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SYNTHESIS AND EVALUATION OF POLYMERS FOR USE IN EARLY WARNING FIRE ALARM DEVICES

by N. R. Byrd and M. B. Sheratte

MCDONNELL DOUGLAS CORPORATION
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16. Abstract

Eight conjugated polyacetylene polymers and one condensation polyene, all containing a high degree of conjugated unsaturation, were synthesized. These polymers were characterized by chemical analysis and by thermogravimetric analysis, as well as for their film-forming capability and gas/polymer interactions. It was found that those that had a high degree of conjugated unsaturation and had resonance - stabilizing groups were very thermally stable to 200°C, e.g., poly(dicyanoacetylene), poly(ethynylferrocene) and poly(phenylacetylene); while those with labile moieties, such as poly(p-formamidophenylacetylene), among others, suffered some degradation when heated in air. When subjected to gas/polymer interaction effects, the greatest change in electrical conductance was observed when ammonia was used as the gas and poly(p-nitrophenylacetylene) was the detector. Other polymers showed similar behavior. For example, poly(ethynylcarborane), considered to be an electron acceptor also showed a change in electrical conductance when exposed to ammonia, while poly(ethynylpyridine) and poly(ethylidenepyridazine) responded to carbon monoxide. However, for "fire gases" (gases from smoldering cotton), poly(ethynylferrocene) was the most responsive. Thus, the concept of polymers with different electronegativities forming charge-transfer complexes with different gases was found to be operable.

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FOREWORD

This document represents the final report for the work accomplished between 2 July 1973 and 30 June 1974 by McDonnell Douglas Corporation for the National Aeronautics and Space Administration, Lewis Research Center, Cleveland, Ohio; under Contract NAS3-17515 on Synthesis and Evaluation of Polymers for use in Early Warning Devices. This work was under the technical direction of first Dr. Tito T. Serafini and later by Dr. Richard E. Gluyas, NASA Project Managers.

Work in the program was conducted at McDonnell Douglas Corporation's Douglas Aircraft Company and McDonnell Douglas Astronautics Company, Long Beach and Huntington Beach, California. Dr. N. R. Byrd was the McDonnell Douglas Program Manager, and the work was performed by Dr. M. B. Sheratte.

TABLE OF CONTENTS

TABLE OF CONTENTS (Con't.)

LIST OF TABLES

LIST OF FIGURES

LIST OF FIGURES

LIST OF PLATES

SYNTHESIS AND EVALUATION OF POLYMERS FOR USE IN EARLY WARNING FIRE ALARM DEVICES

by

N. R. Byrd
M. B. Sheratte

SUMMARY

The objective of this program was to synthesize polymers that can eventually show a demonstrated capability of interacting with gaseous substances and thereby effect a change in some electrical parameter of the polymer; this interaction to be ultimately utilized in developing an early warning fire detector. For this purpose, it had been proposed that poly(phenylacetylene), poly(p-nitrophenylacetylene), poly(p-formamidophenylacetylene), poly(p-aminophenylacetylene), poly(ethynylferrocene), poly(ethynylpyridine), poly-(ethynylcarborane), poly(ethynylnickelocene), poly(dicyanoacetylene) and a polyene from 3, 6-dimethyldihydropyridazine be prepared and tested for their response behavior with a number of gases.

All of the above-mentioned polymers were prepared, except for poly(nickelocenylacetylene). The literature reported that nickelocene does not undergo a Friedel-Crafts reaction (a necessary precursor to the preparation of the ethynyl derivative), therefore the ethynyl derivative could not be prepared by this route. An alternative method was tried, but it, too, was unsuccessful. The next most difficult to prepare was poly(dicyanoacetylene); the problem being the poor yield of monomer. The remaining polymers were straightforward, usually starting with the ethynyl derivative and performing an addition polymerization; except for the polyene from 3, 6-dimethyldihydropyridazine. This latter polymer resulted from a condensation reaction between glyoxal and 3, 6-dimethyldihydropyridazine. However, the resultant

polymer had considerable insoluble material and it was difficult to work with. In the poly(phenylacetylene) series, this polymer was prepared first and the other derivatives, namely, the nitro, formamido and amino prepared in this sequence from the parent polymer. The poly(ethynylferrocene) and the poly(ethynylpyridine) were prepared without too much difficulty, but the poly(ethynylcarborane), although prepared from the monomer that analyzed very well and was presumably of the correct structure, did not result in a polymer that had a good analysis.

The thermogravimetric analysis data showed a good correspondence between degree of conjugation, resonance interaction with aromatic appendage and lack of -CH bonds in the polymer. Thus, poly(dicyanoacetylene), poly(ethynylferrocene) and poly(phenylacetylene) showed less than two percent weight loss out to 200°C (in air).

Of the polymers prepared, poly(phenylacetylene), poly(p-nitrophenylacetylene), poly(p-formamidophenylacetylene), poly(p-aminophenylacetylene) and poly(ethynylferrocene) were the most responsive to various gases and to "fire gas" conditions when they were coated on a lock-and-key electrode geometry. Poly(dicyanoacetylene) was essentially nonresponsive and the other polymers were minimally responsive. Thus, although poly(p-nitrophenylacetylene) was most responsive to ammonia, it did not respond to CO or butadiene and poorly to "fire gases:" while poly(ethynylferrocene) showed some response to CO and butadiene but poor response to NH_3, and was most responsive to "fire gases". Futhermore, poly(ethynylcarborane), an electron-accepting polymer, also showed a response to NH_3, while poly(ethynylpyridine) and poly(ethylidenepyridazine) responded to CO. From the data, it was observed that polymers of varying electronegativity can be prepared and that their interaction with gases will usually relate to their structure, e.g., NH_3 with poly(p-nitrophenylacetylene) and poly(ethynylcarborane)and carbon monoxide with poly(ethynylferrocene), poly(ethynylpyridine)and poly(ethylidenepyridazine).

1.0 INTRODUCTION

The need for fire detection devices has a very high priority in all parts of society whether it be aerospace, military, private dwellings, hotels, office buildings or mines. For example, nursing home fires occur with relatively high frequency; and private dwellings, although involving fewer individuals per dwelling, also have a high incidence of fires. In addition to the loss of lives, there is, of course, generally, a large loss in property.

The President's National Commission on Fire Prevention and Control, chaired by Richard E. Bland, after a lengthy study relating to fires in various dwellings, particularly nursing homes, issued a report in 1973 listing a number of priorities regarding efforts to minimize fire hazards; and number two on that list (after fire prevention) was the need for early warning fire detectors. Thus, there is the constant problem of smoke or fire detection in order to save lives and property in nursing homes, hospitals, private dwellings and aircraft, among others. What is needed, therefore, is a sensor capable of monitoring the atmosphere and rapidly detecting the presence of any contaminant buildup.

Recently, a large number of fire and/or gas detecting devices have been brought into the market that are claimed to be able to detect fires either by heat detection techniques or by gas (combustion products) detection methods. In the former category are infrared sensors and low melting alloys. In the latter are solid state devices and ionization detectors. By far, the most popular are the solid state and ionization detectors; and of the solid solid state type, the most widely used is the TGS gas-sensing semiconductor manufactured by Figaro Engineering, Inc. of Osaka, Japan.

The uniqueness of operation of the TGS device is that it depends upon the interaction of gases with certain metal oxide semiconductors, e.g., tin oxide, zinc oxide and ferric sesquioxide, in conjunction with coils that are made from an alloy of iridium and palladium and that have a resistance of approximately two ohms. The response speed, when gases, such as carbon monoxide, hydrogen or hydrocarbons are adsorbed, is claimed to be quite fast under specific temperature conditions (200°C to 400°C) (Reference 1). However, no specificity exists. All electronegative gases give one type of response and all electropositive gases give another; there is little differentiation within each class of gases. Another drawback is the high temperature used in the operation of the sensor. This, alone, could be a fire hazard in an incipient fire environment.

A promising approach that could obviate the difficulties of the other techniques is a solid state device that uses polymeric organic semiconductors, either alone or in conjunction with an inorganic semiconductor. Polymeric, film-forming organic semiconductors, e.g., substituted polyacetylenes (polyphenylacetylene and its derivatives), among others, have been used as materials for a solid-state sensor (Reference 2). They act as semiconductors, and can also be chemically modified so that the effect of substituents, on their conduction and complexing capability, can be observed. The basic principle upon which the polymeric organic semiconductors depend for their detection capability is a relationship between their electronegativity, adsorption characteristics, complexing behavior, and a change in some of their electrical parameters.

Thus, the purpose of this program was to select and synthesize ten polymeric semiconductors which have varying electronegativity, and the capability of forming films. These semiconducting polymer films were to be deposited on a lock-and-key type of electrode sensor and checked for their gas response behavior. In addition, the polymers prepared were to be evaluated by thermogravimetric analysis (TGA) and isothermal (35°C) gravimetric analysis in order to establish their long term stability and feasibility for use as possible fire detectors in a fire environment.

In essence, the synthesis of poly(phenylacetylene) (I), poly(p-nitrophenylacetylene) (II), poly(p-formamidophenylacetylene) (III), poly(p-aminophenylacetylene) (IV), poly(ethynylferrocene) (V), poly(ethynylpyridine) (VI), poly(ethynylcarborane) (VII), poly(dicyanoacetylene) (VIII), poly(ethynylnickelocene) (IX), and a polyene from 3, 6-dimethyl-dihydropyridazine (X) was attempted. Figure 1 depicts the structures of polymers I-IV, and Figure 2 shows the structures of polymers V-X. Those polymers that were film formers were then evaluated for their response to carbon monoxide, acrolein, butadiene, ammonia, water vapor and the gases from a smoldering cellulosic fire.

2.0 SELECTION OF SEMICONDUCTING POLYMERS

2.1 TYPES OF POLYMERS CONSIDERED FOR DETECTION

The concept behind the development of an early warning fire detector is basically to use organic semiconductors of varying electronegativity so that gases generated by an incipient or smoldering fire, e.g., carbon monoxide, hydrocarbons and water vapor, among others, would be detectable by at least three of these semiconductors in order to have a fire detector. Normally, a multiplicity of detectors would be used since a fire, or smoldering incipient fire, would contain a number of gases, and to have high specificity and minimize false alarms, a sensor specific for each of these gases should be available. However, as a first approximation, a sensor for CO, a hydrocarbon, and water vapor should be sufficient for detection of an incipient fire. Therefore, in addition to the electronic aspect of the early warning fire detector, of equal importance are the materials to be used as coatings on the particular electrode geometry; for it is the chemical structure of these materials upon which the specificity for the particular gas or combination of gases is dependent. In other words, if one were to be detecting ammonia, and since ammonia is an electropositive gas, one would use an electronegative substance with which it could form some type of complex. This could readily be poly(p-nitrophenylacetylene) (II), for example, as has been adequately demonstrated (Reference 2). Alternatively if one were trying to detect an electronegative specie, e.g. an aldehyde, an electropositive polymer would be used for detection purposes, such as, poly(p-aminophenylacetylene)(IV) or poly(ethynylpyridine) (VI).

There are many other organic polymers that have been shown to possess a semiconducting capability, but they are, generally, intractable substances having no capability for being fabricated other than in the form of pressed discs. However, during the course of this program, intrinsic polymeric semiconductors of the polyacetylene type having film-forming capability with varying electronegatives have been developed.

The feasibility of developing a solid state gas detector was first investigaged under contract NAS12-15 for the NASA Electronics Research Center, Cambridge, Massachusetts (Reference 2). Poly(phenylacetylene) (I) and some of its derivatives (polymers II - IV) were synthesized and evaluated for gas/

polymer interaction effects. The present program further expanded this effort by also synthesizing polymers V - X. Polymers I-IV were again prepared, and reevaluated for their response to NH_3 [as in NAS12-15 (Reference 2)], as well as to carbon monoxide, acrolein, butadiene, acetylene, water vapor and "fire gases" from smoldering cellulose. Similarly, V - VIII and X were examined under the same conditions. Polymer IX could not be prepared and consequently was not evaluated.

2.2 RATIONALE FOR CHOICE

Intrinsically, most organic semiconductors have comparatively low conductivity, and it may be that this is what we want, as will be seen later. To increase the conductivity, either the temperature is raised or a complex is formed. In complex formation, one component is an electron-donating substance and another is an electron-attracting material; chloranil/p-phenylenediamine or anthracene/iodine complexes being representative examples. Although the exact mechanism of conduction in the charge-transfer complex is not explicit, it is presumed to be the sharing of electrons, which, in effect, tends to remove electrons from the sphere of the electron donor. This delocalization of electrons subsequently results in a smearing out of the electron cloud throughout the complex which, in turn, can more readily result in a p-or n-type semiconductor. In other words, once the complex is formed, the electrons are more easily excited to an activated singlet or triplet state with consequent availability for electronic conduction.

In order to elucidate the concept of electron delocalization in a conjugated system, let us examine the structure of butadiene. The double bonds involve pi-bond orbitals which consist of an unpaired electron in a p-orbital perpendicular to the molecular axis. It is the interaction of these perpendicular p-orbitals that forms the pi orbital, or what the chemist calls, "a double bond." Figure 3 depicts the bonds in the butadiene molecule showing the sigma and pi bonds, and the resultant "streaming" effect due to the pi bonds. This electron delocalization (uniform distribution of the electron cloud over the entire molecule) occurs in all organic semiconductors whether simple charge-transfer or polymeric. If one now considers the simplest polyene, a polyacetylene, as shown in Figure 4a, (its structure is shown in the form of "streamer" electrons, Figure 4b) it can be seen that there is no localization of electrons, and that they are theoretically capable of being readily displaced in an electric field. Another factor related to the delocalization of electrons is the greater possibility for complexing with gaseous "contaminants," i.e., gas/polymer interaction effects.

One of the uncertainties regarding the mechanism of conduction in organics is that little is known about the effect of "impurities" on the conducting species. For example, Labes, et al., found that the bulk dark conductivity of anthracene was increased when exposed to iodine vapor and was dependent upon the pressure of iodine [a change in pressure of 30 mm caused an increase in conductivity by one order of magnitude (Reference 3)], and p-chloranil, in the presence of amine vapors, also showed an increase in its bulk dark conductivity (Reference 4). Others have also shown that impurities can affect the conductivity of these organic compounds, and it is the very nature of this problem, namely, the change in conductance due to impurities, which allows us to consider using organic semiconductors as detectors for gaseous products to be found in fires. Let us now examine how this behavior applies to our program.

It is fairly well recognized that surface bonding consists of both physical and chemical bonds. Physical bonding results from van der Waals interactions between the gas molecule and the surface and there are usually lower heats of adsorption involved than in chemisorption. In addition, surfaces are rough, both at the microstructure level and in higher dimensions. Thus, in a porous rough surface adsorbed molecules come into more intimate contact with more atoms of the adsorbent that if the surface were a smooth plane; and these cracks and crevices in the rough surface appear to have more "active sites" for van der Waals adsorption (Reference 5). The chemical contribution to bonding concerns itself with chemisorption phenomena caused by an exchange or sharing of electrons between the binding molecule and the substrate.

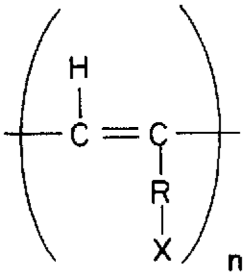
If we consider the adsorption of olefins on a catalyst surface, then in the case of ethylene or acetylene, where an adsorbed molecule becomes attached to a metallic surface, such as nickel or platinum, the pair of electrons in the pi-bond separate and each electron pairs up with an electron from the metal surface (Reference 6). Thus, normal covalent bonds of varying bond strengths may be formed during the chemisorption process when this electron pairing occurs. In addition, coordinate links between molecules having at least one pair of electrons (and acting as an electron donor), and metal surfaces which are acting in an electronegative manner with respect to these compounds, may also lead to chemisorption of these molecules. This can be seen in Figure 5 for the cases of dimethyl sulfide, arsine and pyridine with nickel, platinum and palladium, respectively (Reference 7). It has also been found that the strength of adsorption in any system depends both on the gas and on the metal, and it is possible to have a number of gases in sequence such that any one is more strongly adsorbed by any metal than the ones succeeding it, as shown (Reference 8):

$$O_2 > C_2H_2 > C_2H_4 > CO > H_2 > CO_2 > N_2$$

It is readily observable from the sequence that the greater availability of electrons, (either from a diradical such as oxygen, high electron density in acetylene, or easy separation into atomic species (on a metal surface) as in hydrogen) is the factor which establishes its capability of forming a complex with an electronegative surface.

At this point, let us extrapolate the action on metal surfaces to that of an organic semiconductor, keeping in mind the fact that a conjugated polymer may potentially be a "metallic" conductor or semiconductor. The semiconducting material in question here will be the bonding surface and the feasibility of its action as a probe for contaminant detection will be shown.

Consider a polymer with a conjugated polyunsaturation in its backbone, having either electron-widhdrawing or electron-donating side groups, X:



$$\left(\overset{\displaystyle H}{\underset{}{C}} = \underset{\underset{\displaystyle X}{|}}{\underset{\displaystyle R}{\underset{|}{C}}} \right)_n$$

In the one instance, X is electron-withdrawing and R is a conjugated moiety capable of allowing X to exert its influence on the conjugated backbone. Call this polymer, A. In another instance, X is electron-donating. Call this polymer, B. In a third-instance, there is a polymer with no electron-withdrawing or electron-donating group on R. Call this polymer, C. If a potential were impressed on A, B or C, the conductivity would be in the order

$$A < C < B$$

and would be the beginning of a series of polymers with different electronegativities. Other criteria considered were that the polymer chosen should be capable of effecting a change in some electrical parameter in order to be able to detect the presence of a gas through this change. In addition, the polymer should be able to be deposited as a film, be oxidatively and thermally stable and not hygroscopic. And it was on the basis of this rationale that we chose the various polymers used in this program.

Once the aforementioned criteria had been established for the overall class of polymers, i.e., conjugated polyenes, other factors were considered with regard to the choice of the individual polymers. Polymers I-IV were given primary consideration because their synthesis had been well characterized and they had previously been used in the development of a gas detector (Reference 2), but had not heretofore been used under smoldering fire conditions. Polymers V-X were also considered because in most instances their synthesis had been well-documented in the literature. In addition, they represented either electropositive polymers, such as polymers VI and X, or electronegative substances, such as polymers VII and VIII. Polymers V and IX were considered because of their potential for complexing with gases via d-orbital electrons in the metal atoms.

Since the synthesis and rationale for polymers I-IV have been adequately described elsewhere (Reference 2), it is of interest to examine the synthesis and rationale for choosing polymers V-X. The synthetic route to poly(ethynylferrocene) (V) was through the monomer ethynylferrocene, which had to be prepared first.

Ethynyl ferrocene was prepared from acetyl ferrocene according to the procedure described by Rosenblum (Reference 9).

1. $C_{10}H_{10}Fe$ (Ferrocene) + $CH_3COCl \xrightarrow{AlCl_3} FeC_{10}H_9COCH_3$

2. $FeC_{10}H_9COCH_3 + HCONMe_2 + POCl \longrightarrow FeC_{10}H_9CHCl = CHCHO$

3. $FeC_{10}H_9CHCl = CHCHO + NaOH \longrightarrow FeC_{10}H_9C \equiv CH$

and was reported to polymerize with benzoyl peroxide as the catalyst (Reference 10). The polymer was found to have an electrical resistivity around 10^{10} ohm - cm (Reference 10). This polymer would probably be electropositive and might show interesting complexing behavior with aldehydes, or possibly even hydrocarbons, either saturated or unsaturated, through d-orbital electrons of the iron atom.

For the preparation of poly(ethynylpyridine) (VI), Okamoto and Alia (Reference 11) have reported the preparation of the α, β and γ -pyridylacetylene from the corresponding acetylpyridine derivative. Although the yields were low, they obtained enough to study the polymerization characteristics and report on their electrical properties. Another method of preparation may also be via halogenation and dehydrohalogenation of the corresponding vinylpyridine. The resultant poly(ethynylpyridine) (VI) should be useful for detection of such substances as aldehydes and other electronegative substances.

Originally, it was thought that B - phenyl - B' - ethynyl carborane would be prepared via the following series of reactions:

1. $B_{10}C_2H_{12}$ (Carborane) + $OR^- + 2ROH \longrightarrow B_9C_2H_{12}^- + B(OR)_3 + H_2$
2. $B_9C_2H_{12}^- + H^- \longrightarrow B_9C_2H_{11}^{=} + H_2$
3. $B_9C_2H_{11}^{=} + C_6H_5BCl_2 \longrightarrow C_6H_5B_{10}C_2H_{11} + 2Cl^-$
4. $C_6H_5B_{10}C_2H_{11} + OR^- + 2ROH \longrightarrow C_6H_5B_9C_2H_{11}^- + B(OR)_3 + H_2$
5. $C_6H_5B_9C_2H_{11}^- + H^- \longrightarrow C_6H_5B_9C_2H_{10}^{=} + H_2$
6. $C_6H_5B_9C_2H_{10}^{=} + CHCl = CH - BCl_2 \longrightarrow C_6H_5(CHCl = CH)B_{10}C_2H_{10} + 2Cl^-$
7. $C_6H_5(CHCl = CH)B_{10}C_2H_{10}$ + Base $\longrightarrow C_6H_5(C \equiv C)B_{10}C_2H_{10}$

Reactions 1-5 are known and have been reported by Sheratte (Reference 12). Furthermore, 2-chlorovinylboron dichloride is known (Reference 13) having been prepared by the carbon catalyzed reaction of boron trichloride with acetylene.

However, it was subsequently learned that a C - ethynyl carborane can be easily prepared by the following route (References 14 and 15):

$$B_{10}H_{10}\cdot 2X + HC\equiv C-C\equiv CH \rightarrow B_{10}C_2H_{11}\cdot C\equiv CH$$

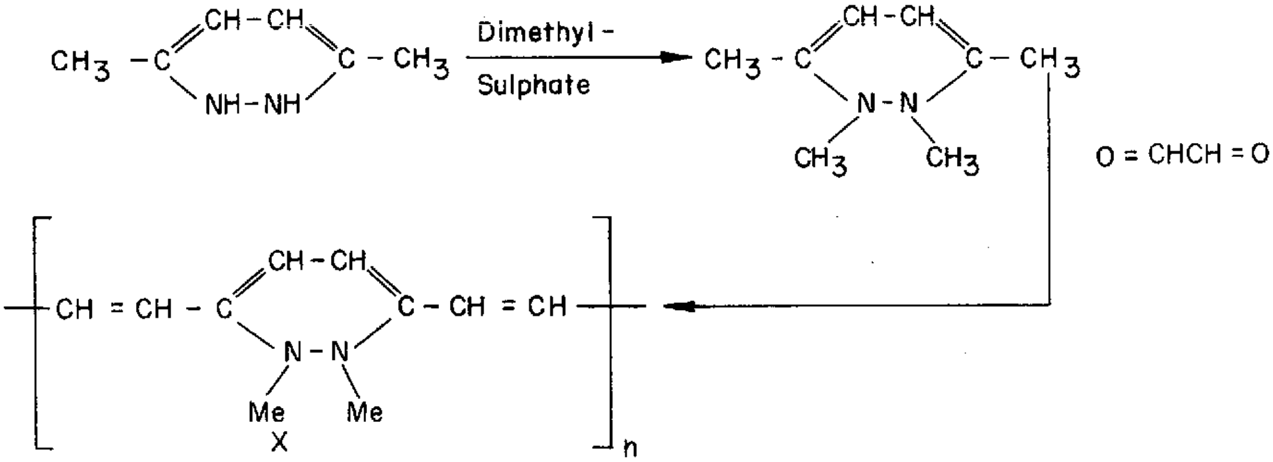
$$\left[B_{10}H_{10}\cdot 2X = \text{Decarborane bis-X } (X = \text{Acetonitrile, } Me_2S,\ Et_2S, \text{ etc.}\right]$$

and it was this approach that was used. The first step was to obtain the butadiyne and then react this with decarborane. Polymer VII was expected to be quite interesting as an electronegative polymer and useful for electropositive gases, e.g., ammonia, CO, etc.

For the preparation of poly(dicyanoacetylene) (VIII) Byrd (Reference 16), followed the technique described by Moureu and Bongrand (Reference 17) and prepared dicyanoacetylene monomer from acetylene dicarboxamide. The yields are very poor. Its polymerization by anionic catalysts had been studied by Benes, et al. (Reference 18) and it was found to polymerize quite readily. Theoretically, the resultant polymer should be extremely interesting as a gas complexing agent as it is very strongly electronegative. Thus, it was thought that even hydrocarbons might complex with this polymer.

To prepare poly(ethynylnickelocene) (IX), it was originally planned that the ethynyl derivative of nickelocene would be prepared, analogously to ethynylferrocene. However, it has been reported that nickelocene does not undergo a Friedel-Crafts reaction (Reference 19), so in view of this, an alternative method was considered. This polymer should be similar to poly(ethynylferrocene) (V) in its complexing capability. The major difference being that the nickelocene polymer should be easily oxidized to the nickelocenium ion and therefore potentially more capable of complexing with electropositive species.

