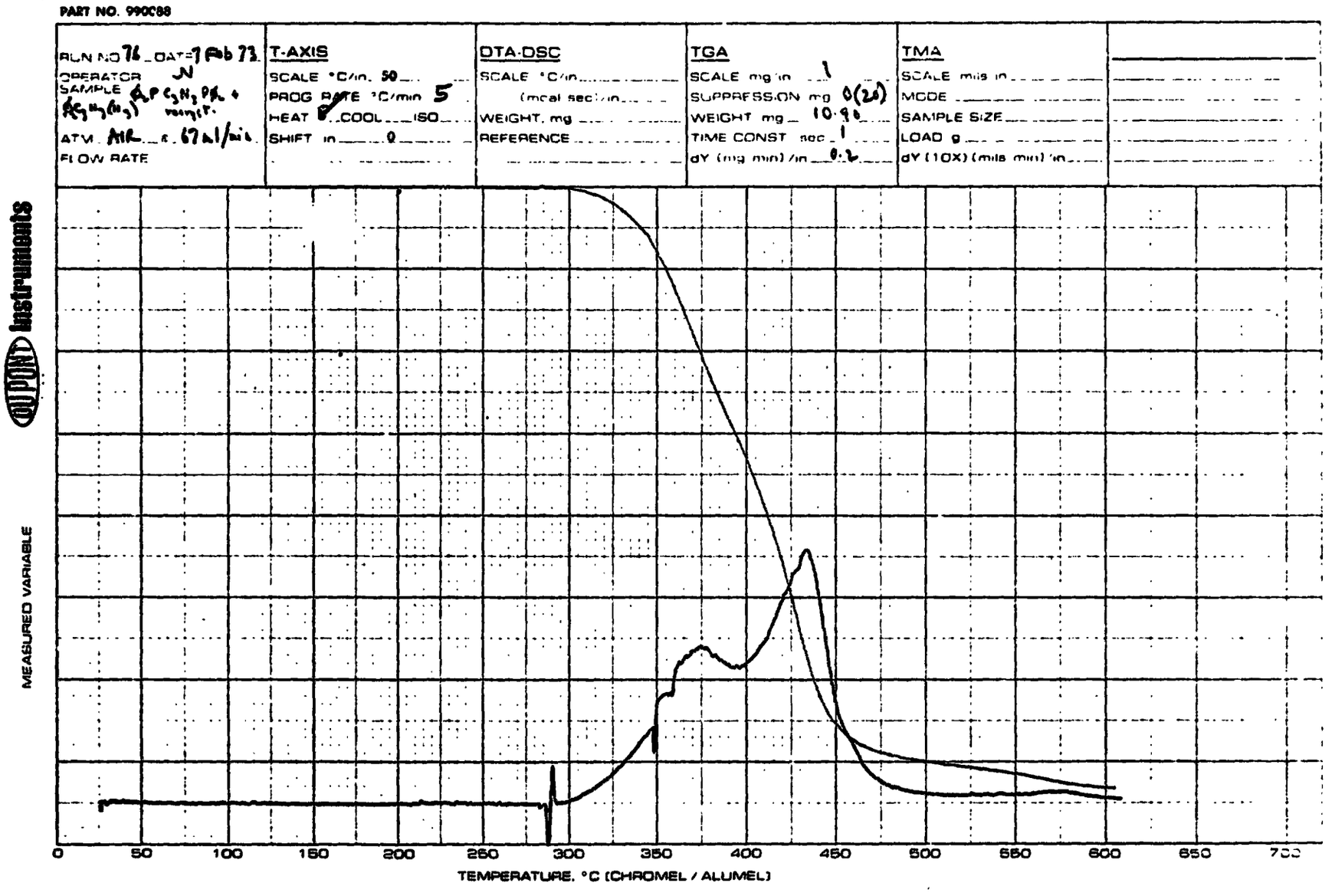

Fig. 28: TGA of $\Phi_2C_3N_3-N=P\Phi_2-C_3N_3(\Phi)-P\Phi_2=N-C_3N_3\Phi_2$ (in air)

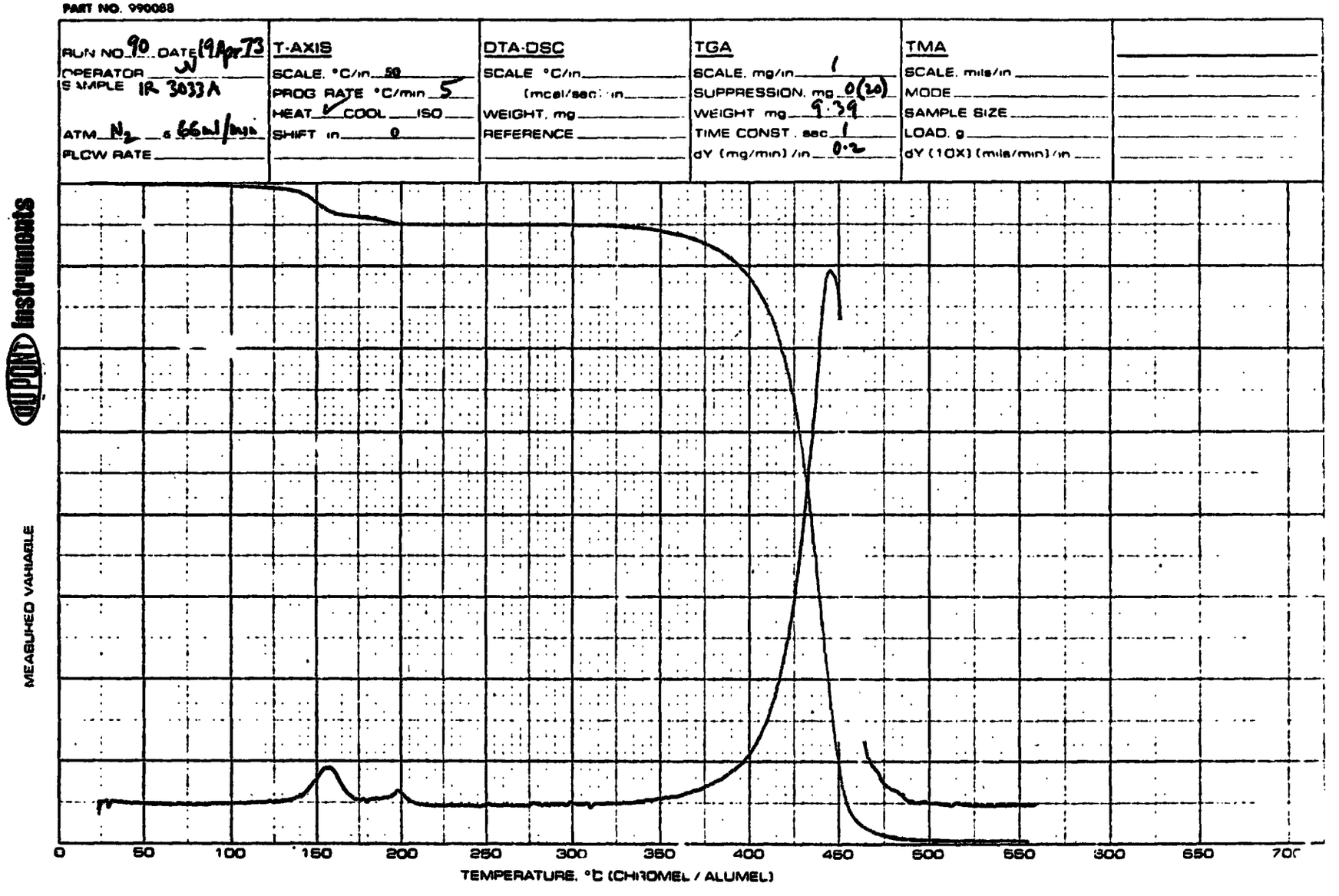

Fig. 29: TGA of $\Phi_3P{=}N{-}P\Phi_2{=}N{-}C_3N_3(\Phi){-}N{=}P\Phi_2{-}N{=}P\Phi_3$ (in N_2)