Overberger and Byrd had previously reacted piperonal with the oxidized product of 3,6-dimethyl -1, 2-dihydropyridazine, viz., 3,6-dimethylpyridazine (Reference 20) and obtained a derivative having carbon-carbon double bonds. It was found that the oxidized compound, e.g., the pyridazine, reacted with piperonal at the methyl groups. It was decided, for this program, that 3, 6-dimethyl-1, 2-dihydropyridazine be treated with dimethylsulfate to obtain the N-methyl derivative and that this compound be treated with glyoxal to get the polyene, as follows:



This polymer should be strongly electropositive and capable of forming complexes with aldehydes, thereby potentially being a very good detector for aldehydes.

3.0 EXPERIMENTAL

A number of methods exist for the preparation of conjugated polyenes; notable among them being the polymerization of ethynyl monomers. However the preparation of the monomer and, in some cases the polymer, frequently results in poor yields and/or difficultly isolable products. Thus, aside from the preparation of the poly(phenylacetylene) class of polymers (polymers I-IV) [which had been well documented elsewhere (Reference 2)], the synthesis of the other polymers called for in this program, in many instances, resulted in low, or no, yield of material. Once prepared, though, regardless of yield, they were all subjected to characterization studies consisting of viscosity measurements, spectroscopic analyses, thermogravimetric analyses, and gas/polymer interaction effects, as determined by changes in electrical conductance. This section will, therefore, contain only experimental methods, while Section 4 will consist of a detailed discussion of the results.

3.1 Synthesis of Polymers

The first task undertaken in this program dealt with the preparation and evaluation of poly(phenylacetylene) (I), poly(p-nitrophenylacetylene) (II), poly(p-formamidophenylacetylene) (III), and poly(p-aminophenylacetylene) (IV). This group of polymers derives from poly(phenylacetylene) and Figure 1 shows the reaction scheme used in preparing them. The next group studied was polymers V - X; none of these being related to each other in the synthesis sequence, as were I-IV.

3.1.1 Poly(phenylacetylene) (I)

Poly(phenylacetylene) (I) was prepared by mixing 75g of phenylacetylene (ethynylbenzene), 200 ml carbon disulfide and 0.5 g aluminum chloride, under nitrogen. An exotherm resulted within two hours bringing the temperature up to 42°C and the exotherm maintained reflux for 1 1/2 hours further. When the mixture started to cool, heat was applied and refluxing continued overnight. The resulting mixture was poured into 1200 ml of isobutanol and a dark tan precipitate, weighing 45 g, was obtained. The softening point of this material (in a capillary tube) was 210-225°C.

Analysis for poly(phenylacetylene):
Calc. for C_8H_6: $C = 94.11$, $H = 5.88$
Found: $C = 94.02$, $H = 6.04$

3.1.2 Poly(p-nitrophenylacetylene) (II)

Fifty grams poly(phenylacetylene) (I) were dissolved in 120 ml of red fuming nitric acid at 0°C and allowed to react at this temperature for one hour. Ice was added to the solution to precipitate the polymer. The mixture was filtered, washed with water until the washings were neutral, washed with alcohol and dried in a vacuum oven at 50°C. Yield was 70 g. Although the elemental analysis of the resultant poly(p-nitrophenylacetylene) (II) shows a low carbon, the hydrogen and nitrogen are excellent. It should be noted that aside from polymers prepared by polymerization of monomer, e.g., phenylacetylene, most polymers that are derivatives prepared via reactions run on a polymer will tend to have poor analyses. This, of course, is most likely due to difficulties in controlling reactions on polymers as well as the difficulty in purifying the product, as compared to a low molecular weight organic compound. Thus, such things as overnitration and/or, oxidation could have occurred here to result in the poor analysis. It is difficult to know to what to attribute the poor carbon analysis.

Analysis for poly(p-nitrophenylacetylene):
Calc. for $C_8H_5NO_2$: $C = 65.31$, $H = 3.40$, $N = 9.52$
Found: $C = 58.81$, $H = 3.34$, $N = 9.53$

3.1.3 Poly(p-formamidophenylacetylene) (III)

Poly(p-formamidophenylacetylene) (III) was prepared by the reduction of II. Ten grams of II were dissolved in 60 ml dimethylformamide (DMF) followed by a solution of 35 g anhydrous stannous chloride in 75 ml DMF plus 45 ml concentrated HCl. The mixture was heated to 100°C for five hours, cooled and poured into 500 ml of H_2O made basic with concentrated NH_4OH. The precipitate was filtered, washed with water and dried. The mixture of polymer and tin salts was extracted with DMF, the extract filtered and then precipitated into water made basic with ammonium hydroxide. The precipitate was filtered, washed with water and dried to yield 7.3g of a black powder.

Analysis for poly(p-formamidophenylacetylene):

Calc. for C_9H_7NO:	C = 74.48, H = 4.83, N = 9.66
Found:	C = 71.96, H = 5.13, N = 11.01

The discrepancies found in this analysis might be explained in similar fashion as was discussed for the nitro polymer (II).

3.1.4 Poly(p-aminophenylacetylene) (IV)

The poly(p-formamidophenylacetylene) (III) was converted to poly(p-aminophenylacetylene) (IV) by hydrolysis of III with concentrated hydrochloric acid.

Analysis for poly(p-aminophenylacetylene):

Calc. for C_8H_7N:	C = 82.05, H = 5.87, N = 11.97
Found:	C = 77.72, H = 5.87, N = 10.33

3.1.5 Poly(ethynylferrocene) (V)

In the preparation of poly(ethynylferrocene) (V), the monomer had been adequately described elswhere (Reference 9), so little difficulty was anticipated. However, it was found that certain precautions had to be taken in the purification steps or the yield and type of polymer would be poor. Once the purification procedure was established, the preparation and purity of the polymer followed accordingly.

To prepare the poly(ferrocenylacetylene) (poly(ethynylferrocene) it was first necessary to prepare ethynylferrocene.

Acetylferrocene (obtained from Research Organic Corp., Sun Valley, Calif.) was first converted to 1-chloro-2-formyl-vinylferrocene then to ethynylferrocene and finally to poly(ethynylferrocene) (V).

A solution of 6 ml phosphorous oxychloride in 200 ml dimethylformamide (DMF) was prepared by adding the $POCl_3$ slowly to the DMF at 0°C under nitrogen.

The vigorous exotherm was controlled with an ice-salt bath.

Acetylferrocene (46g) was dissolved in 200 ml DMF and this was added to the $POCl_3$ solution in DMF at 0°C with stirring under nitrogen. (The published procedure recommends adding the $POCl_3$ solution to the acetylferrocene, but this results in a sticky solid that has to be purified within a day or two or it suffers extensive decomposition.)

After all the acetylferrocene had been added (appproximately 30 minutes), the resultant blue solution was held at 0°C for a half hour and then allowed to warm to room temperature under nitrogen. A solution of 350g sodium acetate in 1000 ml water was added and the mixture stirred under nitrogen overnight.

(CAUTION: The addition of the first 100 ml, or so, of this solution is strongly exothermic!)

Before extraction of the product with methylene chloride, the aqueous layer was saturated with salt. This gave a separation of layers that was quite readily seen. No attempt was made to wash the DMF out of the methylene chloride extract (a procedure recommended in the literature) (Reference 9). Instead, the methylene chloride was stripped out under vacuum, and the resultant deep red solution poured into excess saturated sodium chloride solution. The 1-chloro-2-formyl-vinylferrocene precipitated as glistening deep red needles which were sufficiently pure to be stored indefinitely and could be used in the next step of the synthesis without further purification. Figure 6 depicts the structure of the 1-chloro-2-formyl-vinylferrocene.

Analysis for 1-chloro-2-formyl-vinyl ferrocene:

Calc. for $C_{13}H_{11}Fe\ Cl\ O$:	C = 56.87, H = 4.01, Cl = 12.92, Fe = 20.36
Found:	C = 56.98, H = 4.21, Cl = 12.81, Fe = 20.01

Ethynylferrocene was prepared by dissolving 4.8g of 1-chloro-2-formyl-vinylferrocene in 150 ml dioxane, heating to reflux under nitrogen, adding 100 ml of 0.5N NaOH, and boiling the mixture under nitrogen for ten minutes. After this time, the hot solution was poured over 500g ice. The resultant mixture was saturated with salt and exhaustively extracted into ether. After drying, removal of the ether left three grams of a deep red oil. Chromatographic purification on alumina using benzene as eluant gave 2.4 g of pale yellow, pasty crystals melting at 50° to 53°C [(Literature: 52.5° (Reference 9)]

It has been found that the slow decomposition of ethynylferrocene is caused by traces of impurity. This impurity can best be removed by repeated chromatography on alumina, using hexane as eluant. The leading band is ethynylferrocene, followed very closely by the impurity. By rejecting the last 10% of the band, a sample has been obtained as orange hexagonal crystals, mp. 53°C. This procedure uses hexane as an eluant instead of benzene; and the product has been stable without showing any tendency to decomposition.

Analysis for ethynylferrocene:

Calc. for $C_{12}H_{10}$ Fe:	C = 68.62, H = 4.77, Fe = 26.61
Found:	C = 68.70, H = 4.86, Fe = 26.67

Polymerization of this material for 8 hours at 190°C in the presence of benzoyl peroxide leads to a polymer that is almost completely soluble in benzene.

Analysis for poly(ethynylferrocene):

Calc. for $C_{12}H_{10}$ Fe:	C = 68.62, H = 4.77, Fe = 26.61
Found:	C = 68.62, H = 4.86, Fe = 26.39

3.1.6 Poly(ethynylpyridine) (VI)

Ethynylpyridine, used in the preparation of poly(ethynylpyridine) (VI), was also prepared from a known procedure (Reference 21). The major difficulty here lay in the instability of the 1-(4-pyridyl)-2-bromoethylene and vessicant action of this compound. The preparative route used for VI was that from the bromination of 4-vinylpyridine to the dehydrobromination and on to the polymerization of the ethynyl derivative. The ethynylpyridine was subsequently converted to the corresponding polyacetylene derivative.

4-Vinylpyridine hydrochloride (105g, 0.74 mole) was suspended in 500 ml chloroform and cooled to 0°C. Bromine (82 ml, 1.5 mole) was added so that the temperature remained below 0°C. After the addition was complete (about 35 minutes), the mixture was stirred at 0°C for 1 hour and then allowed to come to room temperature over the next two hours.

About 300 ml ether was added, causing the separation of an orange oil. The supernatant was decanted and the oil was washed with more ether. Finally, about 500 ml acetone was added slowly (causing a moderate exotherm and the generation of a strong lachrymator), and the oil slowly solidified under the acetone to a pale yellow powder, m.p. 146-150°C (Gray) (Reference 21) gives m.p. 148-150°C. The yield was essentially quantitative.

Sixty three grams of the above dibromo salt were dissolved in 1000 ml water, and treated with sodium carbonate until basic. The mixture was then extracted with ether, and after drying over magnesium sulphate, the ether layer was concentrated to 350 ml. A solution of 22g triethylamine in 100 ml tetrahydrofuran was added and the mixture was stirred under nitrogen for two hours at room temperature and then 1 1/2 hours at reflux temperature.

The black precipitate of triethylamine hydrobromide was removed by filtration. Evaporation of the solvents left a mixture of a pale tan solid product and some excess triethylamine, which was washed out of the product using pentane. The yield of 1-(4-pyridyl) -2-bromoethylene was 41g (87%).

After numerous attempts at dehydrobromination of 1-(4-pyridyl)-2-bromoethylene to obtain the ethynylpyridine, it was found that the product depended upon the length of time the bromoethylene derivative was kept before further reaction. It appears that this compound is very unstable. Even if stored at 0°C, and a 24 hour period elapses between its preparation and subsequent dehydrobromination, the yield of 4-ethynylpyridine is drastically reduced. Furthermore, if held at 40-50°C for about 1/2 hour, an exothermic polymerization occurs.

[NOTE: An important word of caution is put forward to those who wish to investigate the synthesis and reactions of the 1-(4-pyridyl)-2-bromoethylene. It is a virulent vessicant, and great care should be exercised in handling it.]

A mixture of 50g paraffin wax and 60g powdered potassium hydroxide was placed in a 500 ml flask equipped with a stirrer, powder addition funnel, thermometer and Claisen take-off head. The Claisen head was connected directly to a flask which was immersed in a dry ice/freon mixture and connected to a vacuum pump. The entire apparatus was evacuated to 200 mm, and the wax/potassium hydroxide mixture was heated to 160°C by immersion of the flask in an oil bath held at that temperature.

Crude 1-(4-pyridyl) -2-bromoethylene was placed in the funnel and admitted in small portions to the reaction flask. After each addition, the temperature in the flask rose considerably. The pressure was held at 200 mm for 2 minutes after each addition, and then slowly lowered to 4 mm while the product distilled and was collected in the recovery flask. The pressure was then raised to 200 mm again, using a nitrogen bleed, and a second batch of reactant was admitted.

After 41g crude 1(4-pyridyl) -2-bromoethylene had been so treated, about 6g product had distilled.

The ethynylpyridine was thermally polymerized to a black solid by heating under nitrogen at 150°C for 20 hours. The polymer was soluble in methanol, but after 2-3 days exposure to air, it was only soluble in glacial acetic acid.

Analysis for poly(ethynylpyridine):
Calc. for C_7H_5N: C = 81.55, H = 4.85, N = 13.59
Found: C = 83.20, H = 6.09, N = 10.59

Poor analysis might be attributable to product being an acetate salt.

3.1.7 Poly (C-ethynylcarborane) (VII)

1,4-Dichloro - 2-butyne (30g) was converted into butadiyne using the method of Herbertz (Reference 22). The butyne was dissolved in 250 ml ethanol and 2g pyridine added. The solution was placed in a 500 ml flask, under nitrogen, and 100g of 40% sodium hydroxide were added slowly with stirring, so that the temperature remained below 50°C.

The addition took one hour, and butadiyne evolved continually during this time. When all the sodium hydroxide had been added, the temperature was raised to 80°C for 1 hour further, while the apparatus was swept with nitrogen.

The butadiyne was passed through two dilute sodium hydroxide wash bottles, and dried over calcium sulphate before being condensed in a dry ice/freon cold trap.

The yield from 30g dichlorobutyne was 10g.

Decarborane (25g) was dissolved under nitrogen in 200 ml refluxing acetonitrile. After about one hour, the bis-acetonitrile complex of decarborane began to precipitate. Refluxing was continued overnight to yield a suspension of the bright yellow complex.

The 10g butadiyne were dissolved in 50 ml acetonitrile, and added slowly to the refluxing decarborane bis-acetonitrile suspension. The mixture was heated at 80°C for four hours, yielding a dark yellow cloudy solution.

The solvent was then stripped out, and the pasty residue treated with ether, in which most dissolved. The ether solution was dried over magnesium sulphate, and stripped to dryness after filtration. The yellow pasty residue was dissolved in pentane and cooled to -80°C, when white crystals of C-ethynyl carborane separated.

The yield was 12g, m.p. 72-76°F. [Hawthorne (Reference 15) gives 75-78°C].

Analysis for C-ethynyl carborane:
Calc. for $C_4B_{10}H_{12}$: C = 28.57, H = 7.14, B = 64.29
Found: C = 28.38, H = 7.28, B = 64.57

The C-ethynyl carborane was thermally polymerized under nitrogen at 130°C for 20 hours. The resultant golden yellow polymer had a softening range from 45-150°C and was soluble in methanol. Using benzoyl peroxide as a catalyst, an apparently higher molecular weight material was prepared with a softening point of over 100°C.

Analysis for poly(ethynylcarborane):
Calc. for $C_4B_{10}H_{12}$: C = 28.57, H = 7.14, B = 64.29
Found: C = 24.09, H = 6.70, B = 47.76

It is difficult to understand this poor analysis other than some possible oxidation and loss of boron.

3.1.8 Poly(dicyanoacetylene) (VIII)

Concentrated ammonium hydroxide (400 ml) and methanol (300 ml) were cooled to -20°C, and diethylacetylene dicarboxylate (100g) was added dropwise with vigorous stirring so that the temperature remained below -10°C. The addition took about five minutes. Stirring was continued without cooling for one hour, during which time the temperature of the mixture rose to 15°C. The product was filtered, washed with a little water, and then with 50 ml ice cold methanol and dried under vacuum. The yield was 55g (97%) of the acetylene dicarboxamide.

An apparatus was constructed by joining short lengths of 8 mm glass tubing to the bottom of a 500 ml Erlenmeyer flask. Each length of tubing passed through a rubber stopper which was plugged into the neck of a 20 mm test tube. The neck of the Erlenmeyer was closed by a rubber stopper through which passed a length of 8 mm tubing, which led to two traps in series, and ultimately a vacuum pump.

An intimate mixture was prepared of 12g acetylene dicarboxamide, 200g sand and 100g phosphorus pentoxide. The mixture was distributed among eight test tubes which were evacuated and flushed with nitrogen two or three times, before finally being evacuated to 2 mm. The two traps were immersed in dry ice/freon, and then the eight tubes containing the amide mixture were simultaneously plunged into an oil bath preheated to 215°C.

After 15 minutes, most of the product had collected in the first trap, with a very small amount in the second trap. Twenty ml tetrahydrofuran were added to each trap and the dicyanoacetylene was washed directly into an addition funnel, from which it was added slowly to approximately 0.05 g n-butyl lithium in hexane at -70°C under nitrogen. During the addition, the solution temperature rose to -50°C, and the mixture started to darken. About one hour after the addition was complete, the temperature had fallen to -70°C again, and the solution was black. The product was allowed to come to room temperature, and removal of the solvent left about 2g black solid.

The preparation of dicyanoacetylene and the polymer have been well documented (References 16-18).

Although the polymerization goes almost quantitatively, the overall yields of polymer from the diamide are poor. The difficulty is in the preparation of the monomer. In addition, it appears that the polymer is quite hygroscopic, and this, too has affected the availability of the material for subsequent use. No analysis is available due to the hygroscopic nature of the polymer.

3.1.9 Poly(ethynylnickelocene) (IX)

Nickelocene (37.8g, 0.2 mole) was partly dissolved in 250 cc pentane under nitrogen and cooled to -78°C. Bromine (48.0g, 0.3 mole) was added slowly with good stirring and cooling below -50°C. The exothermic reaction continued until almost all the bromine had been added.

After all the bromine was in (2 hrs), the suspended solid was stirred for 1 hour at -70°C, and then allowed to warm to room temperature overnight.

The brown solid product (28g) was filtered and washed with a little cold pentane. It was dried for 24 hours in a vacuum dessicator over NaOH to remove residual bromine.

Analysis for brominated nickelocene:

Calc for C_{10} H_{10}Ni Br: C = 44.67, H = 3.72, N = 21.85, Br = 29.74

Found: C = 25.88, H = 2.80, Ni = 36.38, Br = 16.95

It is not clear exactly what this material is, but it evidently is not a bromonickelocene. It contains only 1/3 bromine atom per nickel atom, and it contains too much nickel per carbon atom. No further work was attempted on this material.

3.1.10 Polyene from 3, 6-Dimethyldihydropyridazine (X)

Acetonylacetone [114g (1 mole)] was placed in a 500 ml flask under nitrogen. Hydrazine [32g (1 mole)] dissolved in 68 ml of water was added to the acetonylacetone with cooling to maintain the temperature at less than 30°C (40 minutes). After a further 1 1/2 hours at room temperature, the reaction mixture was heated to 90°C and held under reflux for 20 minutes. After cooling, the mixture was extracted with ether, dried over potassium carbonate and the ether removed to yield a pale gold oil. Rapid distillation at 125°C (2mm) gave 78g (70%) yield of a pale yellow oil of 3, 6-dimethyldihydropyridazine.

3,6-Dimethyl-1, 2-dihydropyridazine (22g, 0.2 mole) was dissolved in 150 ml methanol, under nitrogen, in a 500 ml flask at room temperature and 20 ml of 10% aqueous sodium hydroxide were added, followed by 12g dimethylsulphate. The temperature rose to 43°C in five minutes, and then fell to 40°C over the next ten minutes, at which time a further 20 ml sodium hydroxide and 12g dimethylsulphate were added, causing the temperature to reach 60°C in ten minutes. Further quantities of sodium hydroxide and dimethylsulphate were added, so that gentle refluxing was maintained without cooling, until 48g (0.4 mole) dimethylsulphate had been added. When the final boiling began to slow, 10% sodium hydroxide was added until cloudiness persisted (about 10 ml) and refluxing was continued for another hour, adding more sodium hydroxide each time the solution cleared.

The product was poured over 500g ice and extracted with ether. The ether extract was dried over potassium carbonate and taken to dryness, to yield 21g (75%) dark brown oil, which was distilled at 95°C (2mm).

Analysis: Calc. for $C_8H_{14}N_2$: C = 69.57, H = 10.14, N = 20.28
Found: C = 69.24, H = 10.44, N = 20.21

Polymerization of this product with glyoxal was attempted next by two methods

a. Open Vessel Method

Tetramethylpyridazine (5.5g, 0.04 mole), and 6 ml of 40% aqueous glyoxal were placed in a 50 ml flask with 0.02g hydroquinone and 0.02g pyridine, and heated to 100°C under nitrogen with good stirring for two hours. After cooling, the viscous product was extracted into benzene and dried over potassium carbonate. Removal of the solvent left 6.1g black, sticky, semisolid (X).

b. Sealed Vessel Method

The above quantities of reactants were sealed in a glass tube under nitrogen and heated at 120°C for three hours. The solid black product was largely insoluble in most organic solvents. Boiling m-cresol partly dissolved it.

Of the two methods, the latter appeared to give a better product, but it also gave a difficultly soluble product. It was subsequently found that glacial acetic acid dissolved the most material, but even this solvent did not dissolve all of the polymer. It appears that this polymer is considerably crosslinked. Thus, extracting 56 g of the seemingly crosslinked polymer with hot glacial acetic acid resulted in the recovery of about 5g of material after removal of the acetic acid under vacuum.

Analysis: Calc. for $C_{10}H_{12}N_2$: C = 75.00, H = 7.50, N = 17.50
Found: C = 59.78, H = 6.12, N = 9.03

This poor analysis may be due to the fact that acetic acid was used as a solvent, and the acetate salt may have formed.

3.2 Characterization of Polymers

Once the polymers had been prepared, a number of parameters relative to their properties had to be evaluated. Their structures were determined by infrared and ultraviolet absorption spectra. An indication, but not an absolute value, of their molecular weight was obtained from their relative viscosities. Solubilities were determined to a limited extent; just enough so that films could be put down on the lock-and-key electrode substrate in a uniform manner. Thermogravimetric analyses and isothermal stabilities were also obtained in order to determine the long-term stability of the polymers. Finally, gas/polymer interactions were determined for pure gases under different relative humidities, as well as gases generated by a smoldering wad of cotton.

3.2.1 Physical Data

3.2.1.1 Solubility and Film Forming Characteristics

In order for the polymers prepared in this program to be capable of being incorporated into a useful device, they had to be soluble in a solvent that would be non-corrosive to the substrate, easy to handle, and would not affect the chemical structure of the polymer being dissolved. Furthermore, since it had been demonstrated previously that a four percent solution of the particular polymer would consistently result in a film thickness of about 0.2 microns (Reference 2), it was decided to use the same solution concentration for this program. To this end, poly(phenylacetylene) (I), poly(p-nitrophenylacetylene) (II), and poly(dicyanoacetylene)(VIII)were dissolved in acetone. Poly(p-formamidophenylacetylene) (III) and poly(p-aminophenylacetylene (IV) were dissolved in dimethylformamide (DMF), while poly(ethynylferrocene) (V) was dissolved in benzene. Poly(ethynylpyridine) (VI) and the polyene from 1,2,3,6 - tetramethylpyridazine (X) were dissolved in glacial acetic acid and poly(ethynylcarborane) (VII) was dissolved in methyl alcohol. The poly(ethynylnickelocene (IX) could not be prepared.

Once the solutions were obtained, films of these polymers were placed on the lock-and-key sensor for the necessary gas measurements. The method that consistently gave good films was via the technique described elsewhere (Reference 2). The sensor was kept in a vertical position and then dipped into the polymer solution. By withdrawing the sensor from this slowly, and as gradually as possible, the surface tension of the solution pulled the excess liquid off the surface. The sensor was then stood on edge on a piece of absorbent paper and allowed to dry. While in this position, the paper pulled off any bead which might form at the bottom edge of the sensor. The sensor was now ready for use in gas measurements.

3.2.1.2 Viscosities

Table 1A gives the values for the relative viscosities, at constant concentration, for polymers I - IV. The other polymers were not placed in this Table as their solubilities were different; their viscosities are in Table IB.

It is interesting to note that although polymers II - IV were all made from the same poly(phenylacetylene) (I), the viscosities were greater than that of (I). This increase may be attributable to dipole or hydrogen bonding effects between chains. In other words, association via a dipole - dipole interaction may be occurring between the chains in polymer II and hydrogen bonding in polymers III and IV.