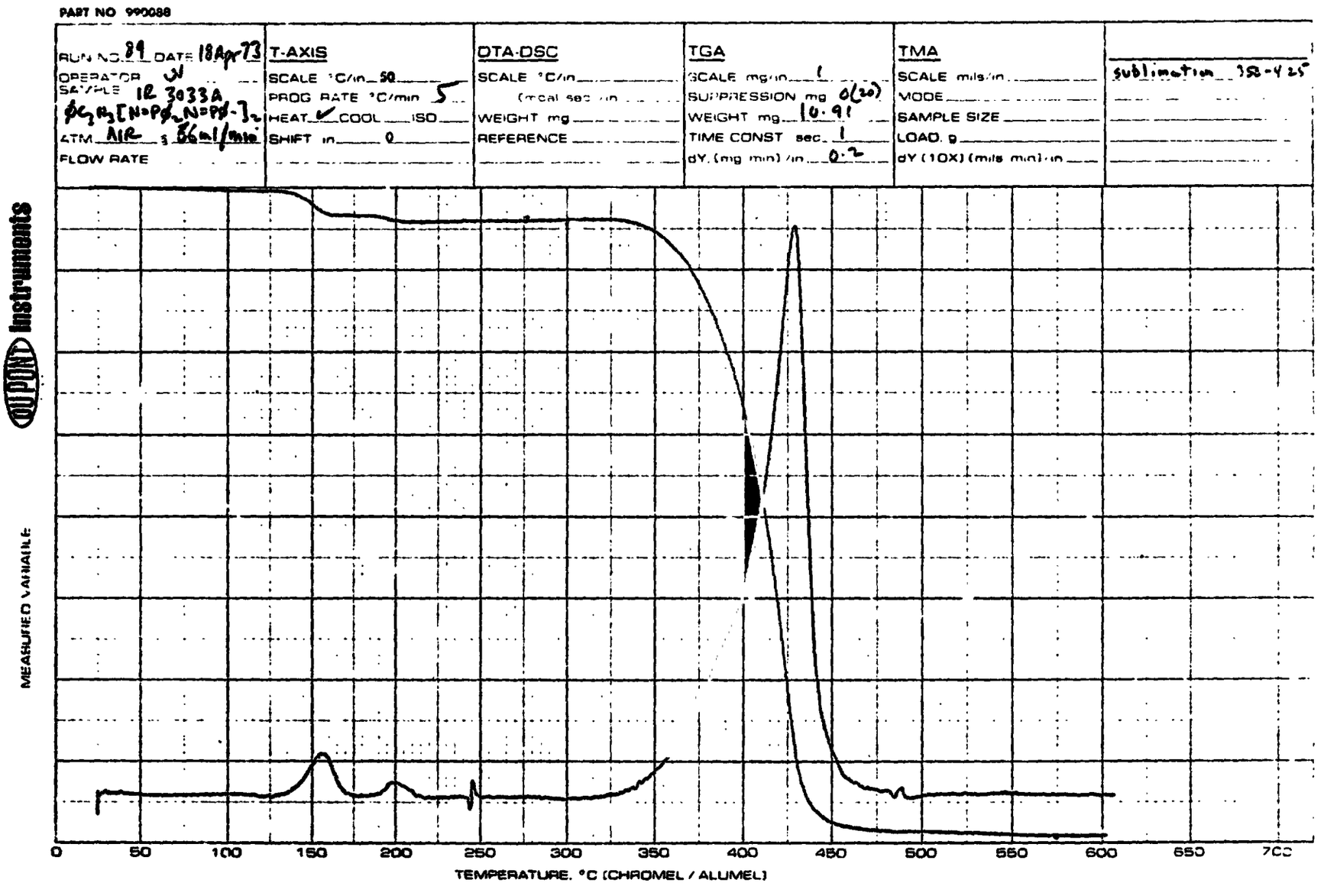

Fig. 30: TGA of $\Phi_3P{=}N{-}P\Phi_2{=}N{-}C_3N_3(\Phi){-}N{=}P\Phi_2{-}N{=}P\Phi_3$ (in air)

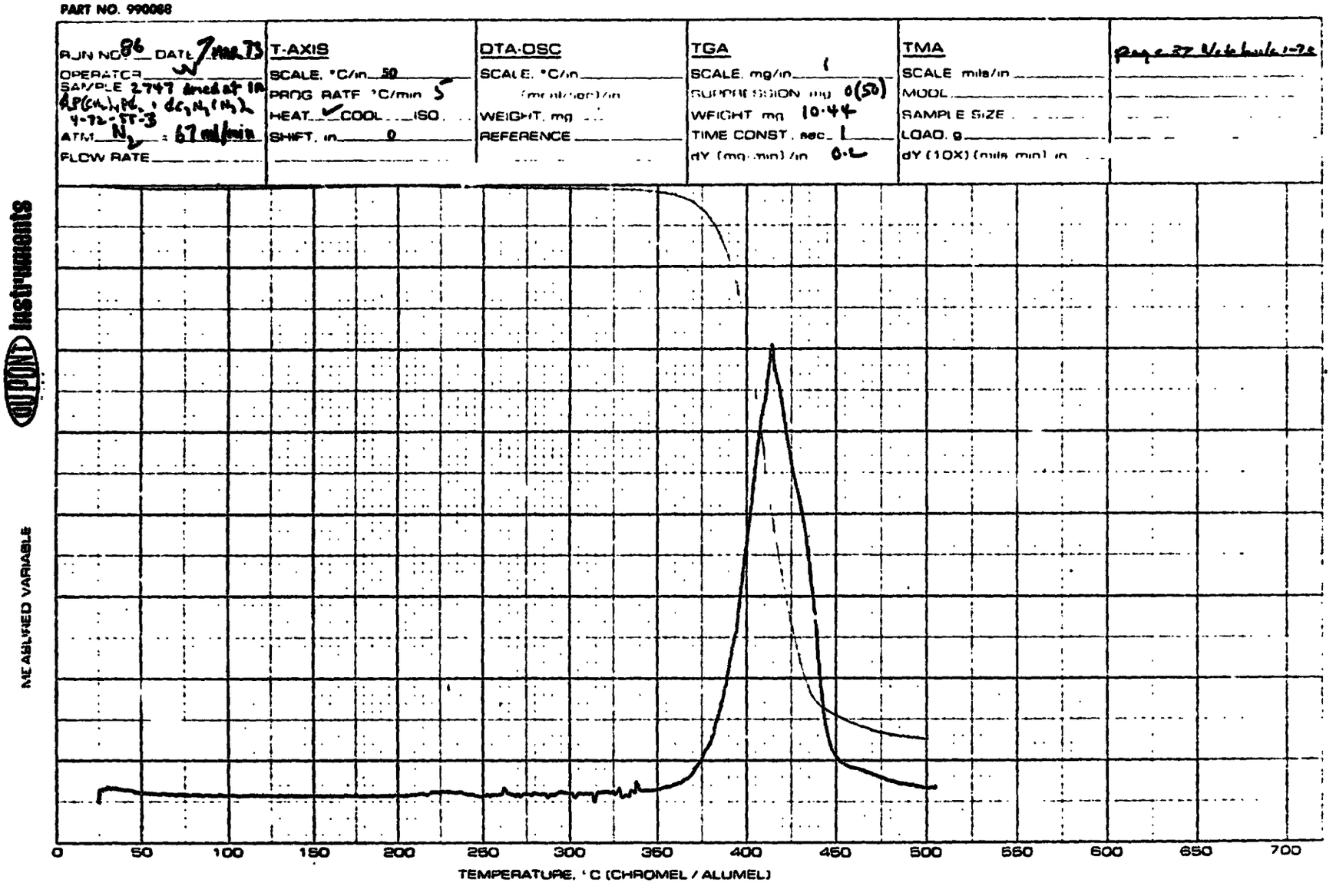

Fig. 31: TGA of $\left[P\Phi_2-(CH_2)_4-P\Phi_2=N-C_3N_3(\Phi)-N\right]_x$, TDA-DPPB (in N_2)

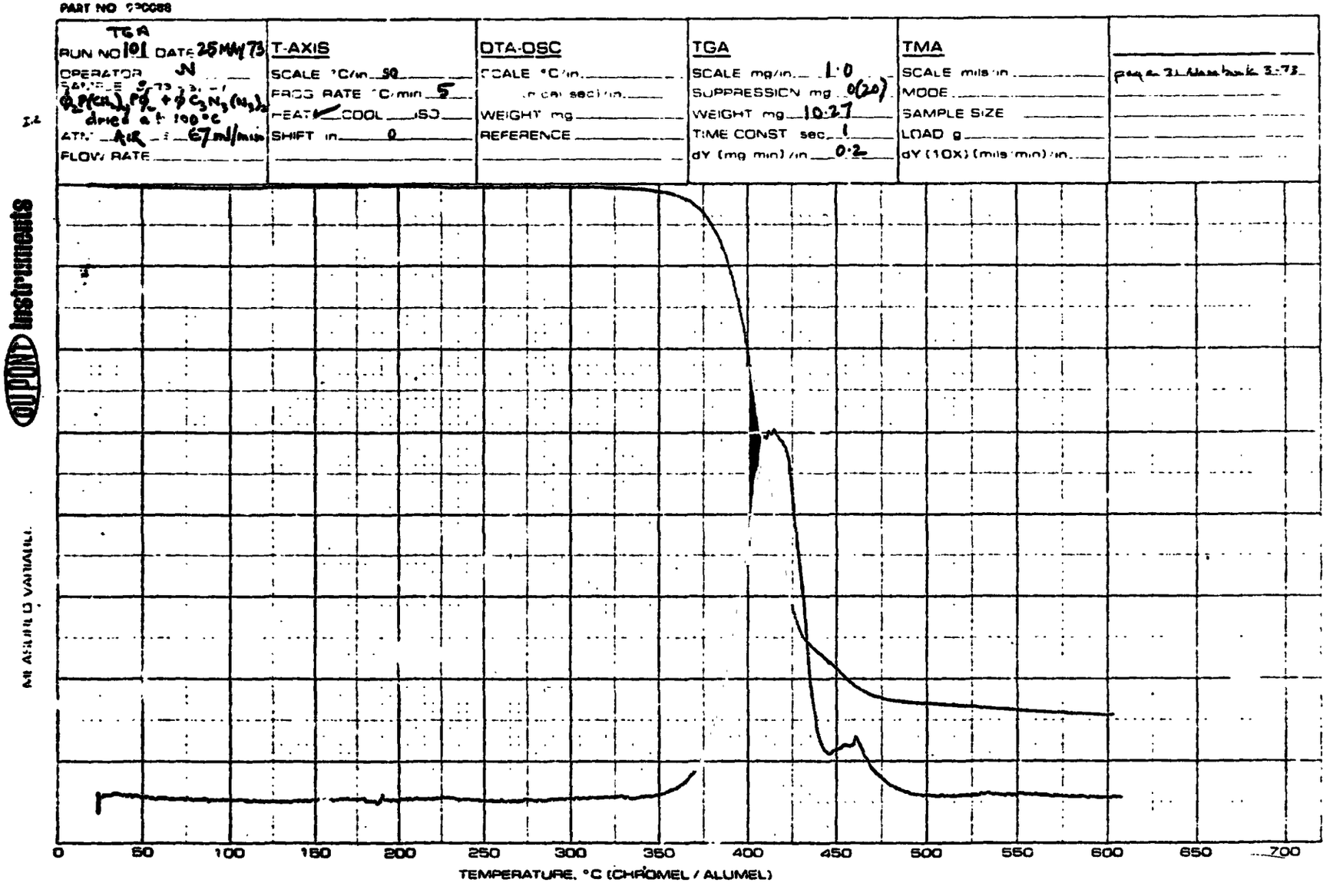

Fig. 32: TGA of $\left[P\Phi_2-(CH_2)_4-P\Phi_2=N-C_3N_3(\Phi)-N=\right]_x$, TDA-DPPB, (in air)