3.2.1.3 Infrared and Ultraviolet Absorption Spectra

3.2.1.3.1 Infrared Spectra

One way of characterizing the chemical structure of an organic compound and/or polymer is its infrared absorption spectrum. Thus, the infrared spectrum for poly(phenylacetylene) is shown in Figure 7, and it compares with that obtained previously (Reference 2). (Note: All IR spectra were obtained on a Perkin-Elmer Model 521 Infrared Spectrophotometer.)

Figure 8 shows the infrared spectrum for poly(p-nitrophenylacetylene) (II), and it is almost identical to that obtained previously (Reference 2), as shown in Figure 9. Figure 10 depicts the spectrum of poly (p-formamidophenylacetylene) (III) and Figure 11 is the infrared curve of poly(p-aminophenylacetylene) (IV).

In following the synthesis of poly(ethynylferrocene), starting with the commercially available acetylferrocene, the respective infrared spectra are shown in Figure 12 for the acetylferrocene, Figure 13 for the 1-chloro-2formyl-vinylferrocene, Figure 14 for the ethynylferrocene and Figure 15 for the poly(ethynylferrocene) (V).

Figures 16-19 are the infrared spectra of compounds either used or generated in the synthesis of poly(ethynylpyridine) (VI).

Figure 20 is the infrared spectrum of C-ethynylcarborane and Figure 21 is that of the poly(ethynylcarborane) (VII).

Figure 22 is the infrared spectrum of poly(dicyanoacetylene) (VIII), and Figure 23 is the infrared spectrum of the brominated nickelocene prepared in the attempt at obtaining poly(ethynylnickelocene) (IX). Finally, in the course of preparing the polyene from 1,2,3,6-tetramethylpyridazine, the infrared spectra of both the monomer and polymer were obtained (Figures 24 and 25, respectively).

3.2.1.3.2 Ultraviolet Spectra

Figures 26-29 are the ultraviolet spectra of polymers I-IV, respectively (all UV spectra were obtained with a Cary 14 recording spectrophotometer). Figures 36-34 are the ultraviolet spectra for polymers V - VIII and X, respectively. Poly(ethynylnickelocene) (IX) could not be prepared, so its spectrum is not available.

3.2.1.4 Thermal Stability Measurements

Quite germane and critical to the program are thermal stability measurements, i.e., stability to high temperatures and to a particular temperature for an extended period of time. For this purpose, thermogravimetric analysis (TGA) curves were run in air using a duPont 950 Thermogravimetric Analyzer, 990 Thermal Analyzer and a Cahn Time Derivative Computer. In the figures containing these curves, there are two types of curves shown. The upper curve represents the rate of weight change with time and temperature while the lower curve shows the absolute weight loss. Figures 35-43 are the TGA curves for all polymers except IX, and Table II gives the isothermal weight losses.

3.2.2 Gas Measurements

Since one of the necessary aspects of this program is to determine gas/polymer interaction effects for possible use in fire detecting devices, the various polymers prepared were applied as films onto a lock-and-key electrode substrate and placed into a 7000 cc stainless steel vacuum chamber which was connected to a vacuum rack.

The lock-and-key (interdigitated) electrodes were prepared on Corning 7059 glass slides that were 1" x 1" x 0.048". These glass slides were degreased in hot (60°C) trichloroethylene then acetone at room temperature, followed by hot (60°C) methyl alcohol, rinsed with deionized (D.I.) water and blown dry with nitrogen. They were then cleaned in concentrated (48%) hydrofluoric acid for two seconds and those substrates that remained clear were kept for processing into the sensor; all others were discarded. The good slides were then given a D.I. water rinse for 30 minutes, blown dry with nitrogen and baked for ten minutes at 180°C in a vacuum oven prior to metallization.

The slides were placed in a vacuum system and the surfaces were reverse sputtered for 30 seconds followed by the sputtering of nickel for 1-1/2 minutes (to get a film 50-100 A thick) and then gold was sputtered on for eight minutes to a thickness of 2000 A. Filtered Hunt photoresist was spun onto the gold surface at 5000 rpm for 40 seconds and then dried in a dessicator, under nitrogen, for 30 minutes, followed by a bake in a vacuum oven for 60 minutes at 66°C. The slides were then masked with the lock-and-key pattern and exposed for eight seconds, developed and then rinsed in D.I. water. This was followed by baking at 125°C for 30 minutes under infrared lamps.

The next step was to etch the gold pattern on the slide with KI gold etchant (consisting of four parts of KI, one part of I_2 and 14 parts of water) at 60°C and then etching the nickel at room temperature in a mixture of one part nitric acid, one part acetic acid and one part acetone. The photoresist was then removed with Room Temperature Hunt Microstrip.

After completion of the above steps, the sensors were tested for shorts and then 0.002" x 0.010" gold ribbon leads were soft soldered to the electrodes. Frequently, incomplete removal of the nickel subsurface or some other conducting short would result and the surface conduction was too high. However, after overcoming these difficulties in obtaining good lock-and-key electrode sensors, gas measurements were made on all polymers that were prepared and that could be put down as films on the electrodes. In all cases, the applied voltage across the 5 mil spacing between the electrodes was 130 volts, d.c., and the film thickness of polymer was about 0.2 - 0.3 microns [actual thickness was not measured in this program, but technique used for depositing films, as described elsewhere, (Reference 2) usually gave films about 0.24 microns].

Plate I shows the overall system with the chamber, its connection to the vacuum rack, and the electrometer used for electrical measurements. Figure 44 depicts the circuit diagram of this setup. Plate II shows the inside of the chamber with a coated sensor and Plate III shows the lock-and-key electrode sensor without the polymer coating on it.

Initially, a number of experiments were run on polymers I-IV to semi-quantitatively determine their response to "fire gases." Experimentally, the barrel of a 20 ml hypodermic syringe, with the needle embedded in a rubber stopper, was held vertically, with the open end down. A burning paper strip was thrust into the syringe where it continued to burn for a few minutes until lack of oxygen extinguished the flame. The unburned paper was withdrawn, and the gases which had been generated by the flame were trapped inside the syringe by inserting the plunger.

The rubber stopper was then removed from the needle and the gases which were trapped inside the syringe were caused to flow over an equilibrated coated sensor by holding the needle within 1/4 inch of the sensor surface and depressing the plunger over approximately five seconds.

Controls were run using a syringe full of room air at 30% RH, a syringe full of ammonia and a syringe full of exhaled breath. Sensitivity to a given gas was indicated by an increase in current during gas flow, followed by a slow return to approximately the original value.

Subsequent to this initial exploratory study of the response of the poly (phenylacetylenes) to "fire gases," etc., a detailed study was made of all the film-forming polymers' response to various gases, as well as to "fire gases," but under more controlled and quantitative conditions.

The experimental procedure was as follows:
The test conditions were in air at zero percent relative humidity (RH), 50% RH and 100% RH; both in the absence of, and the presence of, various gases, i.e., ammonia, carbon monoxide, acrolein, butadiene, etc. In addition, measurements were made on polymers exposed to the combustion products ("fire gases") evolved from smoldering cotton in air at 50% RH.

The coated sensor was placed in the chamber (Plate II), which was then evacuated until the current in the sensor attained equilibrium. The chamber was then filled with dry air, and the current again noted. (No change could generally be detected.) The chamber was then opened, and a beaker was placed inside, and the chamber rapidly closed again. The beaker contained a solution designed to provide a constant relative humidity inside the chamber. For 50% RH, saturated potassium dichromate was used. For approximately 100% RH, pure water was used.

When the current in the sensor had attained equilibrium again, a quantity of air was withdrawn from the chamber equal to the volume of test gas to be injected. This was accomplished using a hypodermic syringe inserted through a rubber septum. The purpose of this was to maintain a maximum of one atmosphere pressure at all times. The test gas was then injected through the septum and any current changes in the sensor were monitored.

For better controlled "fire gas" measurements, a nichrome wire was inserted into the chamber and used as a resistance heater to generate the "fire gases." Plate IV shows the nichrome wire heater inside the chamber. A wad of cotton was then wrapped around the wire and the voltage gradually increased until browning, charring, and smoldering (but not burning with a flame) occurred. Plate V depicts the cotton wrapped around the wire.

Tables III-X show the gas responses for all polymers prepared except poly(dicyanocetylene) (VIII) and poly(nickelocenylacetylene) (IX). The latter could not be prepared as a characterizable polymer, and the former (VIII) was found to be insensitive to adsorbed gases. Even under vacuum, fairly large quantities of ammonia (3000 ppm) were not detected with VIII. Acrolein, acetylene, water vapor and the "fire gases" from burning cotton also were not detectable.

Table XI shows the "fire gas" measurements in air at 50% RH for all polymers that were used for gas measurements.

4.0 DISCUSSION OF RESULTS

4.1 Characteristics of Polymers

4.1.1 Spectral Analysis

In discussing the various spectra obtained (both infrared and ultraviolet), it would be well to briefly point up the relationship between the synthesis and the spectra. For example, where one polymer was derived from another, it is of interest to show how the appearance (or disappearance) of a particular functional group can be followed spectroscopically. This applies equally well to the preparation of a polymer from its monomer, wherein the characteristic absorption peaks attributable to the monomer disappear as it is converted to the polymer.

In view of the fact that polymers I - IV had been quite thoroughly investigated previously (Reference 2), no problem was anticipated in their synthesis for this program. Thus, the products obtained, and the various spectra, corresponded quite closely to what was expected. The infrared spectra (Figures 7-11) showed the characteristic absorption peaks for the particular functional group present in the structure. For example, the infrared spectrum of poly(phenylacetylene) (I), shown in Figure 7, compares favorably with that obtained previously (Reference 2), while the NO_2 absorption in polymer II appears at 1350 cm^{-1}, (Figure 8) and its spectrum compares very favorably with that obtained previously (Figure 9) (Reference 2). Then, in the reduction to the formamide group (polymer III), the NO_2 absorption is found to have disappeared and the appearance of a CO stretch at 1660 cm^{-1} is observed (Figure 10). Subsequently, hydrolysis of the formyl group eliminates the CO stretch and the NH absorption at 3250 cm^{-1} is quite pronounced for polymer IV (Figure 11) (just as it was in the spectrum of the formamide group of polymer III).

Another spectral study made was ultraviolet absorption spectroscopy. Ultraviolet absorption spectroscopy is a useful analytical tool to relate properties to electronic structure. Normally, isolated double bonds absorb in the far ultraviolet region, and with increasing conjugation there is a shifting towards the near ultraviolet and then on into the visible. No visible absorptions were determined in this program, so it is not possible to correlate the color of the polymer with the absorption characteristics of the conjugated polyene backbone. In most instances, there was an aromatic moiety in the polymer, and it was this group that was making the greatest contribution to the UV spectrum.

With poly(phenylacetylene) (I), the maximum (in the ultraviolet) (Figure 26) is lower than what one would expect for the phenyl group (usually found to be around 260 nm), i.e., it is around 245 nm. This might be attributable to the fact that the phenyl groups are not coplanar with the backbone, but are arranged in a close-packed order laterally to the backbone and therefore make little or no contribution to electronic resonance interaction with the backbone (Reference 2), thereby leaving the conjugated polyene as the sole contributor to the UV absorption. In the case of the poly(p-nitrophenylacetylene) (II) Figure 27, however, the possibility for a greater degree of resonance interaction can occur [see discussion in Final Report on Contract NAS12-15 (Reference 2)] and the absorption maximum is shifted to a longer wavelength than I. Polymers III and IV, (Figures 28 and 29 respectively) show a slight absorption shoulder at around 245 nm and at 285 nm (for IV). It is possible that carrying the spectra out to the visible region might have shown some peaks there, but we don't have these data so we cannot be sure. The only argument in favor of this is the deep color exhibited by these two polymers.

In following the synthesis of poly(ethynylferrocene) (IV) starting with the commercially available acetylferrocene, the respective infrared spectra are shown in Figure 12 for the acetylferrocene, Figure 13 for the 1-chloro-2-formylvinylferrocene, Figure 14 for the ethynylferrocene and Figure 15 for the poly(ethynylferrocene) (V). Figure 13 has a $C=C$ stretch at 1590 cm^{-1}, while Figure 14 has a $-C\equiv C-H$ stretch at 3280 cm^{-1} and a $-C\equiv C-$stretch at 2110 cm^{-1} and complete removal of the 1590 cm^{-1} peak. In Figure 15, as would be expected for the polymer, these stretching frequencies are gone. The UV spectrum for V (Figure 30) shows no absorption for aromatic rings, but a decided shift toward the near UV and possibly on into the visible, with absorption peaks at 265-287 nm (plateau), 305 nm and 325 nm.

Figures 16-19 are the infrared spectra of compounds either used or generated in the synthesis of poly(ethynylpyridine) (VI). Again, there is a -C≡C-H stretch at 3280 cm^{-1} for the monomer, 4-ethynylpyridine (shown in Figure 18), and its disappearance in the polymer (shown in Figure 19). The UV spectrum (Figure 31) has its maximum around 260 nm, characteristic of aromatic groups.

The infrared spectrum of C-ethynylcarborane (Figure 20) is probably characteristic of this compound. The -C≡CH stretch at 2110 cm^{-1} is noticeably present, but when polymerized, the 2110 cm^{-1} band has disappeared (Figure 21). Furthermore, it appears that during polymerization, oxidation of the carbon backbone has occurred, as evidenced by the appearance of a carbonyl absorption at 1700 cm^{-1}. Therefore, the UV spectrum (Figure 32 is not truly characteristic of the expected poly(ethynylcarborane) (VII).

Figure 22 is the infrared absorption spectrum of poly(dicyanoacetylene) (VIII). It shows the very characteristic absorption peak at 2200 cm^{-1} for the CN stretch. However, the UV spectrum (Figure 33) is interesting in that, as was expected, since no aromatic moieties are present, no absorption is found in the 240-260 nm region. Instead, the absorption peak is at 300 nm.

Although the preparation of poly(ethynylnickelocene) (IX) was not successful, the intermediate obtained in the course of its attempted preparation, viz., the brominated nickelocene was analyzed by infrared spectroscopy, and its spectrum is shown in Figure 23. However, since the polymer was not obtained, no UV spectrum is available.

Finally, in the course of preparing the polyene from 1,2,3,6-tetramethyl pyridazine, the infrared spectra of both the monomer and polymer were obtained (Figures 24 and 25, respectively). The only characterizable absorption peak is that of the methyl group in the monomer at 1370 cm^{-1} (Figure 24). The UV spectrum (Figure 34) had its absorption peaks at about 255 nm and 290 nm. Since no aromatic groups were present in this polymer, the spectrum could be attributable to a conjugated polyene system with some pseudo aromaticity from the electrons of the pyridazine ring nitrogens interacting with the double bonds in the ring.

4.1.2 Thermal Analysis

Interestingly enough, the thermal stability data appears to correlate reasonably well with the UV spectra, viz., the greater the degree of conjugation and/or aromaticity (therefore the greater the resonance stabilization of electrons), as well as the absence of CH moieties, the greater the thermal stability. Thus, poly(ethynylferrocene) (X), poly(dicyanoacetylene) (VIII) and poly(phenylacetylene) (I) were the most stable, as shown by their TGA curves (Figures 39, 42, and 35) respectively. The least stable was the poly(ethynylcarborane) (VII), as expected. Although the carborane cage is a relatively stable moiety, the fact that we appeared to have an oxidized product and no conjugation in the backbone seemed to correlate with the observed major weight loss on heating. Presumably, after the backbone had been oxidized and eliminated, the remainder of the molecule appeared to stabilize (Figure 41). Next, in order of decreased thermal stability was the poly(ethylidenetetramethylpyridazine) (X). This compound could readily lose nitrogen (possibly as a dimethyl hydrazine moiety) and then leave a polyacetylene residue that would remain stable for a period of time with heating (Figure 43).

The isothermal weight loss data, however, (Table II) show some interesting results. It was difficult to draw correlative conclusions between TGA data and the isothermal data. The isothermal data were obtained at 95°F (35°C), and generally the majority of the polymers did not show evidence for thermal decomposition at this point; particularly since the isothermal data were obtained from runs made over extended periods of time at 95°F (35°C), while the TGA runs saw this temperature for only a few seconds. In addition, if there was a highly conjugated structure with stabilizing moieties, such as a phenyl group or a ferrocenyl group, this, too, would stabilize the polymer. Thus, for example, the poly(ethynylcarborane) (VII) did not give evidence in the UV spectrum of a conjugated polyene, and it demonstrated the poorest stability at 35°C (under isothermal heating for 168 hours). Poly(ethynylferrocene) (V), however, does show excellent stability under isothermal heating conditions. Of special interest, though, is the case of poly(dicyanoacetylene) (VIII). This polymer increased in weight; and this could be attributable to the hygroscopic nature of the polymer.

Thus, for possible home use, for a sensor to be exposed to summer heat, the most likely polymer would be the poly(ethynylferrocene) (V). However, other polymers may also be considered if, after exposure to air and heat, they will stabilize themselves, as, for example, poly(p-aminophenylacetylene) (IV) or poly(ethynylpyridine) (VI). It should be noted that although polymer X showed low weight losses under isothermal conditions, it did not demonstrate the same "fire gas" responsiveness that V did. Thus a sensor prepared with V would show the best stability at an ambiance of 35°C.

4.2 Gas/Sensor Interactions

In addition to the synthesis and characterization of various polymers for potential use as gas detecting substances it is important to know the interaction of these polymers, on a lock-and-key electrode geometry, with various ambiances. As has been frequently stated, a conjugated polyene. e.g., a polyacetylene with various appendages from the acetylene backbone or a linear polyene with no appendages, would probably show the necessary electrical and electronegativity properties for use as a gas detector. Thus, as has been demonstrated for the poly(phenylacetylene) series of polymers, i.e., I-IV, the interaction of these polymers with certain gases such as ammonia, for example, has resulted in a change in the electrical conductance of these polymers; with II being the most responsive. However, in a "fire gas" environment, III was the most responsive of this series of polymers (as seen in Table XI).

Of all the polymers that could be prepared, the only one that showed absolutely no detectable gas response was poly(dicyanoacetylene) (VIII). It appears from these data that the better a polymer conducts, the more insensitive it is to the presence of electron-donating or electron- withdrawing species (Reference 23). The conductance of VIII is around 2.7×10^{-7} amps versus about 10^{-10} to 10^{-11} amps for the other polymers. Apparently, we require a relatively low conductance material to effect major conductance changes when charge-transfer complex formation occurs, thereby enhancing the sensitivity of the system.

Of the remaining polymers, only five, i.e., polymers I-V, showed a reasonably large response to the various gases and "fire gas" used; and in almost every instance, the electronegativity relationship between the polymer and gas was found to be operable.

Initially, the gas/polymer interactions were studied by first evacuating the chamber and then introducing small amounts of the gas expected to be present in a cotton fire. Next, the measurements were made under smoldering conditions where the gases generated were from smoldering cotton (no flame). In addition, these measurements were made in dry air, and in air at 50 percent relative humidity (RH) and approximately 100 percent RH. Essentially, the results obtained substantiated the data obtained under vacuum conditions with regard to electronegativity effects and with regard to the detectability of ammonia, carbon monoxide and even the gases generated from smoldering cotton. Thus, examining the data in Table VII for gas responses of poly(ethynylferrocene) (V), it is seen that it was minimally, but quite decidedly, responsive to such gases as CO and butadiene, and very responsive to "fire gases" (as seen in Table XI). Another observation of significance is that both poly(ethynylpyridine)(VI) (Table VIII) and poly(ethylidenetetramethylpyridazine) (X) (Table X) showed sensitivity to CO, with the former polymer being more responsive. This is interesting in that it substantiates the fact that a strong electron donor would be needed to detect CO, further supporting the electronegativity concept of gas/polymer interactions.

Table XI also depicts the response of the various other polymers exposed to smoldering cotton in air at 50% RH. It is noted that the response times are quite rapid and that in all cases the sensor came back to its original value. The reason for the long time to return to the original value was that the sensor was in a closed chamber with no fresh air being brought in so that it took time for the gases to equilibrate in the adsorption equilibrium. Furthermore, there was grease between the cover of the chamber and the chamber; and this grease could be a solvent for many of the gases, thereby gradually removing them from the chamber. A still further contributing factor to possible removal of the gases from the environment is the beaker of water or salt solution used to regulate the RH. This, too, could be a solvent for some of the gases, also removing them from the atmosphere in the chamber.

A comment should be made at this point relative to the long term stability of the sensors. It is recognized that should a fire detector be made, it would have to be able to withstand ambient conditions of various gases, dust, etc. and should be operable after a long period of time. In the course of performing on this program, and while waiting for new sensors to be prepared, it was found that a poly(p-nitrophenylacetylene) sensor prepared in 1967 for use on Contract NAS12-15 (Reference 2), and that had been exposed to dust, dirt and all kinds of laboratory ambiances over the six years, still responded in similar fashion to ammonia gas, compared to what had previously been reported (Reference 2). Thus, since conjugated polyenes of this nature are readily stabilized (as further evidenced by the thermal stabilities obtained for the various polymers prepared), long term stability can be expected from devices that will utilize conjugated polyenes as sensing polymers.

A further matter of concern in this program has been that of the effect of changes in humidity on the operation of the sensor. Table XI depicts the speed of response of a sensor to smoldering cotton compared to the longer time required for a change in relative humidity. It has been demonstrated that exposing the sensor to different relative humidity conditions has a pronounced effect on the conductance of the sensor. However, rapid changes in RH are not likely to occur (Reference 24). It is well established that humidity changes are relatively long-timed events; and going from 50% RH to approximately 100% RH, in real operating conditions could take as little as one hour, or longer. Usually, in any situation of change in humidity (even in the case of a fog bank rolling in) there are gradients dependent upon temperature and dew point; and these take longer to occur than the development of gases from a nearby fire. Therefore, since the sensor has time to equilibrate to the change in humidity, this won't cause the alarm to sound due to sudden changes in conductance. A fire, on the other hand, will be a rapid event and exhibit a drastic sudden change in concentration of many gases in the ambiance from what was present immediately before the fire started smoldering or burning, including the generation of water. This change in concentration and type of gas will be capable of causing a rapid change in conductance of a sensor and thereby sound an alarm if differential rate of change circuitry is used. The following example, which concerns itself with the detectability of a fire in the presence of water vapor from such activities as washing, showering, scrubbing floors, etc., as well as cigarette smoke, will demonstrate the concept and feasibility of a differential fire detection circuit.

Most of the polymers we have developed, and even the bare sensor, are sensitive to water vapor. For this reason, sudden increases in relative humidity in a real situation could trigger a false alarm.

Another possible cause of false alarms would be tobacco smoke, which, of course, contains all the components of cellulosic fire products.

To prevent false alarms in these common household situations, it will be necessary to have at least three sensors in any sensing circuit. These will be:

1. The main sensor, sensitive to fire gas vapors. This would be the multiple gas sensor to be developed in this program.

2. A secondary sensor, insensitive to fire gases, but sensitive to water.

3. Another secondary sensor, insensitive to fire gases, but sensitive to some component of tobacco smoke not normally found in a cellulosic fire.

All these sensors would be integrated into the same circuit which would be designed so that in the case of a sudden increase in humidity, sensor #2 would tell #1 that such an increase had occurred and to ignore the changes in conductivity caused by the humidity. In a fire, sensor #1 would have the fire gas input over and above the humidity input, which would be uncompensated by sensor #2.

Similarly, in the presence of tobacco smoke, sensor #3 would tell #1 to ignore concentrations of fire gas equivalent to the amount of tobacco smoke present. Any fire gas products in excess of that related to the tobacco smoke present would trigger the alarm.

In order to determine how much water vapor is actually present in the atmosphere of either our test chamber, or a room, and what amount of water vapor would be added to these enclosures upon total combustion of cotton, the following exercises are of interest. From handbooks it is determined that at 50% RH, the partial pressure of water at 25°C is 12 mm. In 7000cc of air (the volume of our test chamber), there are n moles of water. Thus, from

$$PV = nRT$$

we get

$$P = \frac{12}{760}, \; V = 7000, \; R = 82 \text{ and } T \approx 300°K$$

$$n = \frac{\frac{12}{760} \cdot 7000}{82 \cdot 300} = 0.00045 \text{ mole } H_2O$$

Then, since cellulose will burn in air to yield CO_2 and H_2O, viz.,

$$(C_{12}H_{22}O_{11}) + 12\, O_2 \longrightarrow 12\, CO_2 + 11\, H_2O$$

and approximately 50% of the cellulose is water (actually 58%), the burning of 0.4g of cotton will result in about 0.2gH_2O. Therefore, completely burning the 0.4g of cotton is enough to cause the RH to go from 50% to 100% in the chamber.

As a further exercise on the effect of burning cotton, let us consider the case of an "average" room of 10 feet by 10 feet by 8 feet. Thus, the 800 cubic feet equals 21,600,000cc, or $V = 2.16 \times 10^7$, and at 50% RH we get,

$$n = \frac{\frac{12}{760} \cdot 2.16 \cdot 10^7}{82 \cdot 300} = 14 \text{ moles } H_2O$$

with 14 moles equalling 252 grams of water. Therefore, burning one pound of cotton will release about 250 grams of water, thereby increasing the RH to 100%. However, under smoldering conditions, it is unlikely this amount of cotton would be consumed unless smoldering continued for a long time. Therefore, detection of a fire would not rest solely with detection of the water generated; particularly, since at <u>low levels of combustion</u>, oxidation is incomplete and mostly intermediate products, e.g., CO, hydrocarbons and aldehydes, among others, would be the more likely products.

Thus, there have been two general observations with regard to the responses obtained under various humidity conditions:

1. At low humidity (0.1%, or essentially dry air conditions), the sensors' response at 760 mm first with dry nitrogen and then dry air from a gas cylinder are essentially identical to their response at 10^{-1} mm (vacuum conditions). In other words, no changes in reading on the electrometer. Increasing the humidity causes the sensor to become more conductive; and the absolute value of the response to some gases - particularly ammonia seems to be higher, but the sensitivity, as measured by absolute response divided by background conductivity, is distinctly lower at higher humidities.

2. When smoldering conditions were set in the chamber containing a solution to regulate humidity, the conductivity of the sensors rose rapidly in the first minutes following the beginning of smoldering, but within an hour or so, when the original humidity equilibrium situation has had a chance to reestablish itself, the conductivity of the sensor returned to the value it had before the smoldering began.

It would thus appear, from the first observation, that relatively high concentrations of water vapor, e.g., 50% RH, would mask the responsiveness of the sensor to the gas to which it would normally be expected to be sensitive. The significance of the second observation is that after the sensor has equilibrated itself to a particular RH, the change in conductance is then due to either a change in RH or a particular gas, or both. When the adsorption-desorption equilibrium has reestablished itself by having the gases that were generated by the fire either seep out of the chamber or dissolve in the solution used to regulate the 50% RH, the sensor's conductance should return to the base line value present before the fire. Thus, water vapor that is suddenly introduced into the environment, if not from a fire, could generate misleading results unless balanced out of the circuit by a sensor sensitive only to water vapor.

5.0 CONCLUSIONS

The synthesis of polymers of varying electronegativity that can eventually show a demonstrated capability of interacting with gaseous substances, and thereby effect a change in some electrical parameter that potentially can be used in developing an early warning fire detector has been demonstrated. Of the polymers prepared, poly(phenylacetylene) (I), poly(p-nitrophenylacetylene) (II). poly(p-formamidophenylacetylene) (III), poly(p-aminophenylacetylene) (IV, poly(ethynylferrocene) (V), poly(ethynylpyridine) (VI) and poly(ethylidenetetramethylpyridazine) (X) seemed to be most responsive to the various ambiances. Of special interest was the CO detectability by the latter two polymers (VI and X), thereby reinforcing the electronegativity concept of electron donor/electron acceptor relationships in gas/polymer interactions.

In addition, as was expected, a conjugated polyene structure is quite thermally stable. This was amply borne out by the thermal stability of poly(phenylacetylene), poly(ethynylferrocene) and poly(dicyanoacetylene). In the latter case, it is likely that considerable dipole-dipole interactions, as well as resonance effects, could be enhancing the thermal stability of the polymer; plus the fact that no hydrogens are present to act as labile sites in the molecule. Thus, developing a fire sensor from a conjugated polyene should result in long term stability.

Finally, after the sensor has equilibrated itself to a particular relative humidity caused by metereological conditions and household activities, e.g., washing, showering, etc., its only change due to moisture in the ambiance would now be attributable to the water vapor generated by a smoldering fire; and this amount of water is probably low due to incomplete combustion.

Thus, based upon the electronegativity or electron configuration of a particular polymer, e.g., the d-orbital electrons of iron, as in poly(ethynylferrocene), or the high electron density of poly(ethynylpyridine), for example, it is possible to develop a number of sensors, each of which is specific for a particular gas, and to combine these into a multiple sensor detector for an early warning fire alarm.

6.0 RECOMMENDATIONS

In view of the fact that conjugated polyene polymers have been capable of electrical conduction, and gas/polymer interaction effects, as evidenced by changes in conductance, it is suggested that this type of effort be continued. There are two major areas to investigate further: (1) Practical device development - including both chemistry and electronics: (2) Basic program relating to gas/polymer interaction effects.

Under the first category, we have to consider the chemistry, as follows: Based upon the response behavior of poly(ethynylferrocene), the possibility of using other organometallic polymers for specific gas/polymer interaction effects is indicated. Representative metal-containing polymers may be phthalocyanines, poly(ethynylnitroferrocene), poly(ethynylcobaltacene), etc. By varying the metal atom, but maintaining a conjugated polyene structure for the electrical conductance, it may be possible to obtain a high degree of specificity for various gases, e.g., CO, hydrocarbons, aldehydes, etc. Other polymers that may prove equally interesting, and capable of demonstrating specificity, would be poly(imidazoles), polymeric Schiff-bases and poly(p-dimethylaminophenylacetylene), among others. A still further polymer of interest is a copolymer of some internal alternating electron acceptor/electron donor type thereby showing enhanced sensitivity to combinations of electron acceptor and electron donor gases, e.g., CO and NH_3.

With regard to the electronics, consideration should be given to other types of measurement than conductance. Thus, capacitance measurements should be very sensitive and responsive to gas/polymer interactions. Absorption of gases into polymers should change the dielectric constant of the medium which should be readily detectable by capacitance measurements. Furthermore, use of discriminatory or compensatory circuits should eliminate interference from the humidity of the ambiance with respect to a sensor's response to a smoldering fire.

Another important practical problem is to study the response behavior of various polymers prepared for use in sensors when exposed to smoldering of other materials, e.g., nylon, wool, urethanes, acrylics, vinyls, phenolics, etc. In addition, these measurements should be made at different temperatures, e.g., 0°C, 25°C, 50°C, 100°C, etc.

Under the second category (basic program), the question arises as to what effect water vapor has on the sensor's operation. It is not known how much water gets into the polymer being used as a sensor. Putting each polymer on an electrode substrate and using a microbalance, it should be possible to determine weight increases upon exposure to water vapor. Similarly, the same technique could apply to the gases, e.g., CO, hydrocarbons, aldehydes, etc., as well.

Related to this, a spectral (infrared and ultraviolet) study could be made of the various polymers upon exposure to gases. A correlation between spectral changes (upon exposure to various gases at different partial pressures) and electrical response should indicate which polymer, and the functional group in that polymer, is responsible for greatest specificity with a particular gas. Furthermore, in trying to design a polymer that will show maximum interaction effects, it would be of interest to compare the properties of those polymers that have their functional group as an appendage, e.g., ferrocenyl moiety, or if it is a conjugated part of the backbone, such as a ferrocenyl moiety in a Schiff's base structure.

Tied in with this latter study, would be a detailed study of the ultraviolet absorption spectra of the various compounds, and their relationship to conductivity and complexing capability. This information would more readily enable the design of a polymer which would show maximum interactions with gases. For example, the UV spectrum of a conjugated polyene will be different if it is isolated from the appendage attached to it or in resonance interaction with the appendage; if in interaction, it will be more related to the electronegativity of the appended moiety and therefore more capable of maximum interaction effects.

Finally, another area of importance to investigate is the molecular weight of the polymers prepared.A study should be undertaken with regard to molecular weight distribution and electrical conductance. Increasing the molecular weight should probably increase the electrical conductance due to the fact there will be fewer hoppings necessary from chain-to-chain.

TABLE IA
POLYMER VISCOSITIES

Solvent: Dimethylformamide
Temp.: 20°C±0.1°
Concentration: 0.05%

Polymer	Relative Viscosity(t/t_o)
Poly(phenylacetylene) (I)	1.19
Poly(nitrophenylacetylene) (II)	1.34
Poly(formamidophenylacetylene) (III)	1.24
Poly(aminophenylacetylene) (IV)	1.31

TABLE IB
RELATIVE VISCOSITIES AT 20°C±0.1°
CONCENTRATION 0.05%

Polymer	Solvent	Rel. Vis.
Poly(ethynylferrocene)	Toluene	1.04
Poly(ethynylpyridine)	Acetic Acid	1.08
Poly(ethynylcarborane)	Methanol	1.10
Poly(tetramethylpyridazine)	Acetic Acid	1.10
Poly(dicyanoacetylene)	Acetone	1.09

TABLE II
ISOTHERMAL WEIGHT LOSS AT 35°C IN AMBIENT AIR

Polymer	Weight Loss (Percent) After Hours Shown*				
	24 hrs.	48 hrs.	72 hrs.	96 hrs.	168 hrs.
Poly(phenylacetylene) (I)	0.71%	0.83%	0.87%	0.87%	0.89%
Poly(p-nitrophenylacetylene) (II)	0.10%	0.29%	0.25%	0.32%	0.32%
Poly(p-formamidophenylacetylene) (III)	0.75%	1.46%	1.93%	1.90%	1.94%
Poly(p-aminophenylacetylene) (IV)	0.80%	0.76%	0.84%	0.84%	0.80%
Poly(ethynylferrocene) (V)	0	-	-	0	0
Poly(ethynylpyridine) (VI)	0.24%	-	-	0.28%	0.28%
Poly(ethynylcarborane) (VII)	1.03%	-	-	1.88%	2.01%
Poly(ethylidenetetramethylpyridazine) (X)	0	-	-	0	0.08%
Poly(dicyanoacetylene) (VIII)	+0.10	-	-	+1.30%	+2.15%

*Weighed amounts of polymer were placed in porcelian crucibles and loosely covered. They were placed in a circulating air oven at 35° ± 1°C. Weight losses were recorded at 24 hour intervals up to 96 hours and then at 168 hours.

TABLE III

GAS RESPONSES OF POLY(PHENYLACETYLENE)

R.H.	GAS	VOLUME INJECTED	TOTAL PRESSURE	SENSOR CURRENT (AMPS)
0	Air Only	-	10^{-1} mm	7.8×10^{-10}
0	Air Only	-	760 mm	7.8×10^{-10}
0	NH_3	1 cc (1.4 ppm)	↓	74×10^{-10}
0	NH_3	5 cc (7 ppm)		320×10^{-10}
0	C_2H_2	20 cc (29 ppm)		7.8×10^{-10}
0	C_2H_2	100 cc (140 ppm)		7.8×10^{-10}
0	CO	100 cc (140 ppm)		7.8×10^{-10}
50%	Air Only	-		3.4×10^{-6}
50%	NH_3	1 cc (1.4 ppm)		3.4×10^{-6}
50%	NH_3	5 cc (7 ppm)		3.5×10^{-6}
50%	NH_3	20 cc (29 ppm)		3.8×10^{-6}
50%	C_2H_2	200 cc (290 ppm)		3.4×10^{-6}
50%	CO	200 cc (290 ppm)		3.4×10^{-6}
100%	Air Only	-		4.8×10^{-4}
100%	NH_3	20 cc (29 ppm)		4.9×10^{-4}
100%	NH_3	100 cc (140 ppm)		5.1×10^{-4}
100%	C_2H_2	200 cc (290 ppm)		4.8×10^{-4}
100%	CO	200 cc (290 ppm)		4.8×10^{-4}

TABLE IV

GAS RESPONSES OF POLY(NITROPHENYLACETYLENE)

R.H.	GAS	VOLUME INJECTED	TOTAL PRESSURE	SENSOR CURRENT (AMPS)
0	Air Only	-	10^{-1} mm	8.9×10^{-10}
0	Air Only	-	760 mm	8.9×10^{-10}
0	NH_3	1 cc (1.4 ppm)	↓	140×10^{-10}
0	NH_3	5 cc (7 ppm)		610×10^{-10}
0	C_2H_2	20 cc (29 ppm)		8.9×10^{-10}
0	C_2H_2	200 cc (290 ppm)		8.9×10^{-10}
0	CO	200 cc (290 ppm)		8.9×10^{-10}
50%	Air Only	-		1.1×10^{-5}
50%	NH_3	1 cc (1.4 ppm)		1.1×10^{-5}
50%	NH_3	5 cc (7 ppm)		1.3×10^{-5}
50%	NH_3	20 cc (29 ppm)		1.7×10^{-5}
50%	C_2H_2	200 cc (290 ppm)		1.1×10^{-5}
50%	CO	200 cc (290 ppm)		1.1×10^{-5}
50%	Acrolein	100 μ L (Liq)		1.1×10^{-5}
100%	Air Only	-		1.7×10^{-3}
100%	NH_3	20 cc (29 ppm)		1.9×10^{-3}
100%	NH_3	100 cc (140 ppm)		2.4×10^{-3}
100%	C_2H_2	200 cc (290 ppm)		1.7×10^{-3}
100%	CO	200 cc (290 ppm)		1.7×10^{-3}
100%	Acrolein	100 μ L (Liq)		1.7×10^{-3}

TABLE V

GAS RESPONSES OF POLY(FORMAMIDOPHENYLACETYLENE)

R.H.	GAS	VOLUME INJECTED	TOTAL PRESSURE	SENSOR CURRENT (AMPS)
0	Air Only	-	10^{-1} mm	7.4×10^{-10}
0	Air Only	-	760 mm	7.4×10^{-10}
0	NH_3	1 cc (1.4 ppm)	↓	9.7×10^{-10}
0	NH_3	5 cc (7 ppm)		450×10^{-10}
0	C_2H_2	20 cc (29 ppm)		7.4×10^{-10}
0	C_2H_2	200 cc (290 ppm)		7.4×10^{-10}
0	CO	200 cc (290 ppm)		7.4×10^{-10}
50%	Air Only	-		8.4×10^{-6}
50%	NH_3	1 cc (1.4 ppm)		8.5×10^{-6}
50%	NH_3	5 cc (7 ppm)		8.7×10^{-6}
50%	NH_3	20 cc (29 ppm)		11.1×10^{-6}
50%	C_2H_2	200 cc (290 ppm)		8.5×10^{-6}
50%	CO	200 cc (290 ppm)		8.5×10^{-6}
100%	Air Only	-		8.4×10^{-4}
100%	NH_3	20 cc (29 ppm)		9.7×10^{-4}
100%	NH_3	100 cc (140 ppm)		12.6×10^{-4}
100%	C_2H_2	200 cc (290 ppm)		8.4×10^{-4}
100%	CO	200 cc (290 ppm)		8.4×10^{-4}

TABLE VI

GAS RESPONSES OF POLY(AMINOPHENYLACETYLENE)

R.H.	GAS	VOLUME INJECTED	TOTAL PRESSURE	SENSOR CURRENT (AMPS)
0	Air Only	-	10^{-1} mm	2.3×10^{-10}
0	Air Only	-	760 mm	2.3×10^{-10}
0	NH_3	1 cc (1.4 ppm)		25×10^{-10}
0	NH_3	5 cc (7 ppm)		98×10^{-10}
0	C_4H_8	20 cc (28.6 ppm)		2.3×10^{-10}
0	C_4H_8	200 cc (290 ppm)		2.5×10^{-10}
0	CO	200 cc (290 ppm)		2.3×10^{-10}
0	Acrolein	100 μ L (Liq)		2.5×10^{-10}
50%	Air Only	-		7.8×10^{-6}
50%	NH_3	1 cc (1.4 ppm)		7.9×10^{-6}
50%	NH_3	5 cc (7 ppm)		8.9×10^{-6}
50%	NH_3	20 cc (29 ppm)		11.7×10^{-6}
50%	C_4H_8	200 cc (290 ppm)		7.8×10^{-6}
50%	CO	200 cc (290 ppm)		7.8×10^{-6}
50%	Acrolein	100 μ (Liq)		7.8×10^{-6}
100%	Air Only	-		8.4×10^{-4}
100%	NH_3	20 cc (29 ppm)		9.7×10^{-4}
100%	NH_3	100 cc (140 ppm)		13.5×10^{-4}
100%	C_4H_8	200 cc (290 ppm)		8.4×10^{-4}
100%	CO	200 cc (290 ppm)		8.4×10^{-4}
100%	Acrolein	100 μ L (Liq)		8.4×10^{-4}

TABLE VII

GAS RESPONSES OF POLY(ETHYNYLFERROCENE)

R.H.	GAS	VOLUME INJECTED	TOTAL PRESSURE	SENSOR CURRENT (AMPS)
0	Air Only	-	10^{-1} mm	3.4×10^{-9}
0	Air Only	-	760 mm	3.4×10^{-9}
0	NH_3	1 cc (1.4 ppm)	↓	45×10^{-9}
0	NH_3	5 cc (7 ppm)		185×10^{-9}
0	C_4H_8	20 cc (29 ppm)		3.6×10^{-9}
0	C_4H_8	100 cc (140 ppm)		4.1×10^{-9}
0	CO	100 cc (140 ppm)		3.5×10^{-9}
0	CO	300 cc (430 ppm)		3.7×10^{-9}
0	Acrolein	100 μ L (Liq)		3.4×10^{-9}
50%	Air Only	-		9.0×10^{-6}
50%	NH_3	5 cc (7 ppm)		9.2×10^{-6}
50%	NH_3	20 cc (29 ppm)		9.7×10^{-6}
50%	CO	200 cc (290 ppm)		9.0×10^{-6}
50%	CO	cc (570 ppm)		9.0×10^{-6}
50%	Acrolein	100 μ L (Liq)		9.0×10^{-6}
100%	Air Only	-		1.2×10^{-3}
100%	NH_3	100 cc (140 ppm)		1.3×10^{-3}
100%	CO	500 cc (715 ppm)		1.2×10^{-3}
100%	Acrolein	100 μ L (Liq)		1.2×10^{-3}

TABLE VIII

GAS RESPONSES OF POLY(ETHYNYLPYRIDINE)

R.H.	GAS	VOLUME INJECTED	TOTAL PRESSURE	SENSOR CURRENT (AMPS)
0	Air Only	-	5×10^{-2} mm	1.0×10^{-12}
0	Air Only	-	760 mm	1.0×10^{-12}
0	CO	100 cc	↓	1.0×10^{-12}
0	CO	200 cc		1.0×10^{-12}
0	Air Only	New Sensor(1)		1.0×10^{-12}
0	NH_3	100 cc		1.0×10^{-12}
0	NH_3	200 cc		1.0×10^{-12}
0	C_2H_2	100 cc		1.0×10^{-12}
0	Acrolein	1000 μ L (Liq)		1.0×10^{-12}
50%	Air Only	- (1)		4.4×10^{-4}
50%	CO	10 cc		4.1×10^{-4}
50%	CO	50 cc		3.5×10^{-4}
50%	CO	100 cc		2.9×10^{-4}
50%	CO	150 cc		2.6×10^{-4}
0%	CO	200 cc		2.2×10^{-4}
50%	Air Only	- (1)		8.8×10^{-5}
50%	NH_3	10 cc		6.2×10^{-4}
50%	NH_3	100 cc		30×10^{-4}
50%	NH_3	200 cc		36×10^{-4}
50%	Air Only	- (1)		1.1×10^{-4}
50%	Acrolein	100 μ L (Liq)		1.1×10^{-4}
50%	Acrolein	1000 μ L (Liq)		1.1×10^{-4}
50%	Air Only	- (1)		9.8×10^{-5}
50%	C_2H_2	100 cc		9.8×10^{-5}
50%	C_2H_2	300 cc		9.8×10^{-5}

(1) New sensor means the sensor was cleaned of polymer and recoated in order to minimize contamination from absorbed gases.

TABLE VIII (cont'd)
GAS RESPONSES OF POLY(ETHYNYLPYRIDINE)

R.H.	GAS	VOLUME INJECTED	TOTAL PRESSURE	SENSOR CURRENT (AMPS)
100%	Air Only	- (1)	760 mm	2.1×10^{-4}
100%	NH_3	200 cc	↓	2.1×10^{-4}
100%	Air Only	- (1)		4.8×10^{-4}
100%	CO	200 cc		4.8×10^{-4}
100%	Air Only	- (1)		3.7×10^{-4}
100%	C_2H_2	200 cc		3.7×10^{-4}
100%	Air Only	- (1)		5.1×10^{-4}
100%	Acrolein	100 μ L (Liq)		5.0×10^{-4}
100%	Acrolein	1000 μ L (Liq)		5.0×10^{-4}

TABLE IX

GAS RESPONSES OF POLY(ETHYNYLCARBORANE)

R.H.	GAS	VOLUME INJECTED	TOTAL PRESSURE	SENSOR CURRENT (AMPS)
0	Air Only	-	10^{-1} mm	1.1×10^{-9}
0	Air Only	-	760 mm	1.1×10^{-9}
0	NH_3	10 cc		1.6×10^{-9}
0	NH_3	50 cc		4.6×10^{-9}
0	NH_3	100 cc		27×10^{-9}
0	Air Only	- (1)		3.6×10^{-9}
0	CO	50 cc		3.7×10^{-9}
0	CO	100 cc		3.9×10^{-9}
0	CO	200 cc		4.1×10^{-9}
0	Air Only	- (1)	5×10^{-2}mm	2.8×10^{-9}
0	Acrolein	10 μ L (Liq)	> 2 mm	2.8×10^{-9}
0	Acrolein	100 μ L (Liq)	> 2 mm	2.8×10^{-9}
0	Air Only	- (1)	760 mm	1.9×10^{-9}
0	C_2H_2	100 cc		1.9×10^{-9}
0	C_2H_2	500 cc		1.9×10^{-9}
50%	Air Only	- (1)		1.6×10^{-5}
50%	CO	50 cc		1.6×10^{-5}
50%	CO	100 cc		0.50×10^{-5}
50%	CO	150 cc		0.19×10^{-5}
50%	CO	200 cc		0.20×10^{-5}
50%	Air Only	- (1)		2.2×10^{-6}
50%	NH_3	10 cc		2.7×10^{-6}
50%	NH_3	50 cc		4.4×10^{-6}
50%	NH_3	100 cc		13×10^{-6}
50%	NH_3	200 cc		28×10^{-6}
50%	Air Only	- (1)		2.5×10^{-6}
50%	Acrolein	10 μ L (Liq)		2.5×10^{-6}
50%	Acrolein	100 μ L (Liq)		2.5×10^{-6}
50%	Air Only	- (1)		3.1×10^{-6}

(1) New sensor

TABLE IX (Cont'd)

GAS RESPONSES OF POLY(ETHYNYLCARBORANE)

R.H.	GAS	VOLUME INJECTED	TOTAL PRESSURE	SENSOR CURRENT (AMPS)
50%	C_2H_2	100 cc	760 mm	3.1×10^{-6}
50%	C_2H_2	500 cc		3.3×10^{-6}
50%	C_2H_2	1000 cc		3.4×10^{-6}
100%	Air Only	- (1)		2.9×10^{-4}
100%	CO	100 cc		2.8×10^{-4}
100%	CO	300 cc		2.8×10^{-4}
100%	Air Only	- (1)		1.8×10^{-4}
100%	NH_3	10 cc		1.8×10^{-4}
100%	NH_3	100 cc		2.2×10^{-4}
100%	NH_3	200 cc		2.7×10^{-4}
100%	Air Only	- (1)		1.9×10^{-4}
100%	Acrolein	10 μ L (Liq)		1.9×10^{-4}
100%	Acrolein	1000μ L (Liq)		1.9×10^{-4}
100%	Air Only	- (1)		3.2×10^{-4}
100%	C_2H_2	500 cc		3.2×10^{-4}

(1) New sensor

TABLE X

GAS RESPONSE OF POLY(ETHYLIDENETETRAMETHYL PYRIDAZINE)

R.H.	GAS	VOLUME INJECTED	TOTAL PRESSURE	SENSOR CURRENT (AMPS)
0	Air Only	-	5 x 10^{-2} mm	0.2 x 10^{-11}
0	Air Only	-	760 mm	0.2 x 10^{-11}
0	CO	100 cc	↓	0.2 x 10^{-11}
0	CO	200 cc	↓	0.3 x 10^{-11}
0	CO	500 cc	↓	0.3 x 10^{-11}
0	Air Only	- (1)	↓	0.2 x 10^{-11}
0	NH_3	100 cc	↓	0.4 x 10^{-11}
0	NH_3	200 cc	↓	0.7 x 10^{-11}
0	NH_3	400 cc	↓	1.0 x 10^{-11}
0	Air Only	- (1)	↓	0.2 x 10^{-11}
0	C_2H_2	200 cc	↓	0.2 x 10^{-11}
0	Air Only	- (1)	5 x 10^{-2} mm	0.2 x 10^{-11}
0	Acrolein	100 μ L (Liq)	> 2 mm	0.2 x 10^{-11}
0	Acrolein	1000 μ L (Liq)	> 2 mm	0.2 x 10^{-11}
50%	Air Only	- (1)	760 mm	1.8 x 10^{-4}
50%	CO	100 cc	↓	1.1 x 10^{-4}
50%	CO	200 cc	↓	x 10^{-4}
50%	Air Only	- (1)	↓	2.2 x 10^{-5}
50%	NH_3	100 cc	↓	8.9 x 10^{-5}
50%	NH_3	200 cc	↓	1.2 x 10^{-4}
50%	Air Only	- (1)	↓	1.8 x 10^{-5}
50%	C_2H_2	200 cc	↓	1.8 x 10^{-5}
50%	Air Only	- (1)	↓	8.4 x 10^{-5}
50%	Acrolein	100 μ L (Liq)	↓	8.4 x 10^{-5}
50%	Acrolein	1000 μ L (Liq)	↓	8.4 x 10^{-5}

(1) New sensor

TABLE X (Cont'd)

GAS RESPONSES OF POLY(ETHYLIDENETETRAMETHYL PYRIDAZINE)

R.H.	GAS	VOLUME INJECTED	TOTAL PRESSURE	SENSOR CURRENT (AMPS)
100%	Air Only	- (1)	760 mm	2.2×10^{-4}
100%	NH_3	200 cc	↓	2.3×10^{-4}
100%	Air Only	- (1)		4.5×10^{-4}
100%	CO	200 cc		4.3×10^{-4}
100%	Air Only	- (1)		3.8×10^{-4}
100%	C_2H_2	200 cc		3.8×10^{-4}
100%	Air Only	- (1)		8.9×10^{-4}
100%	Acrolein	1000 μ L (Liq)		8.9×10^{-4}

(1) New sensor

TABLE XI

FIRE GAS RESPONSES AT 50% R.H.