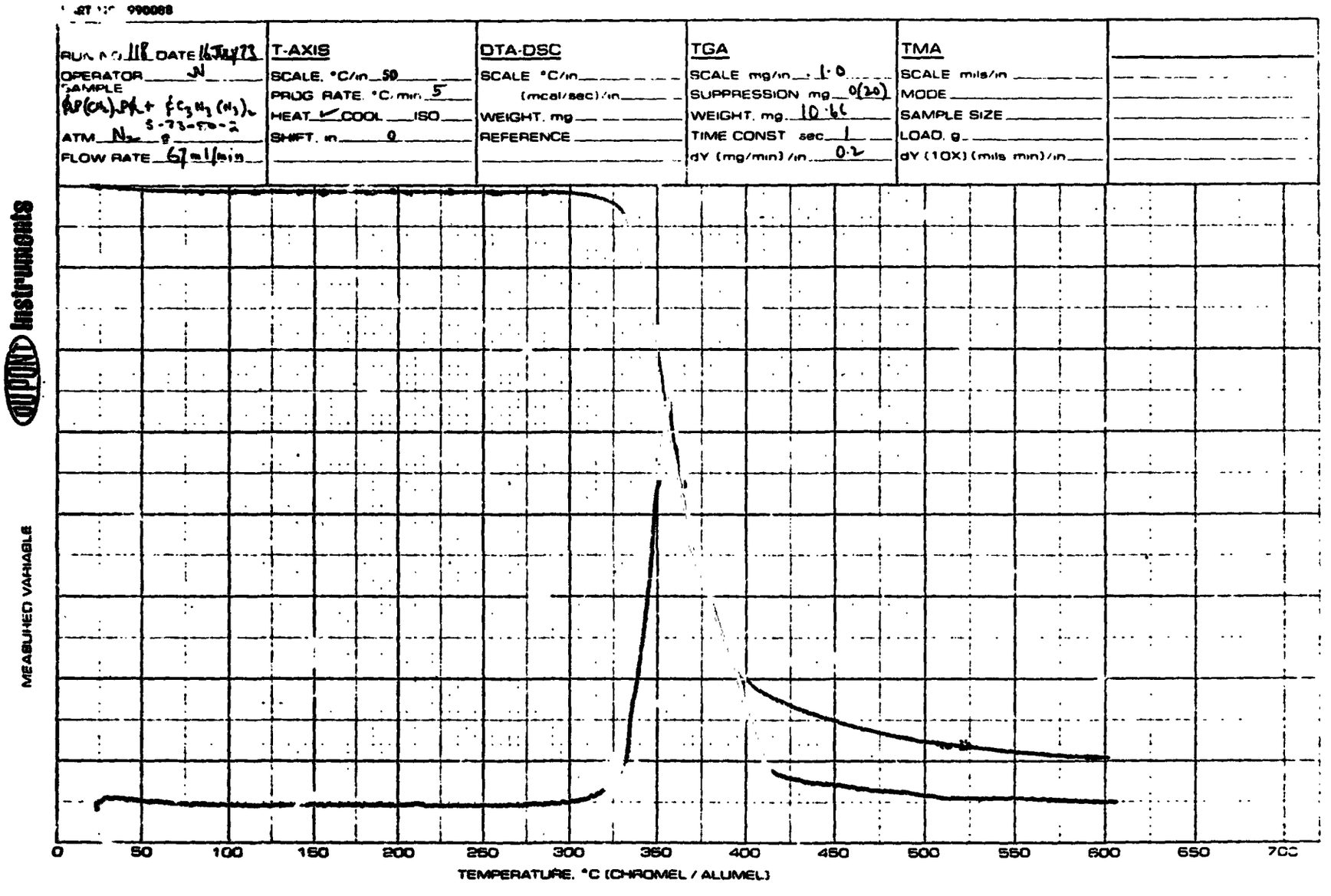

Fig. 33: TGA of $\left[P\Phi_2-(CH_2)_2-P\Phi_2=N-C_3N_3(\Phi)-N=\right]_x$, TDA-DPPE, (in N_2)

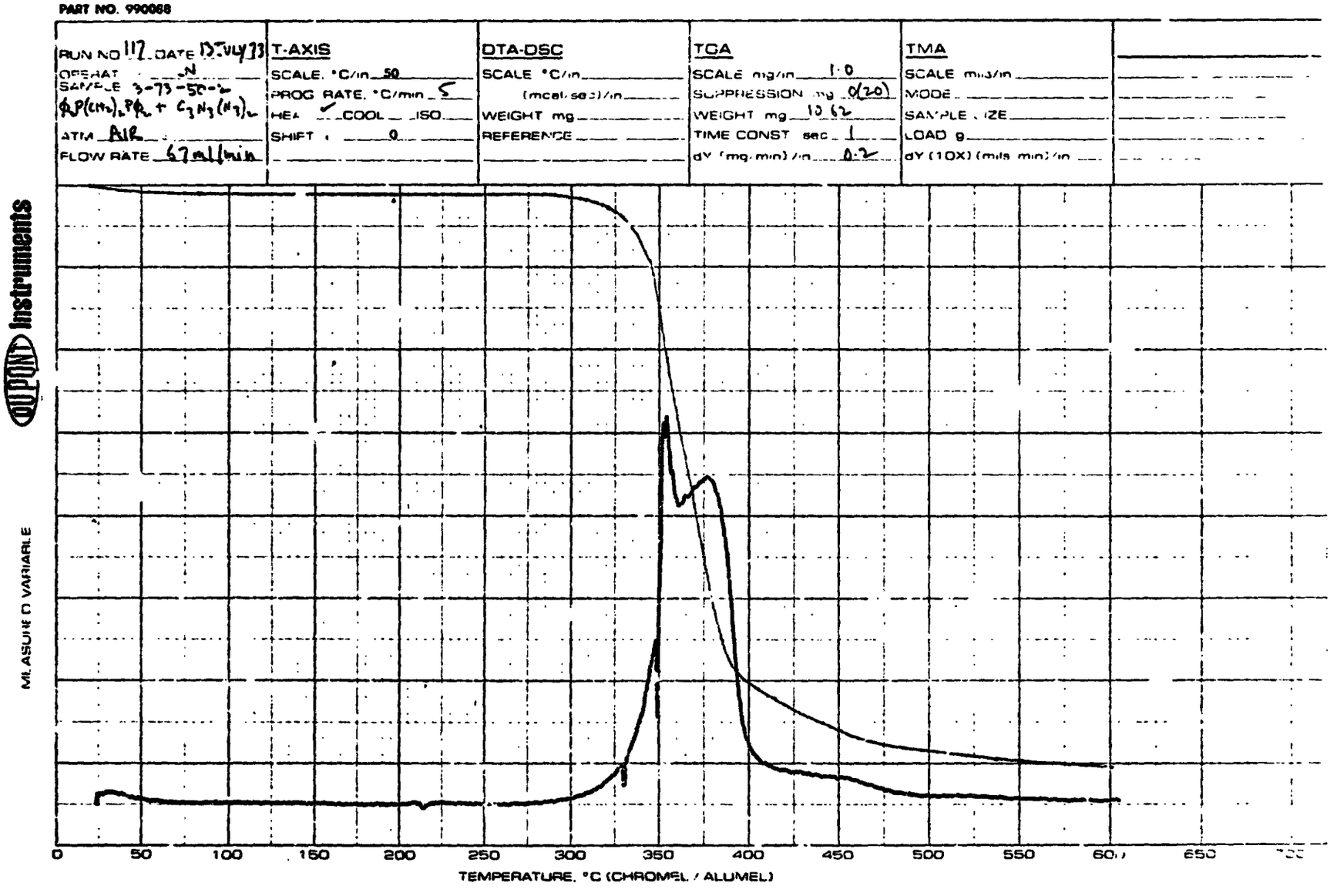

Fig. 24: TGA of $[P\Phi_2-(CH_2)_2-P\Phi_2=N-C_3N_3(\Phi)-N=]_x$, TDA-DPPP (in air)