POLYMER	I_0	I_F	$I_{MAX.}$	$T_{MAX.}$	I_{60}	I_{300}
Poly(phenylacetylene)	3.4×10^{-6}	8.5×10^{-6}	120×10^{-6}	10 Min.	7.4×10^{-6}	3.4×10^{-6}
Poly(nitrophenylacetylene)	1.1×10^{-5}	9.7×10^{-5}	104×10^{-5}	10 Min.	8.8×10^{-5}	1.1×10^{-5}
Poly(formamidophenylacetylene)	8.5×10^{-6}	63×10^{-6}	415×10^{-6}	15 Min.	24×10^{-6}	8.5×10^{-6}
Poly(aminophenylacetylene)	7.8×10^{-6}	47×10^{-6}	320×10^{-6}	10 Min.	18×10^{-6}	7.8×10^{-6}
Poly(ethynylferrocene)	9.0×10^{-6}	84×10^{-6}	470×10^{-6}	10 Min.	31×10^{-6}	9.0×10^{-6}
Poly(ethynylcarborane)	2.7×10^{-6}	7.4×10^{-6}	102×10^{-6}	10 Min.	8.0×10^{-6}	3.7×10^{-6}
Poly(ethynylpyridine)	1.7×10^{-5}	6.1×10^{-5}	74×10^{-5}	10 Min.	5.8×10^{-5}	1.9×10^{-5}
Poly(ethylidenetetramethyl pyridazine)	3.4×10^{-5}	7.9×10^{-5}	95×10^{-5}	15 Min.	7.2×10^{-5}	3.8×10^{-5}

Symbols

I_0 = Sensor current before fire

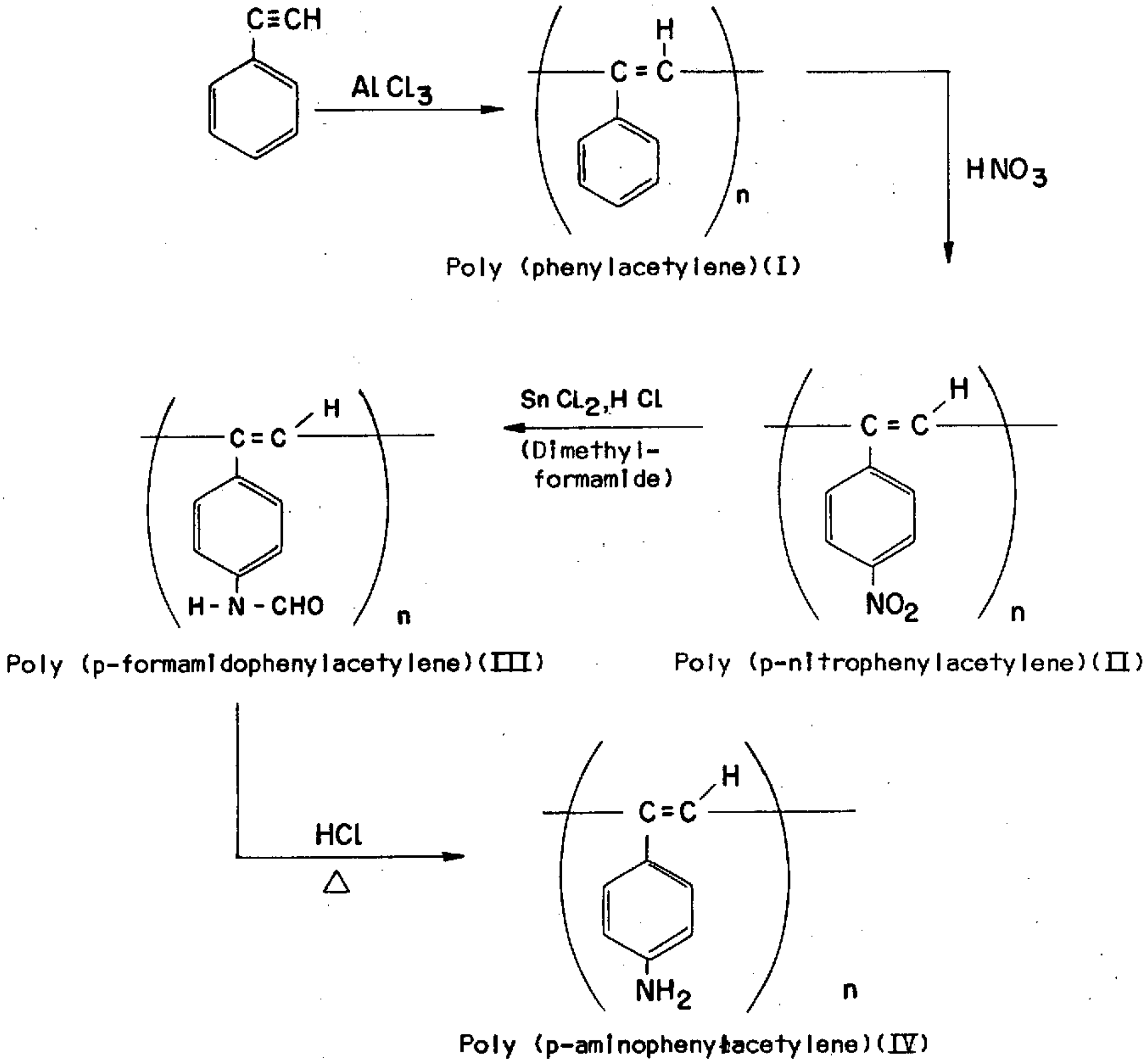
I_F = Current within 5 sec. of ignition

$I_{MAX.}$ = Maximum current observed

$T_{MAX.}$ = Time after ignition for max. current

I_{60} = Current 60 min. after ignition

I_{300} = Current 300 min. after ignition



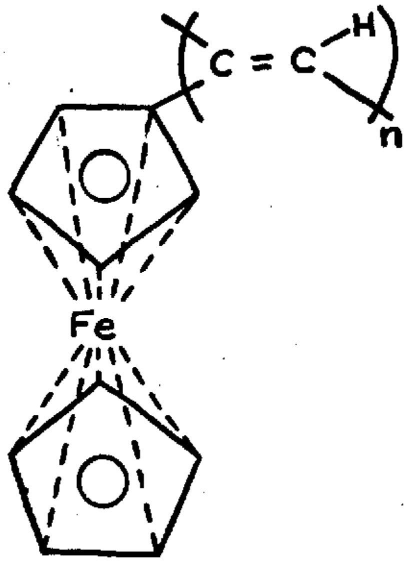
Poly (phenylacetylene)(I)

Poly (p-nitrophenylacetylene)(II)

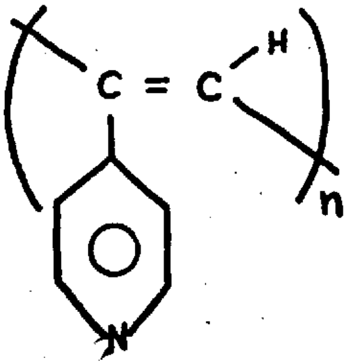
Poly (p-formamidophenylacetylene)(III)

Poly (p-aminophenylacetylene)(IV)

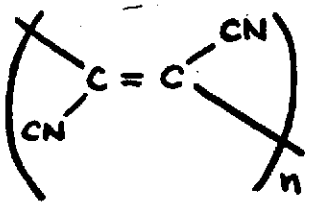
FIGURE I. REACTION SEQUENCE USED IN PREPARATION OF SOME POLY(PHENYLACETYLENES)



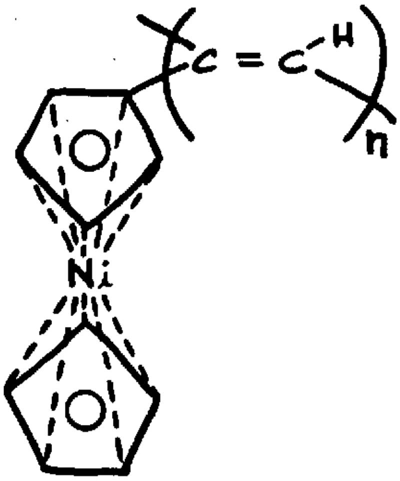
POLY(ETHYNYLFERROCENE)(V)



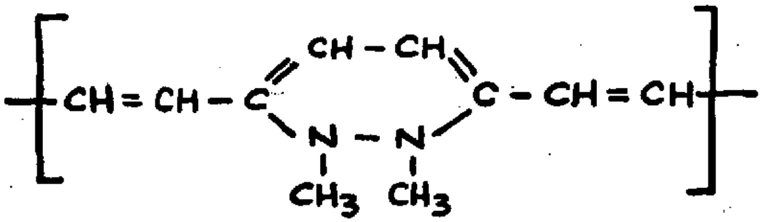
POLY (ETHYNYLPYRIDINE) (VI)



POLY (DICYANOACETYLENE)(VIII)

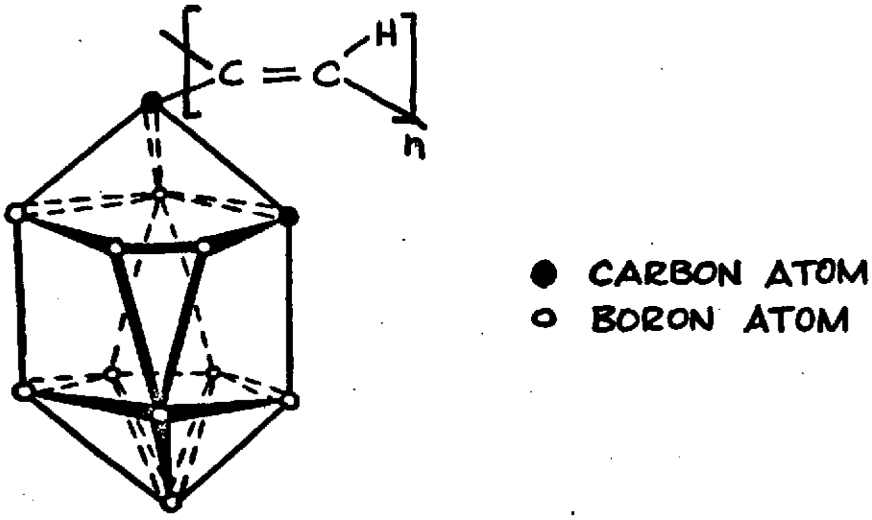


POLY(ETHYNYLNICKELOCENE) (IX)



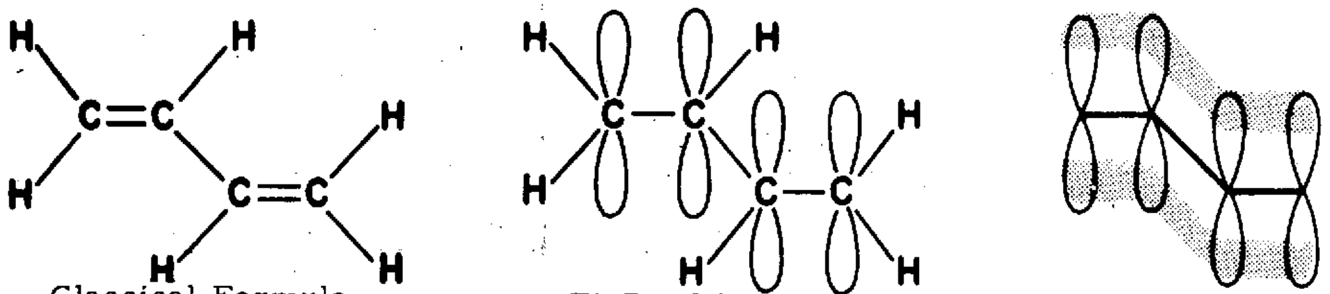
$$\left[-CH=CH-C\overset{\displaystyle CH-CH}{\underset{\displaystyle \underset{CH_3}{N}-\underset{CH_3}{N}}{\quad}}C-CH=CH-\right]$$

POLYENE FROM 1,2,3,6-TETRAMETHYL-PYRIDAZINE (X)



POLY(ETHYNYLCARBORANE) (VII)

FIGURE 2. POLYMERS V - X



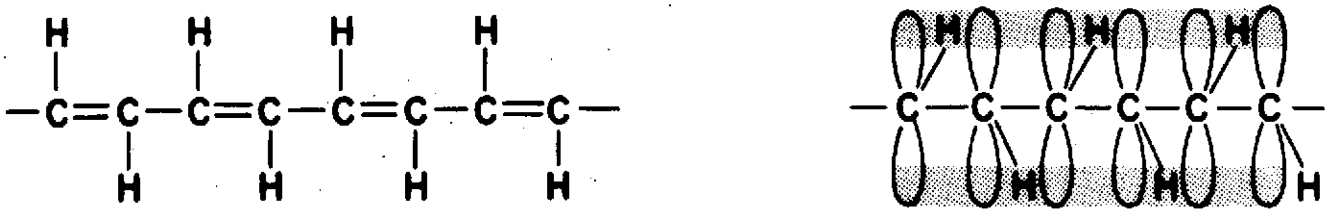
Classical Formula of Butadiene

Pi-Bond Picture of Butadiene

"Streamer" picture of Butadiene

C0341

FIGURE 3. BONDS IN BUTADIENE SHOWING ELECTRON CLOUD



(a)

(b)

C0342

FIGURE 4. (a) STRUCTURAL CLASSICAL FORMULA OF A POLYACETYLENE
(b) "STREAMER" PICTURE SHOWING SMEARING OUT OF ELECTRON CLOUD

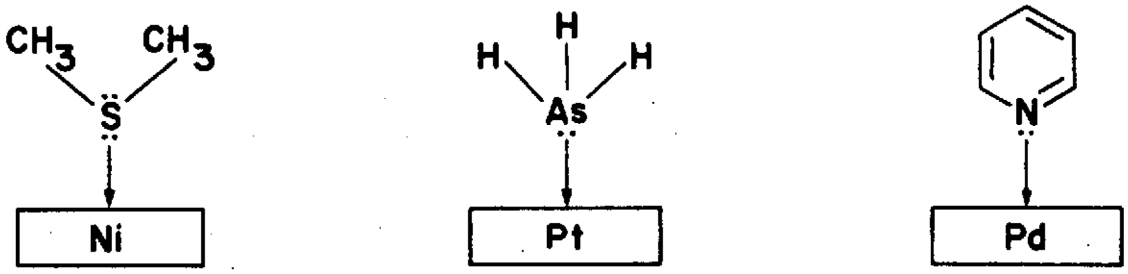


FIGURE 5. ADSORPTION ON A METALLIC SURFACE

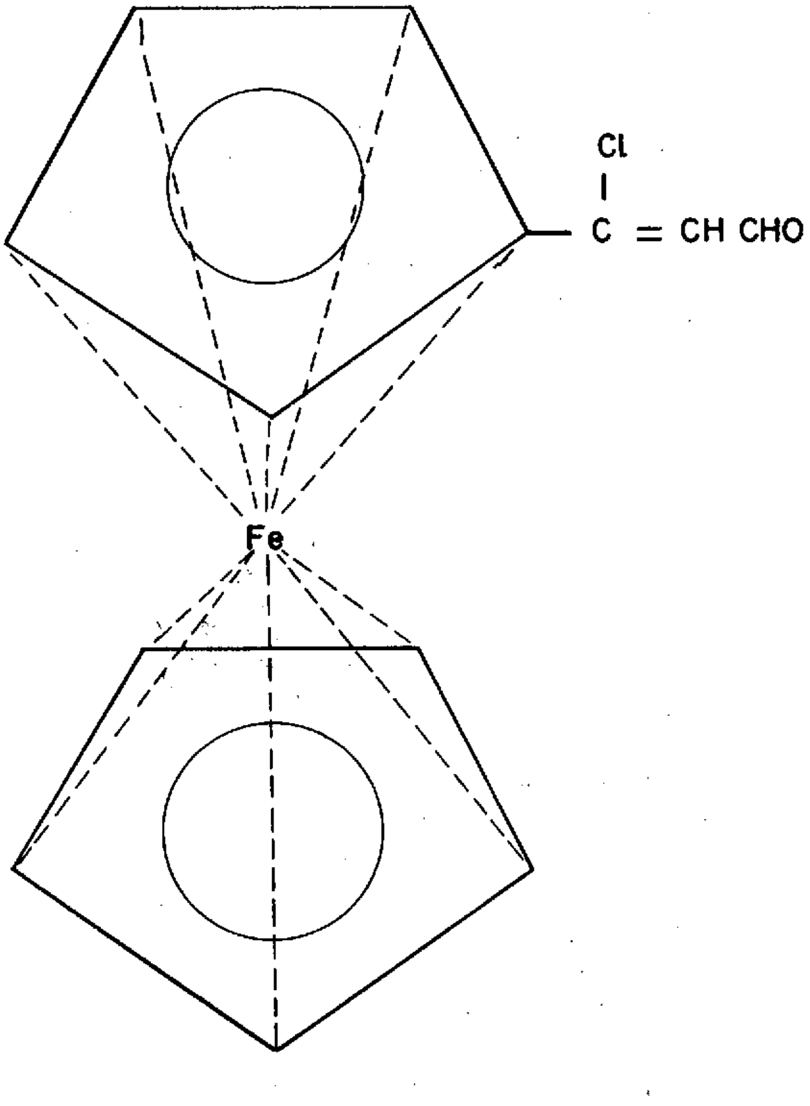


FIGURE 6. STRUCTURE OF 1-CHLORO-2-FORMYLVINYLFERROCENE

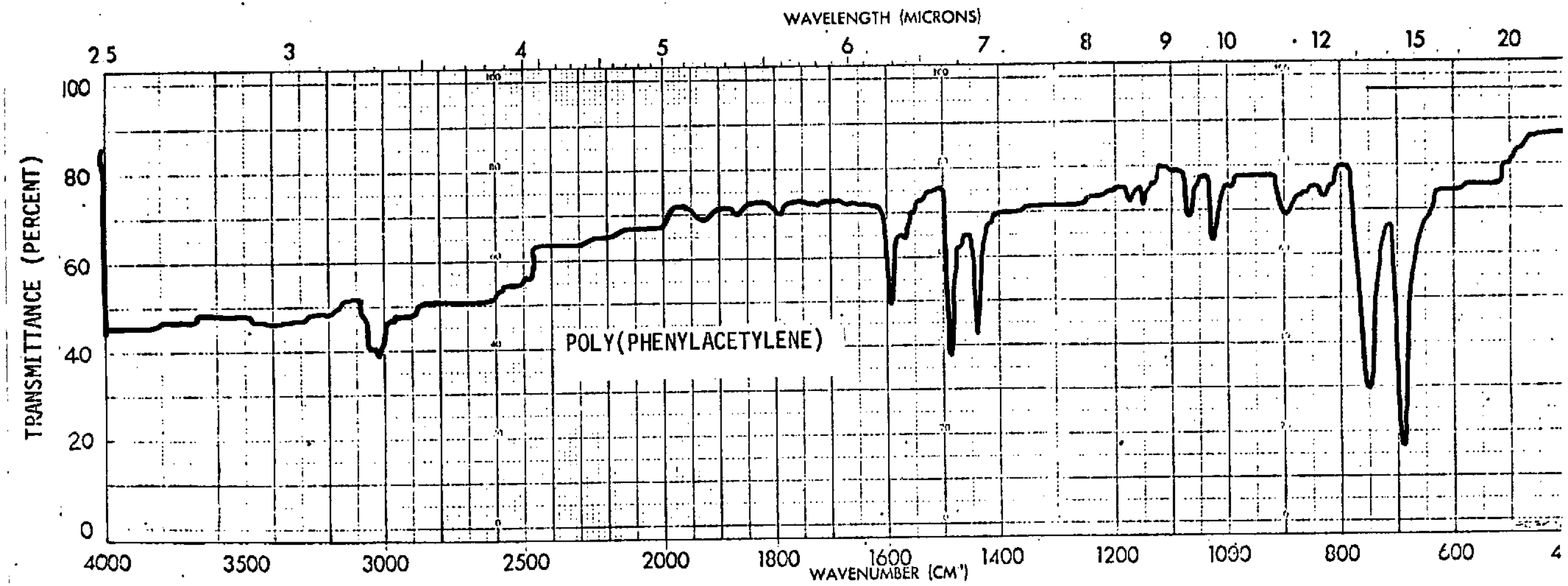


FIGURE 7. INFRARED SPECTRUM OF POLY(PHENYLACETYLENE)

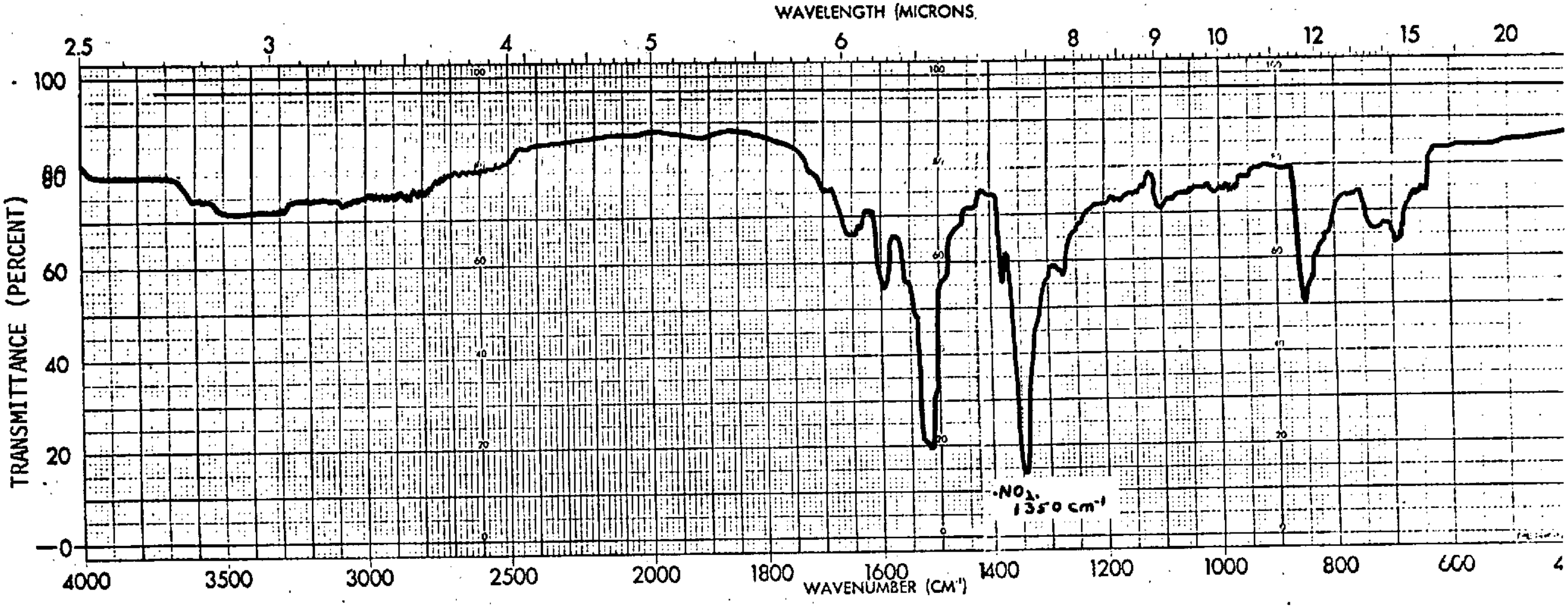


FIGURE 8. INFRARED SPECTRUM OF POLY(NITROPHENYLACETYLENE)