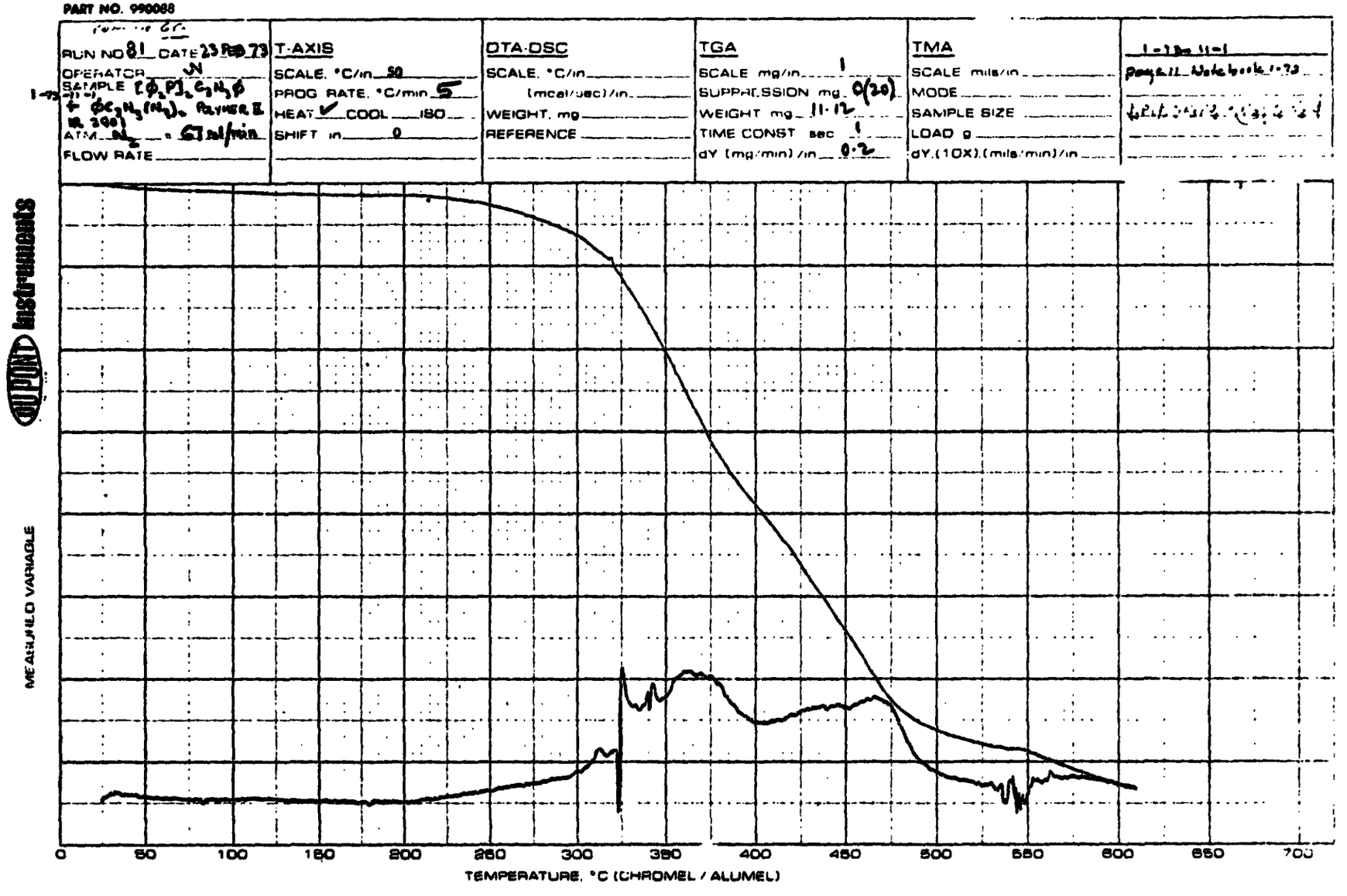

Fig. 35: TGA of $\left[P\Phi_2\text{-}C_3N_3(\Phi)\text{-}P\Phi_2\text{=}N\text{-}C_3N_3(\Phi)\text{-}N\right]_x$, TDA-DPPT (in N_2)

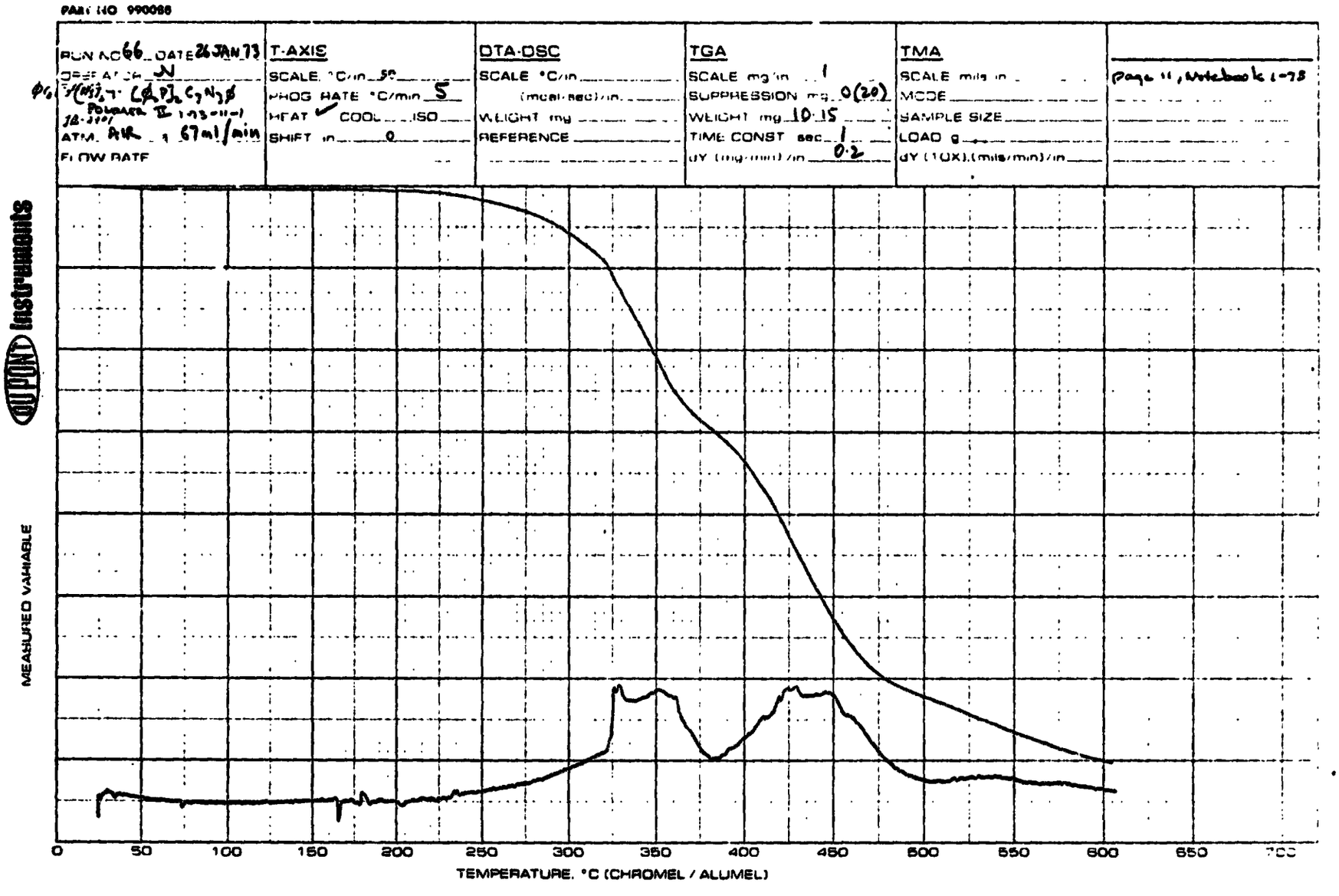

Fig. 36: TGA of $\left[P\Phi_2\text{-}C_3N_3(\Phi)\text{-}P\Phi_2\text{=}N\text{-}C_3N_3(\Phi)\text{-}N\right]_x$, TDA-DPPT, (in air)