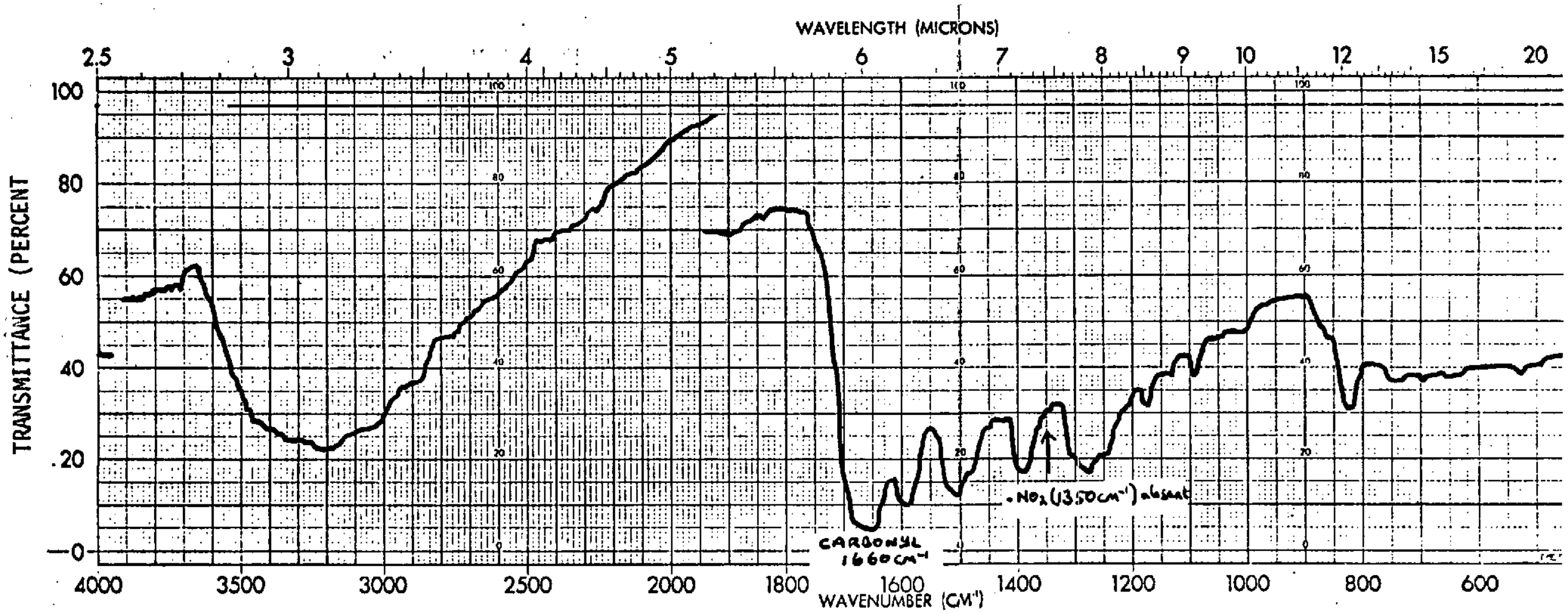


FIGURE 9. INFRARED SPECTRUM OF POLY(NITROPHENYLACETYLENE) (REFERENCE 2)

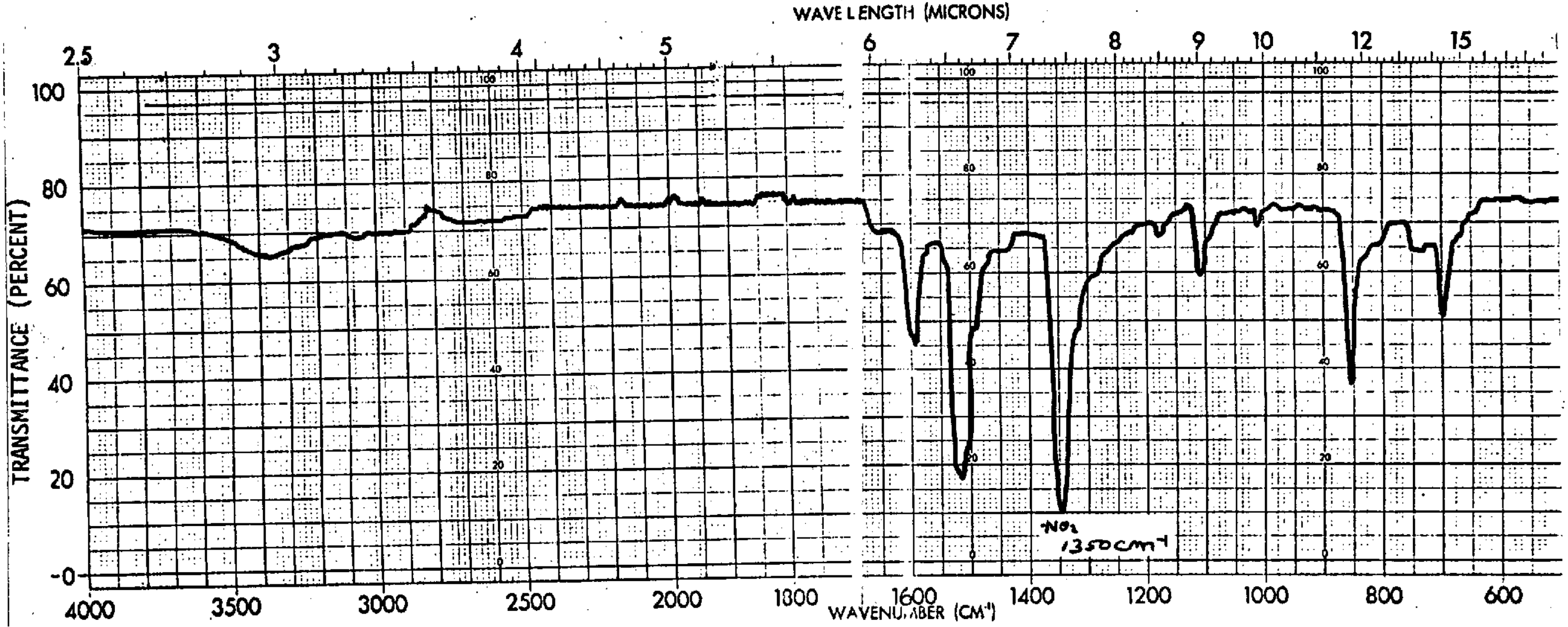


FIGURE 10. INFRARED SPECTRUM OF POLY(FORMAMIDOPHENYLACETYLENE)

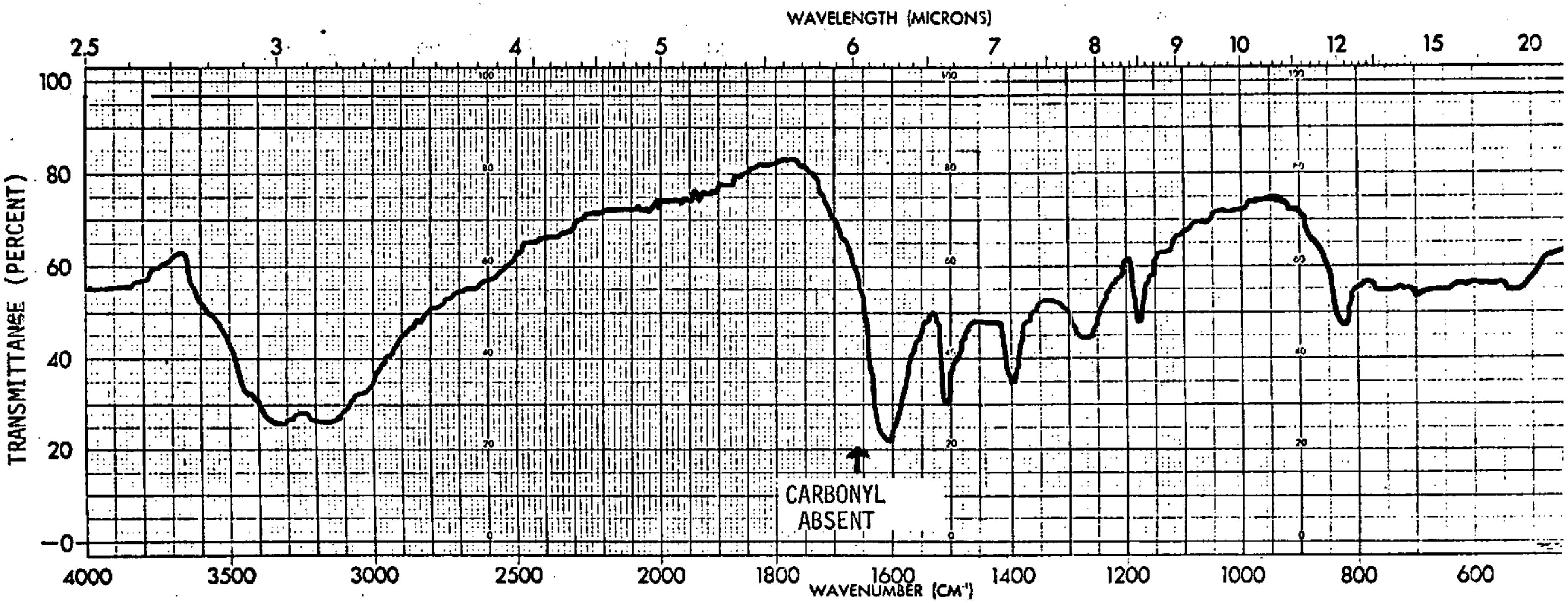


FIGURE 11. INFRARED SPECTRUM OF POLY (AMINOPHENYLACETYLENE)

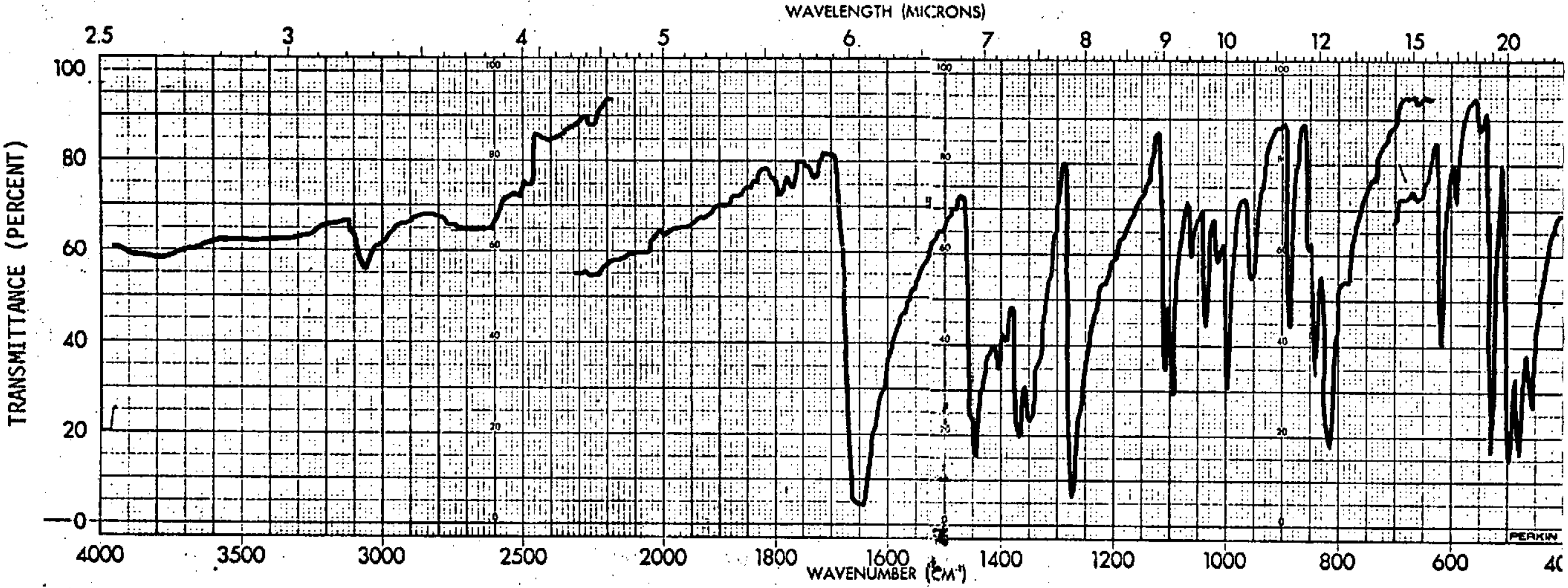


FIGURE 12. INFRARED SPECTRUM OF ACETYL FERROCENE (COMMERCIAL MATERIAL)

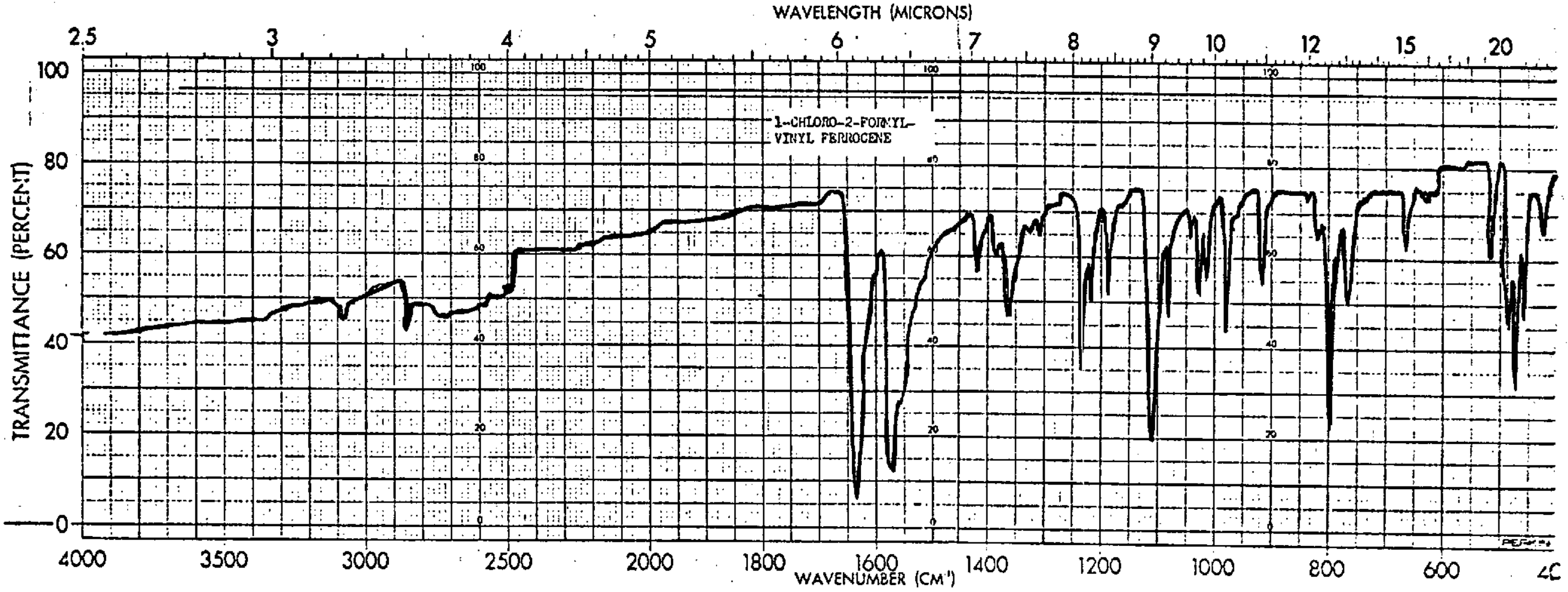


FIGURE 13. INFRARED SPECTRUM OF 1-CHLORO-2-FORMYL-VINYLFERROCENE

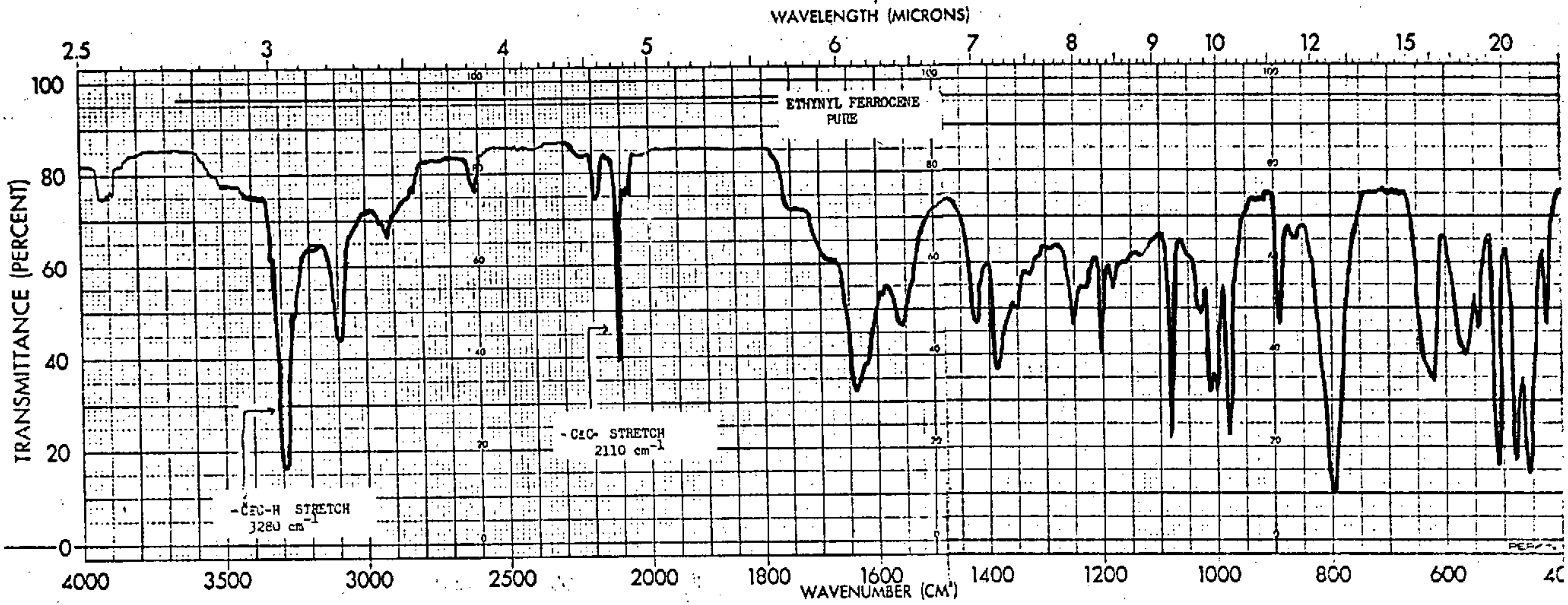


FIGURE 14. INFRARED SPECTRUM OF ETHYNYLFERROCENE

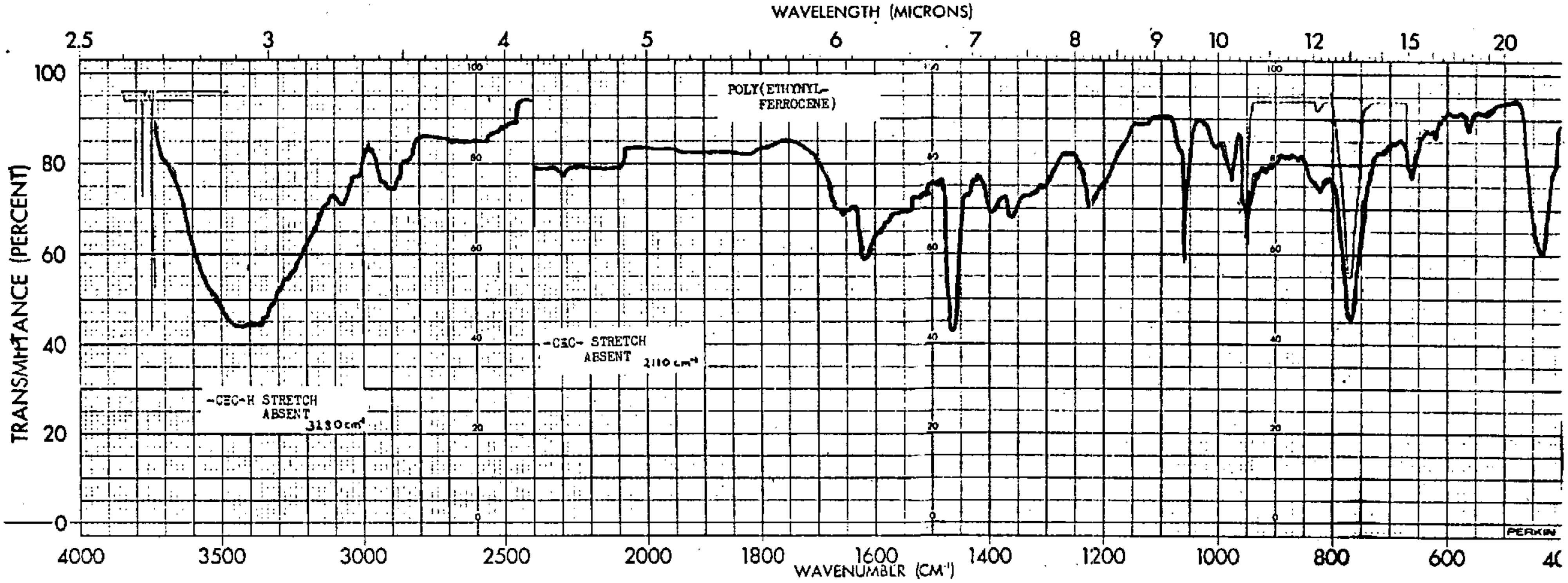


FIGURE 15. INFRARED SPECTRUM OF POLY(ETHYNYLFERROCENE)

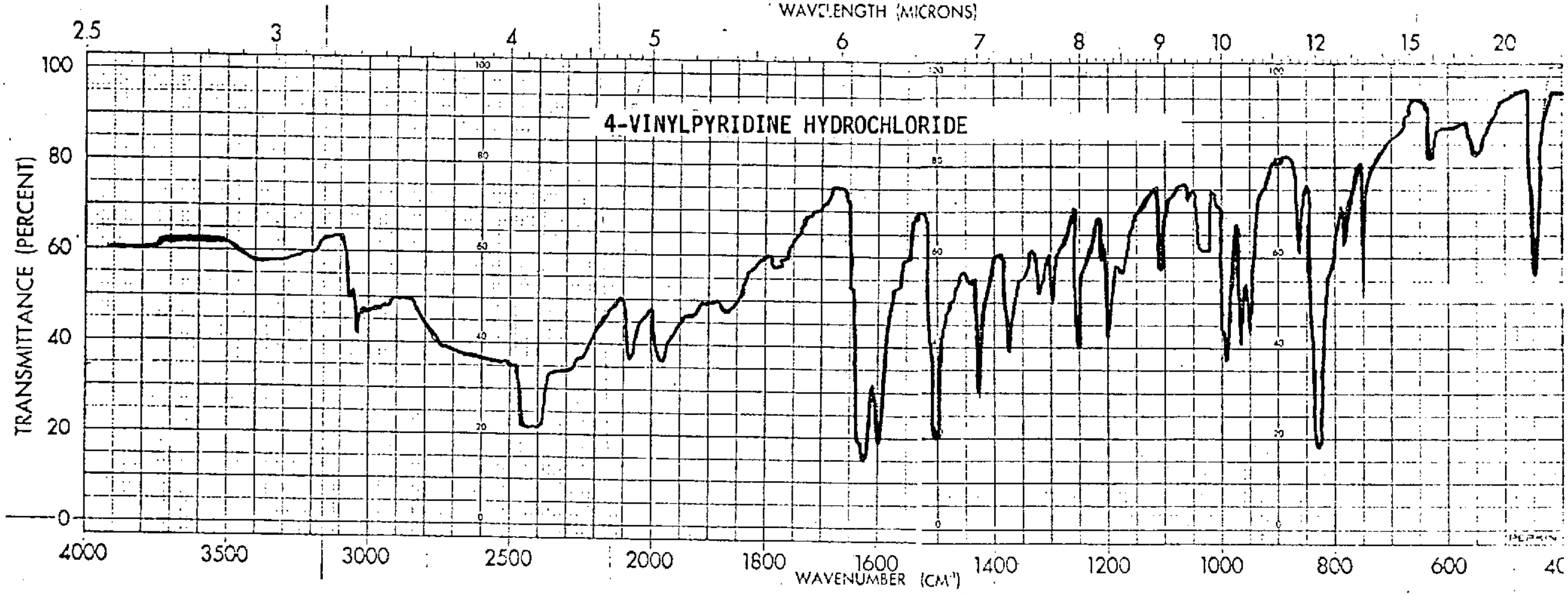


FIGURE 16. INFRARED SPECTRUM OF 4-VINYLPYRIDINE HYDROCHLORIDE

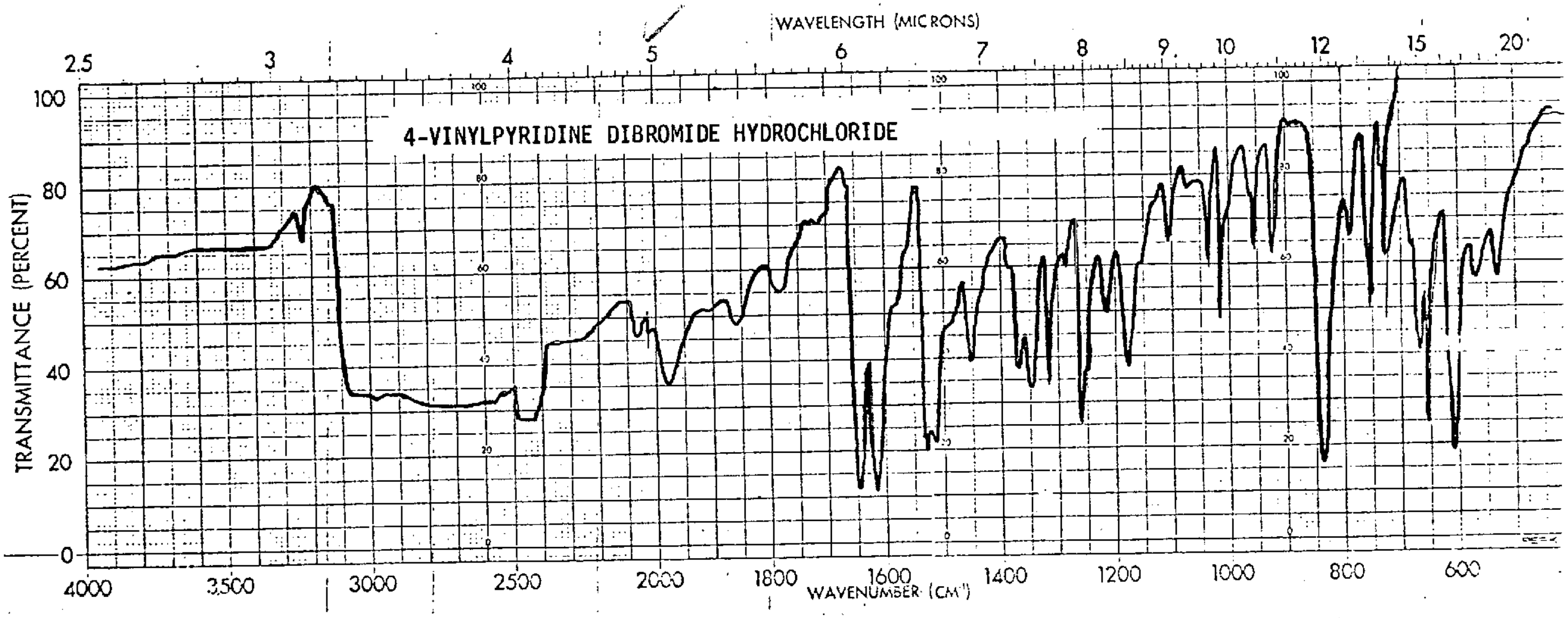


FIGURE 17. INFRARED SPECTRUM OF 4-VINYLPYRIDINE DIBROMIDE HYDROCHLORIDE

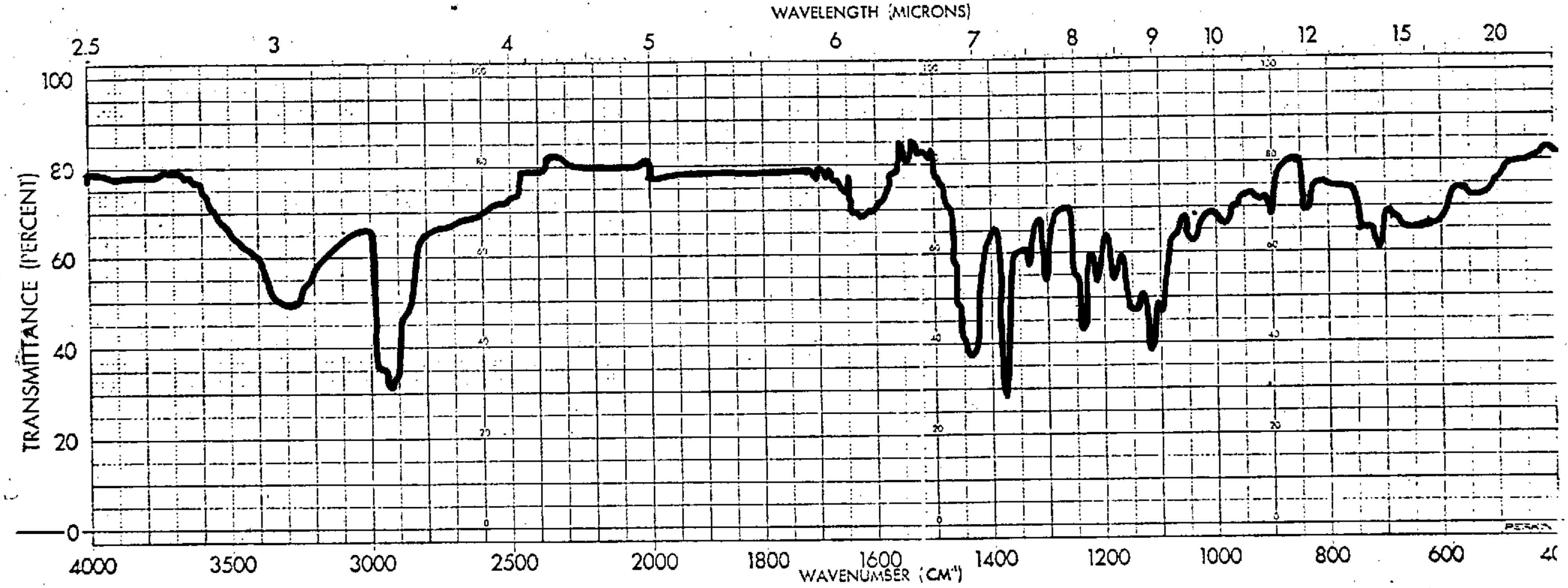


FIGURE 18. INFRARED SPECTRUM OF 4-ETHYNYLPYRIDINE

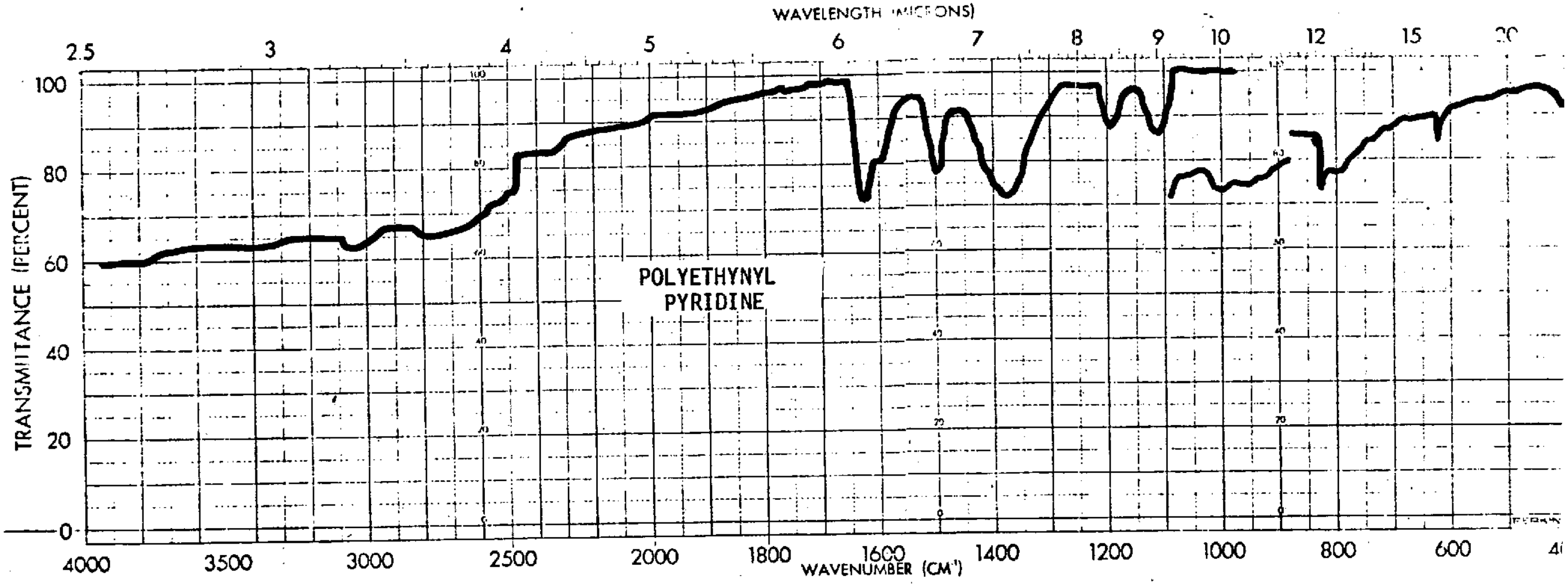


FIGURE 19. INFRARED SPECTRUM OF POLYETHYNYL PYRIDINE

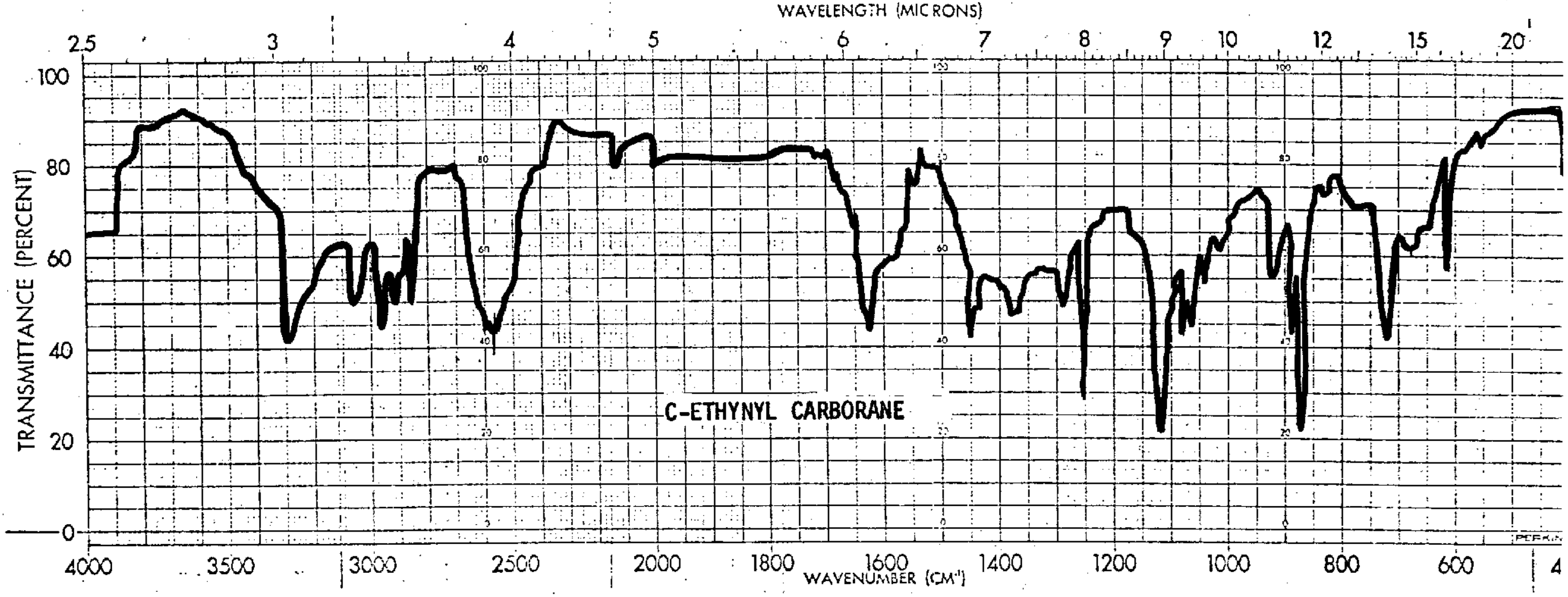


FIGURE 20. INFRARED SPECTRUM OF C-ETHYNYLCARBORANE

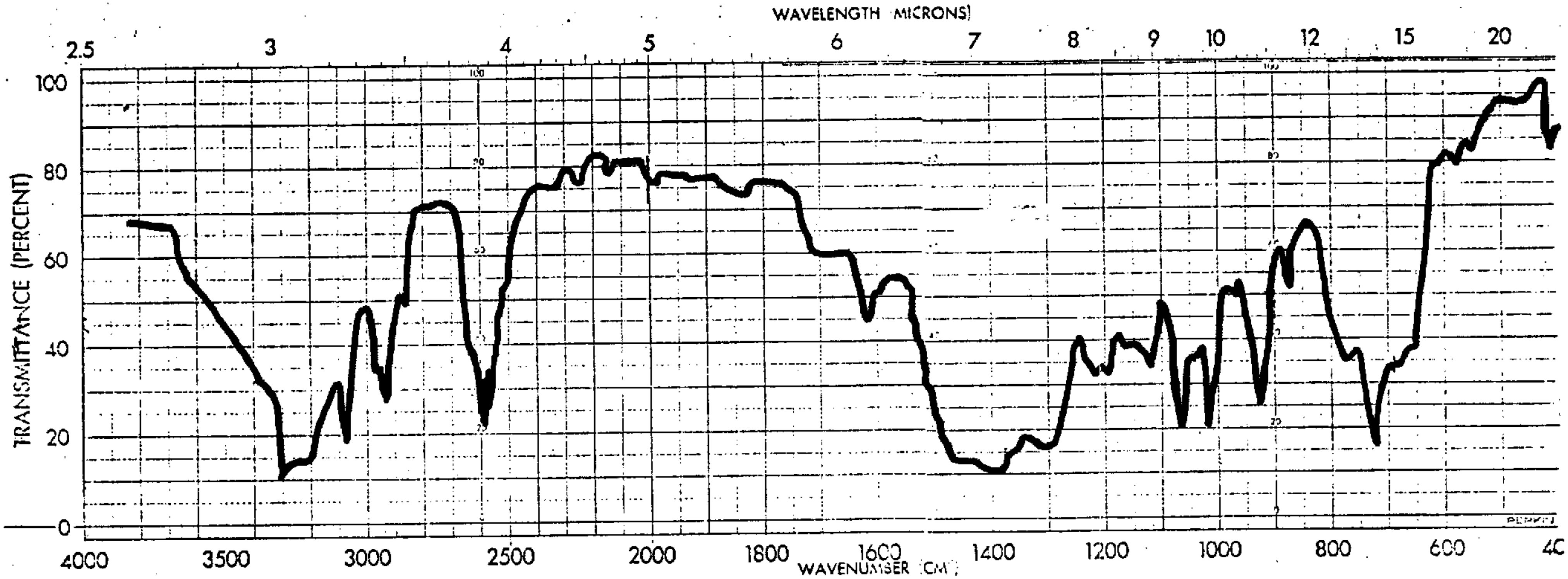


FIGURE 21. INFRARED SPECTRUM OF POLYETHYNYL CARBORANE

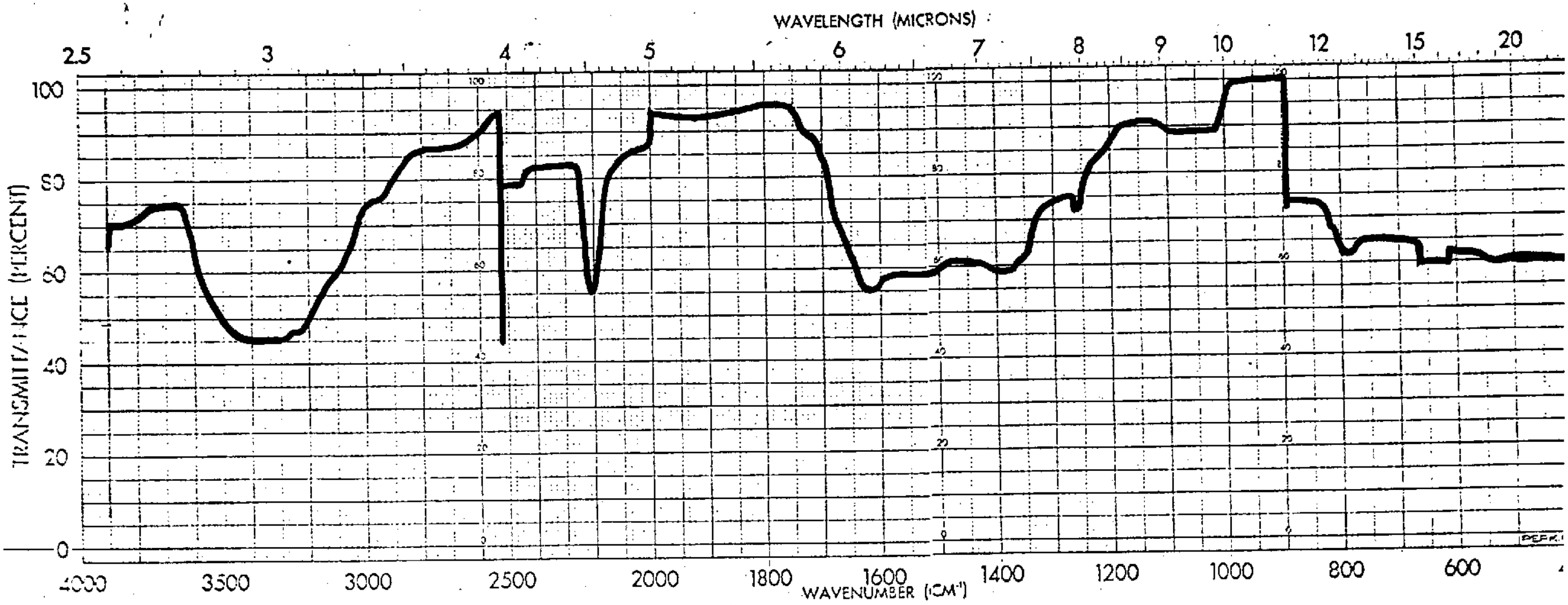


FIGURE 22. INFRARED SPECTRUM OF POLY(DICYANOACETYLENE)