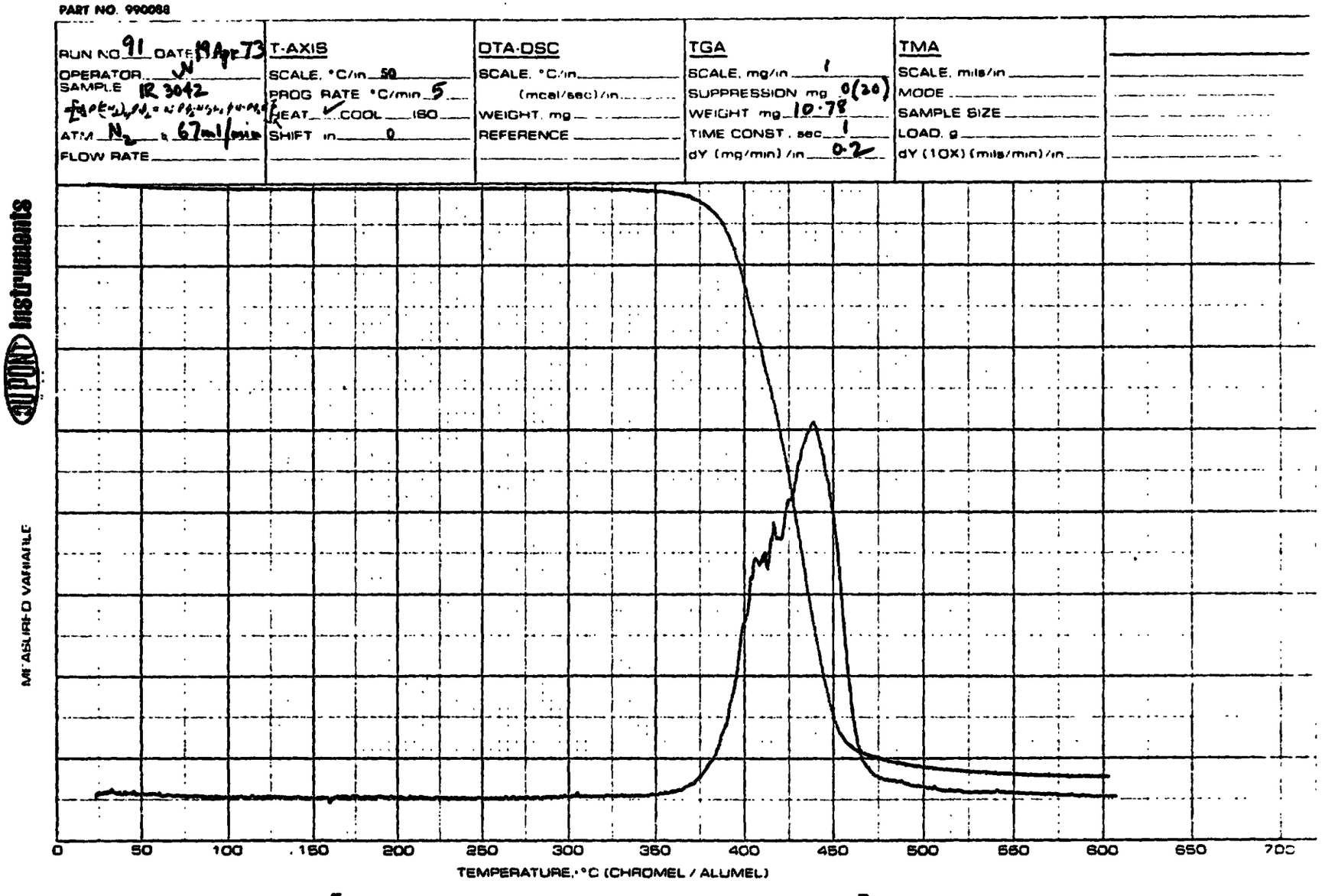

Fig. 37: TGA of $\left[P\Phi_2\text{-}(CH_2)_4\text{-}P\Phi_2\text{=}N\text{-}P\Phi_2\text{=}N\text{-}C_3N_3(\Phi)\text{-}N\text{=}P\Phi_2\text{-}N \right]_x$, TDPA-DPPB (in N_2)

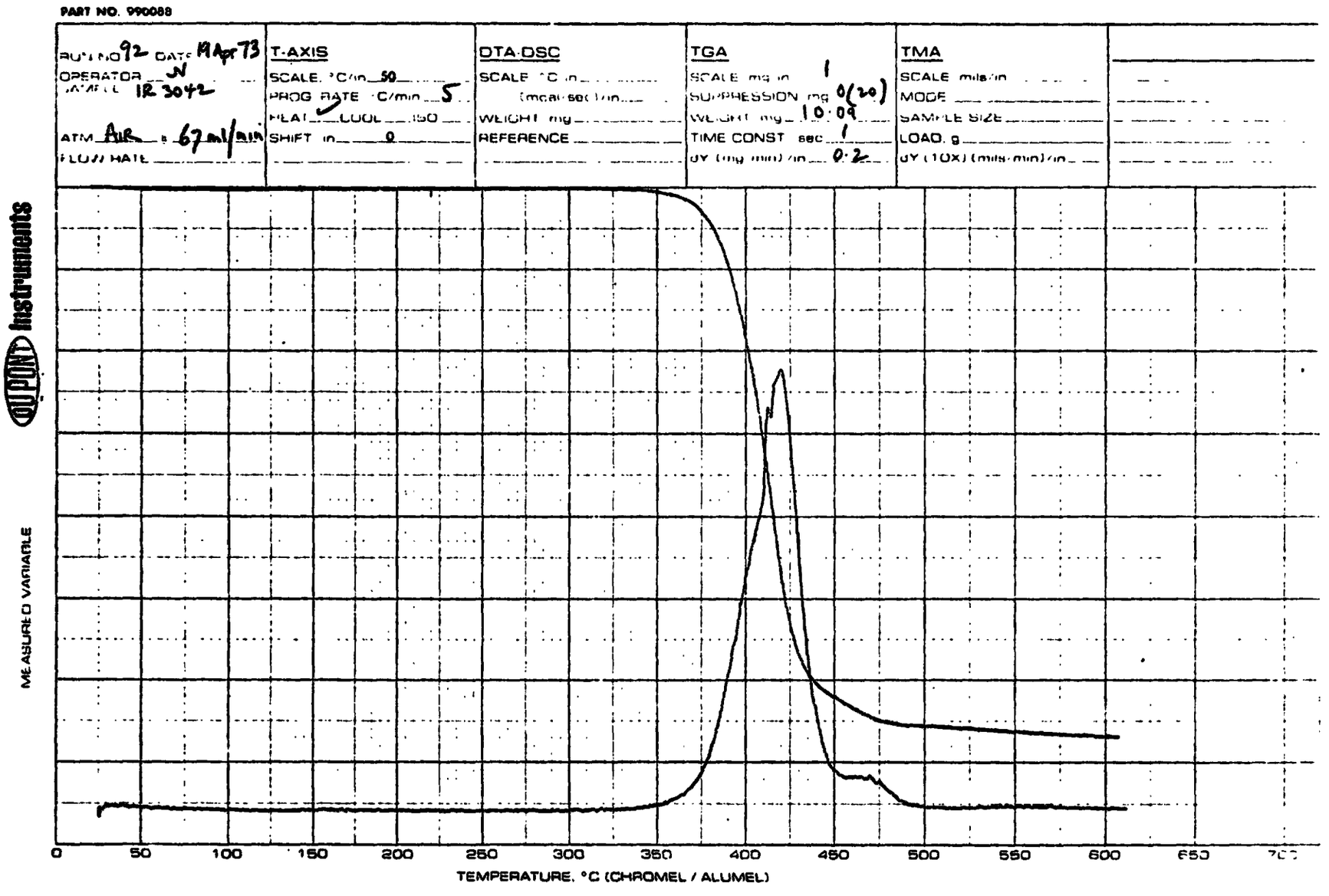

Fig. 38: TGA of $\left[P\Phi_2-(CH_2)_4-P\Phi_2=N-P\Phi_2=N-C_3N_3(\Phi)-N=P\Phi_2-N\right]_x$, TDPA-DPPB (in air)

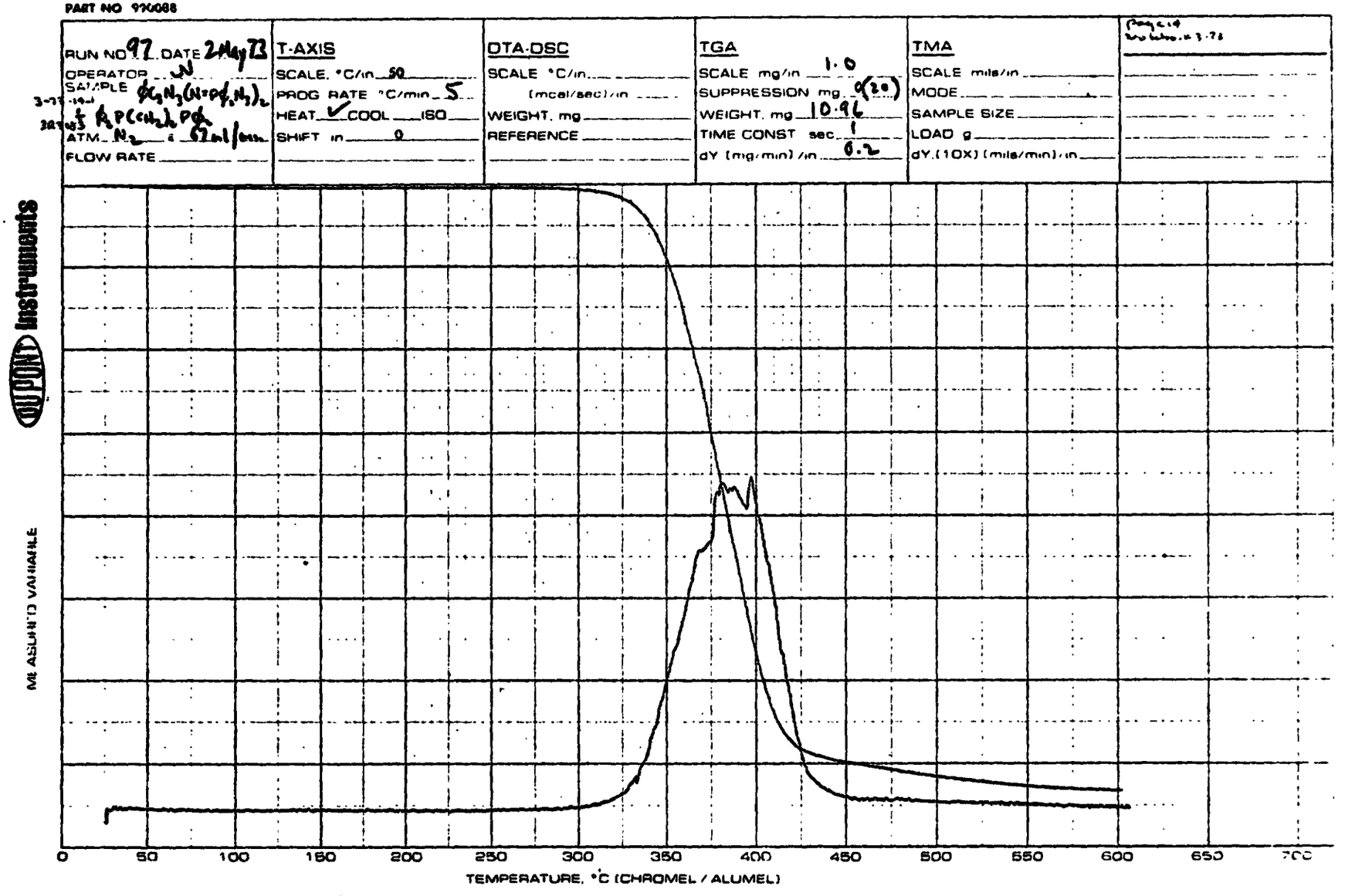

Fig. 39: TGA of $\left[P\Phi_2-(CH_2)_2-P\Phi_2=N-P\Phi_2=N-C_3N_3(\Phi)-N=P\Phi_2-N\right]_x$, TDPA-DPPE (in N_2)

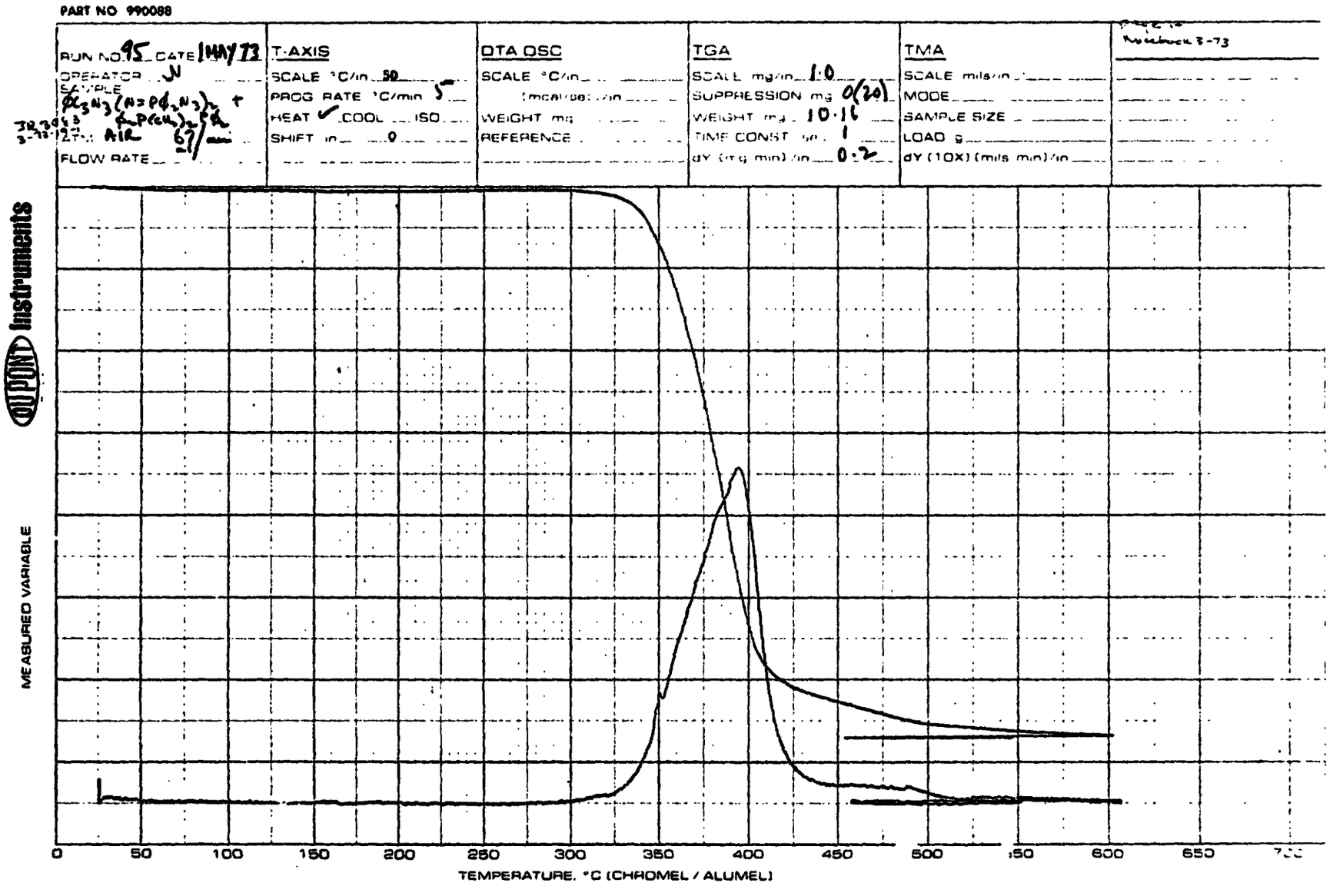

Fig. 40: TGA of $\left[P\Phi_2\text{-}(CH_2)_2\text{-}P\Phi_2\text{=}N\text{-}P\Phi_2\text{=}N\text{-}C_3N_3(\Phi)\text{-}N\text{=}P\Phi_2\text{-}N\text{=} \right]_x$, TDPA-DPPE (in air)

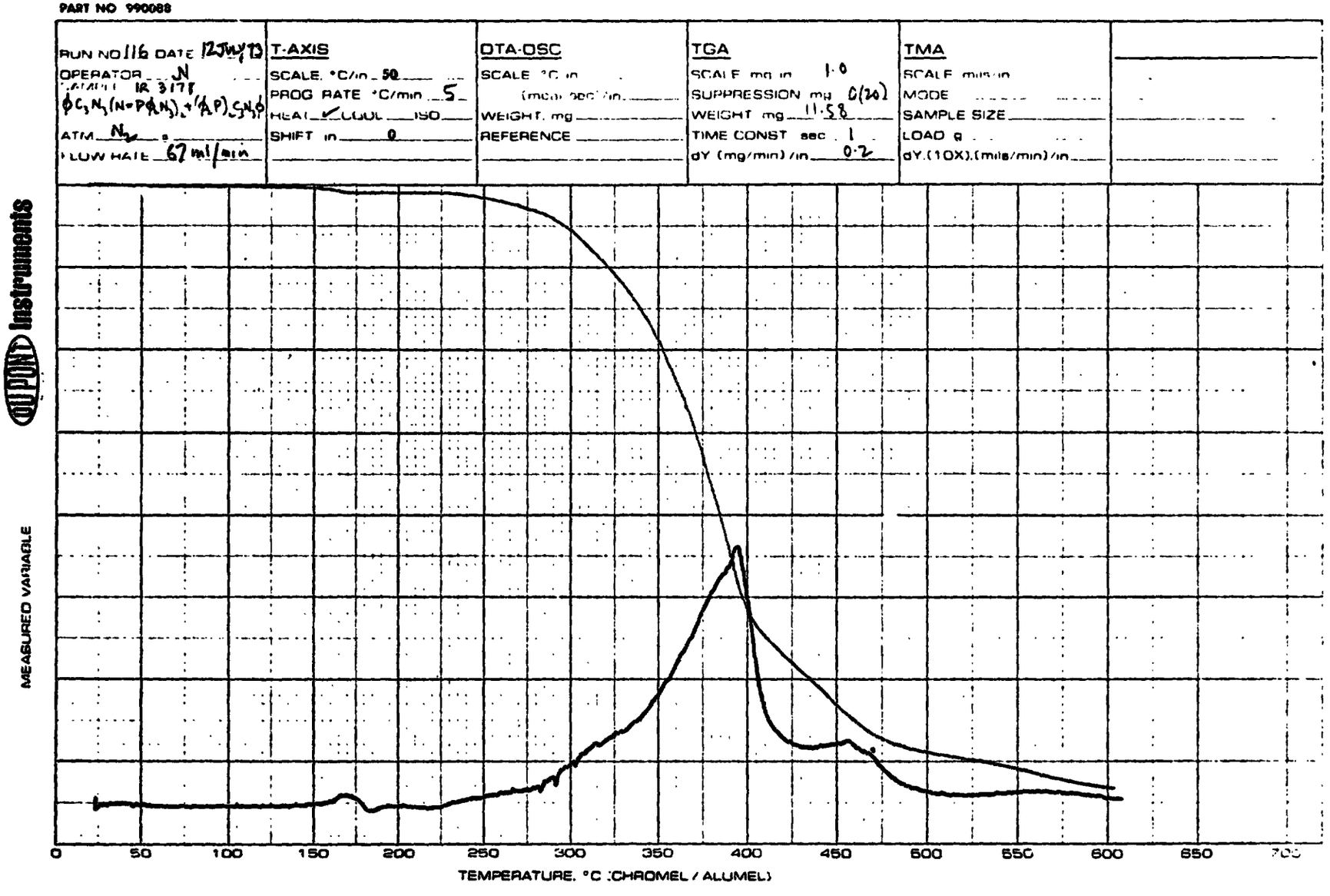

Fig. 41: TGA of $\left[P\Phi_2\text{-}C_3N_3(\Phi)\text{-}P\Phi_2\text{=}N\text{-}P\Phi_2\text{=}N\text{-}C_3N_3(\Phi)\text{-}N\text{=}P\Phi_2\text{-}N\right]_x$, TDPA-DPPT, (in N_2)

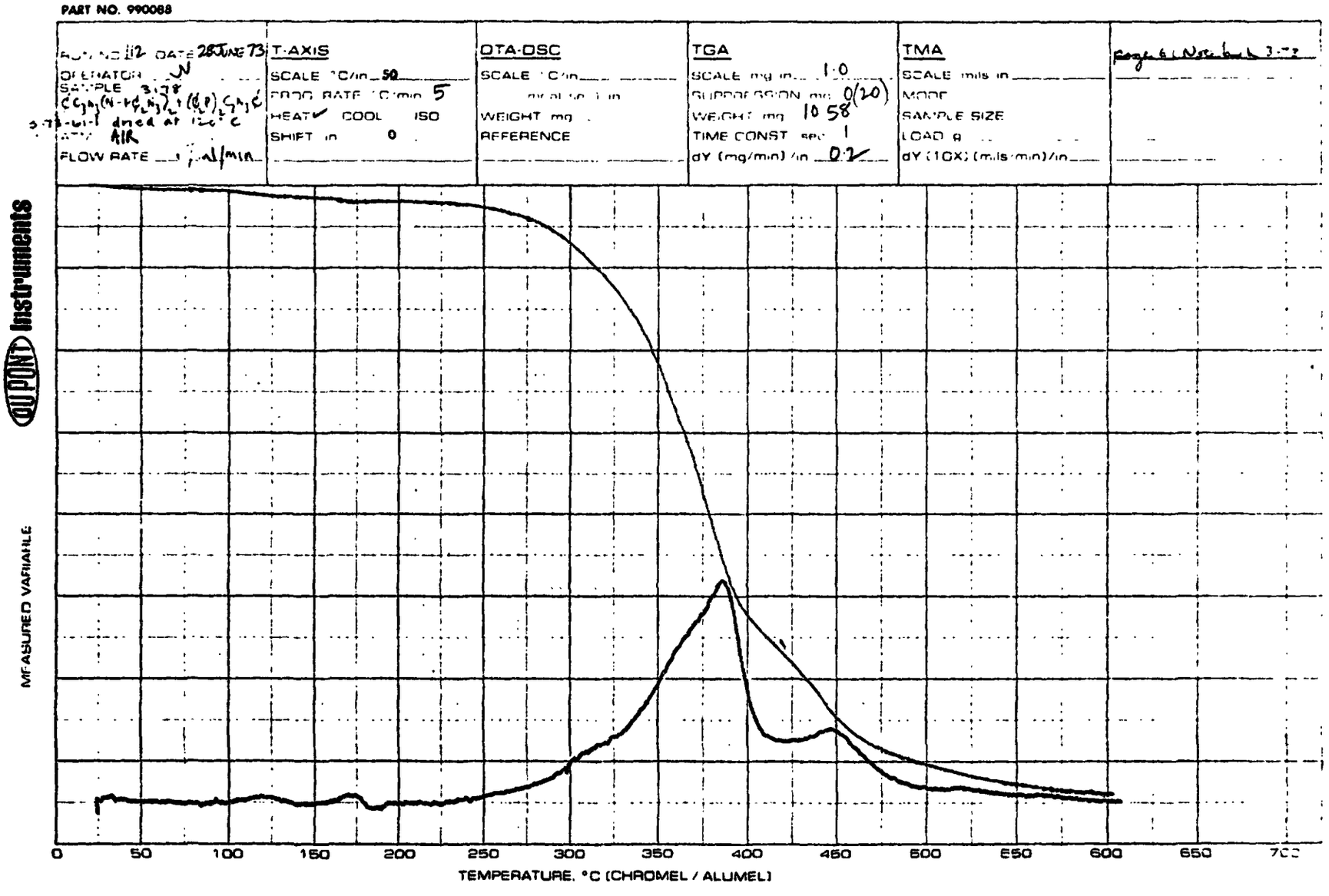

Fig. 42: TGA of $\left[\mathrm{P\Phi_2\text{-}C_3N_3(\Phi)\text{-}P\Phi_2{=}N\text{-}P\Phi_2{=}N\text{-}C_3N_3(\Phi)\text{-}N{=}P\Phi_2\text{-}N}\right]_x$, TDPA-DPPT, (in air)