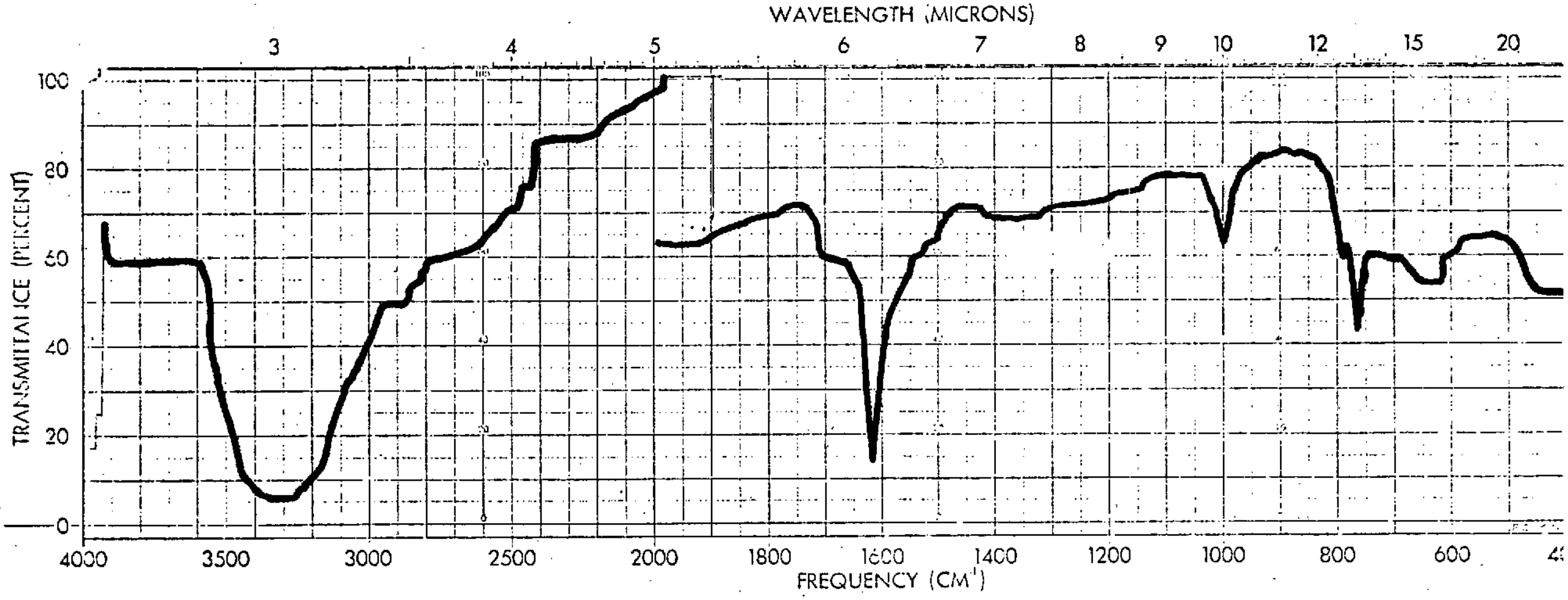


FIGURE 23. INFRARED SPECTRUM OF BROMINATED NICKELOCENE

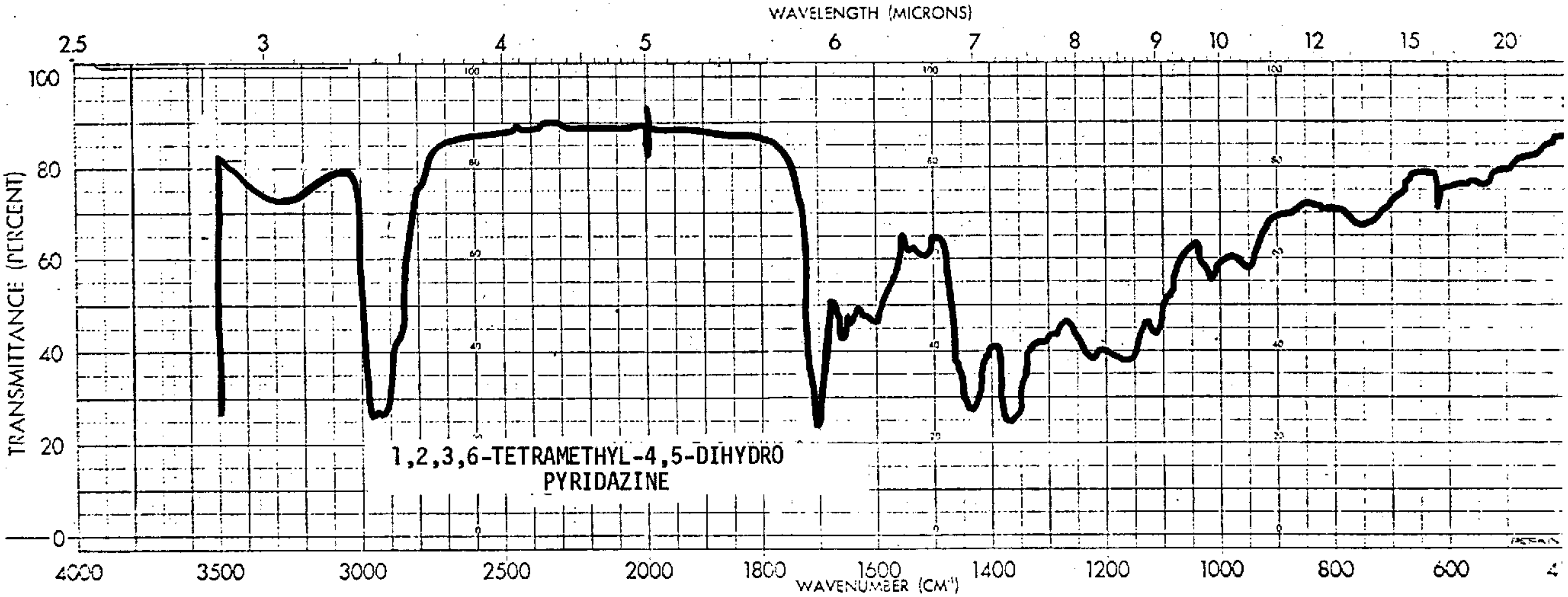


FIGURE 24. INFRARED SPECTRUM OF 1, 2, 3, 6-TETRAMETHYLPYRIDAZINE

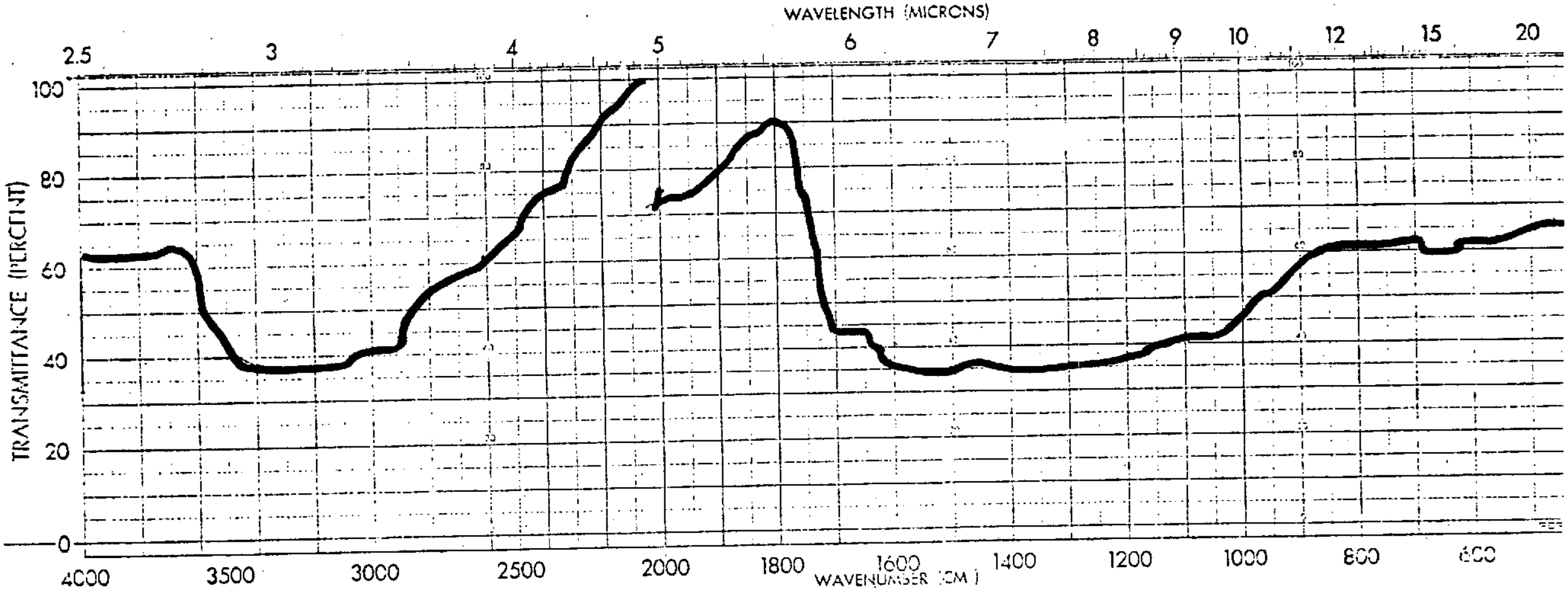


FIGURE 25. INFRARED SPECTRUM OF POLYETHYLIDENE TETRAMETHYL PYRIDAZINE

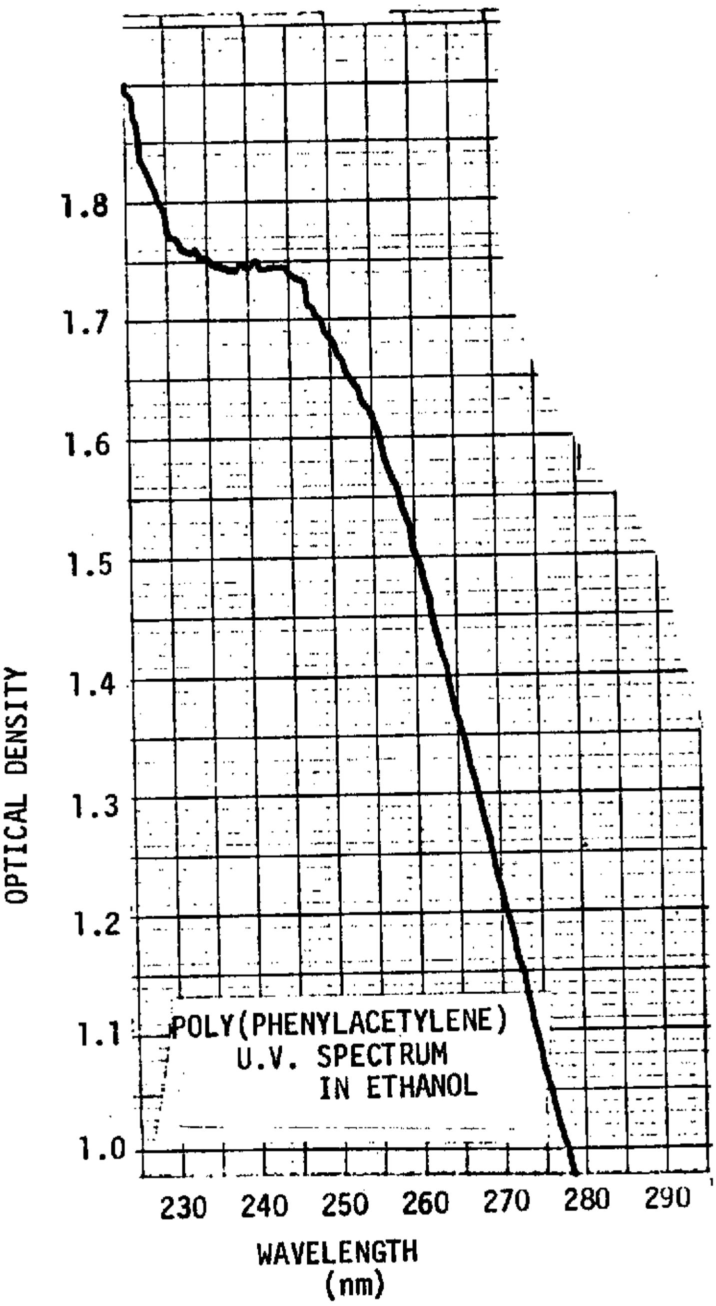


FIGURE 26. ULTRA VIOLET ABSORPTION SPECTRUM OF POLY(PHENYLACETYLENE)

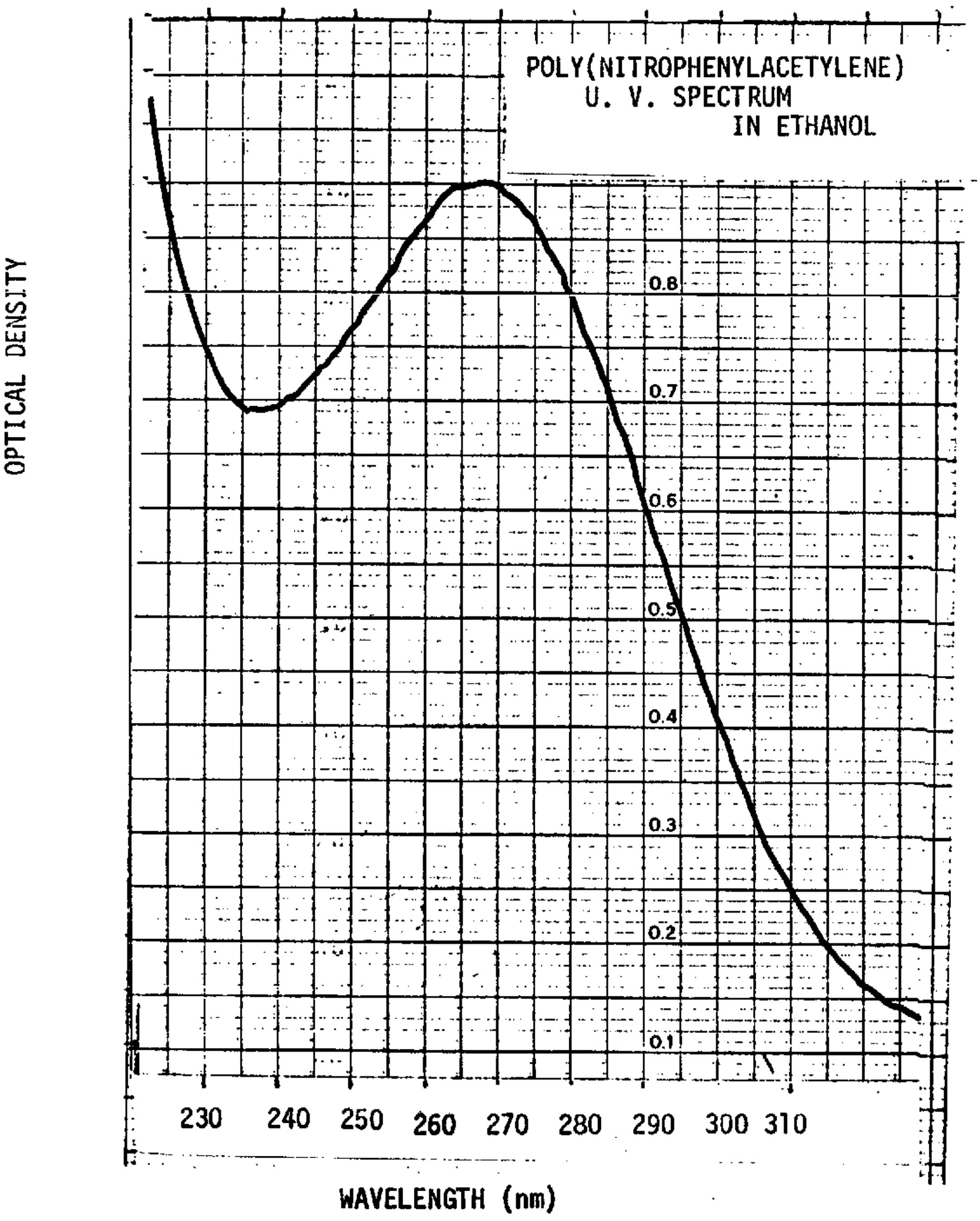


FIGURE 27. ULTRAVIOLET ABSORPTION SPECTRUM OF POLY(NITROPHENYLACETYLENE)

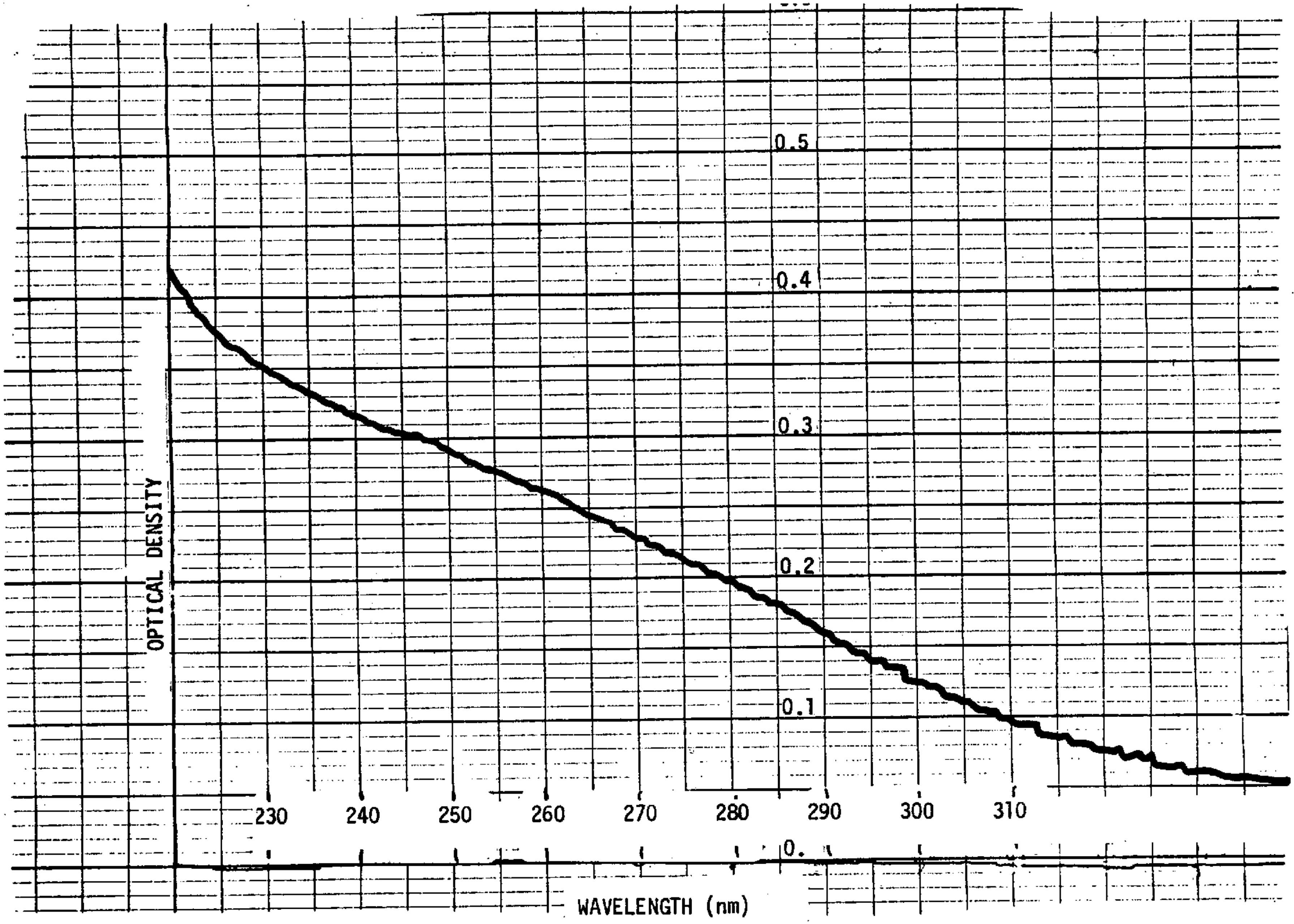


FIGURE 28. ULTRA VIOLET ABSORPTION SPECTRUM OF POLY(FORMAMIDOPHENYLACETYLENE)

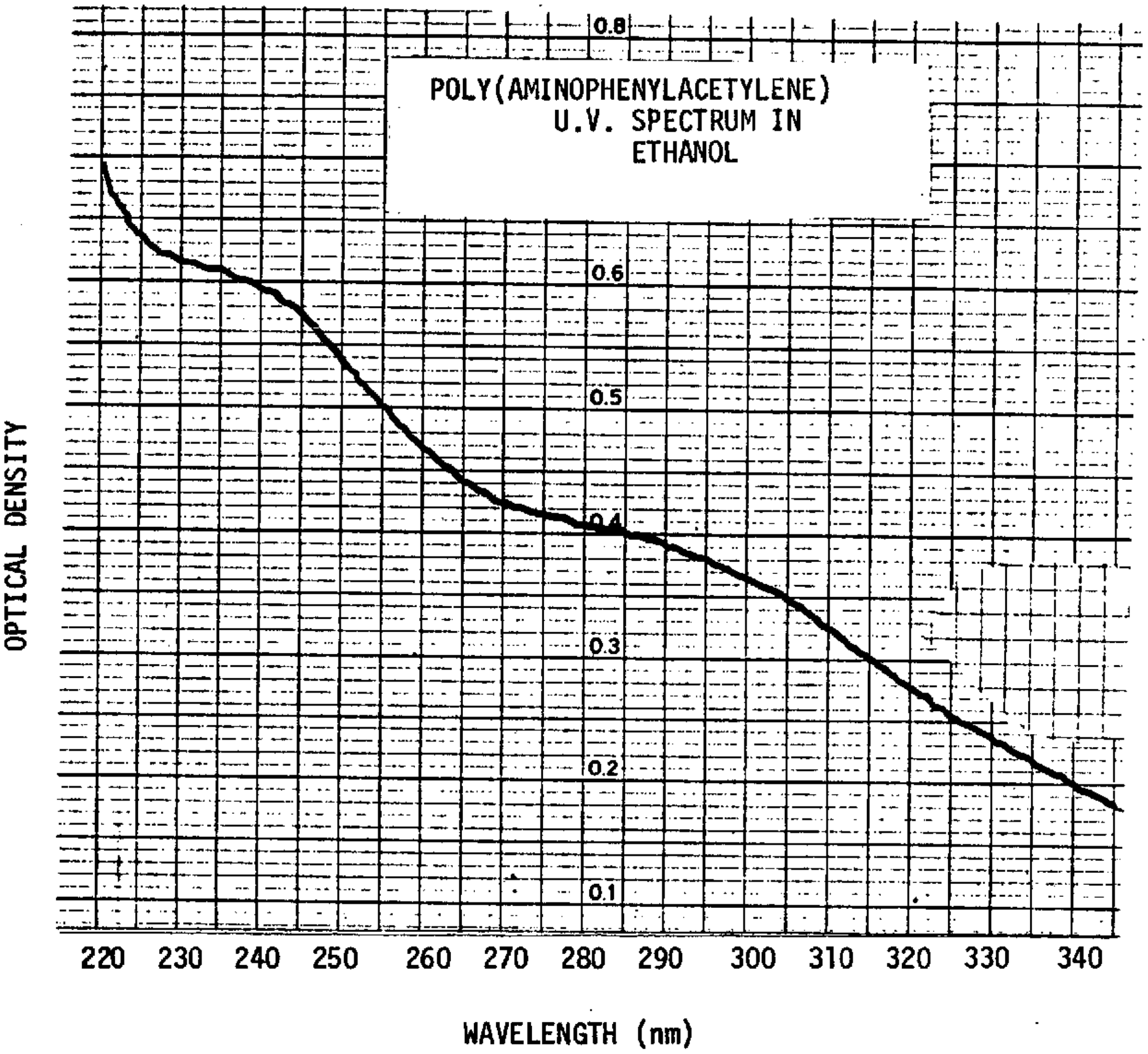


FIGURE 29. ULTRA VIOLET ABSORPTION SPECTRUM OF POLY(AMINOPHENYLACETYLENE)

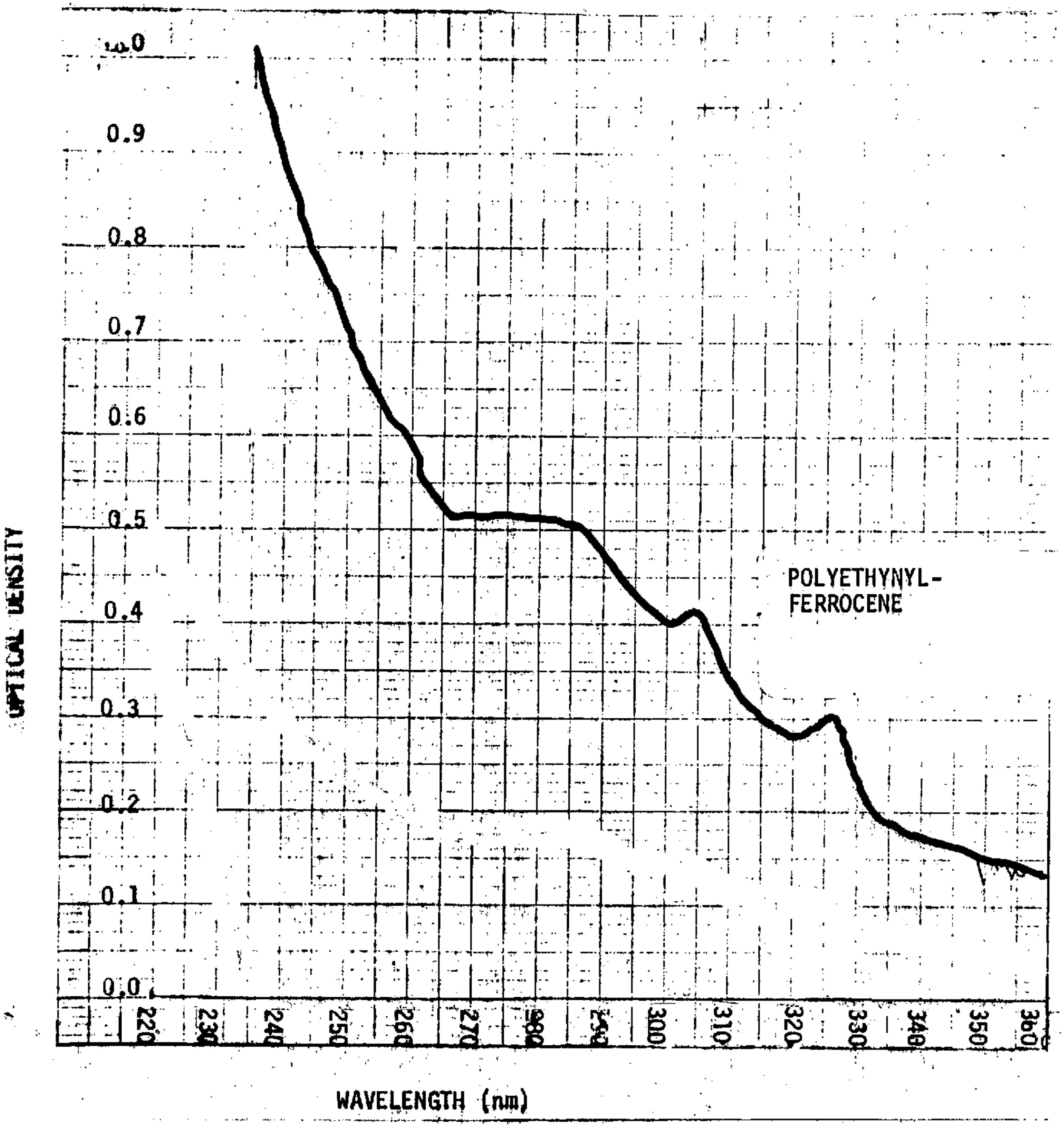


FIGURE 30. U.V. SPECTRUM OF POLYETHYNYLFERROCENE

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OF POOR QUALITY

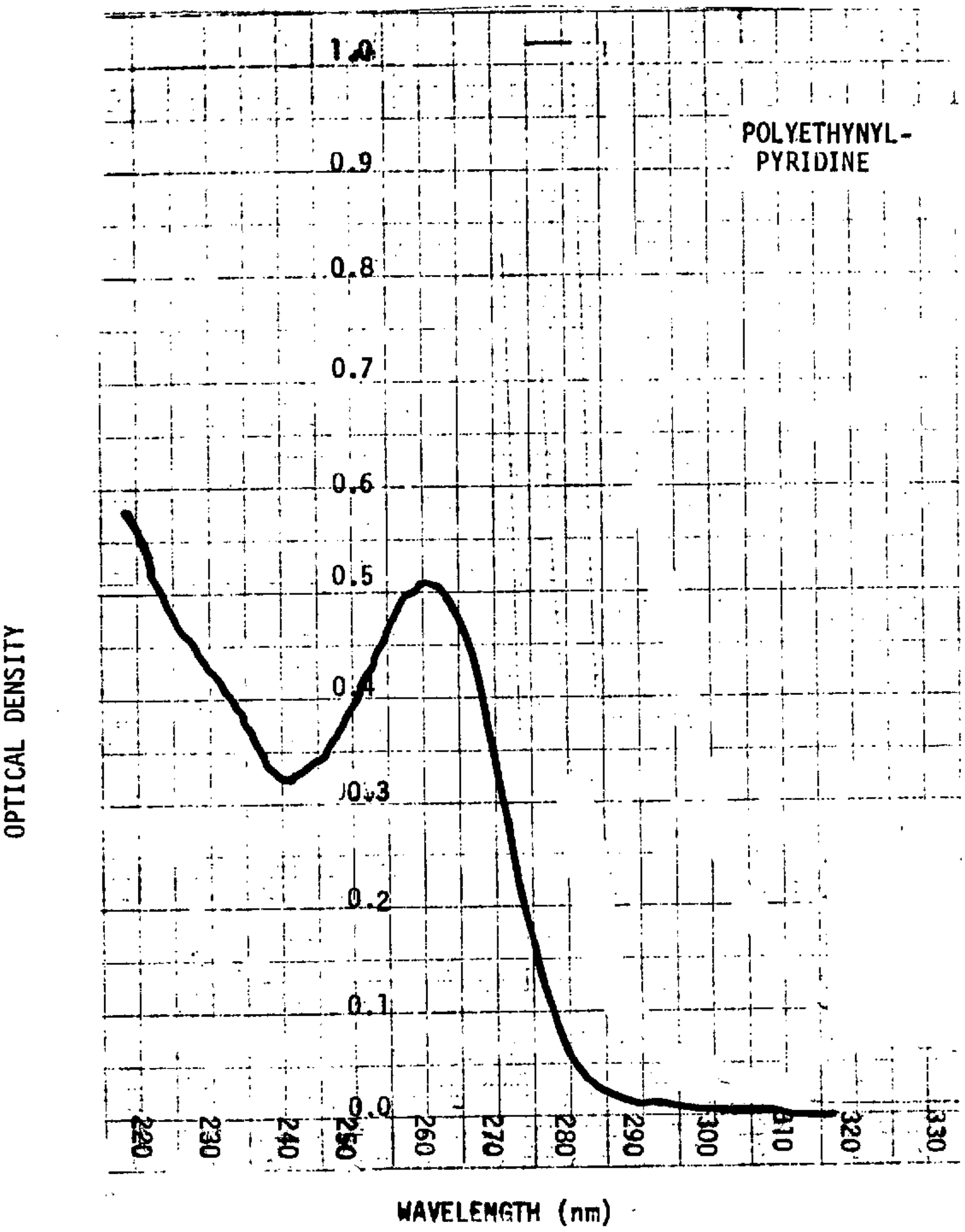

FIGURE 31. U.V. SPECTRUM OF POLYETHYNYL PYRIDINE

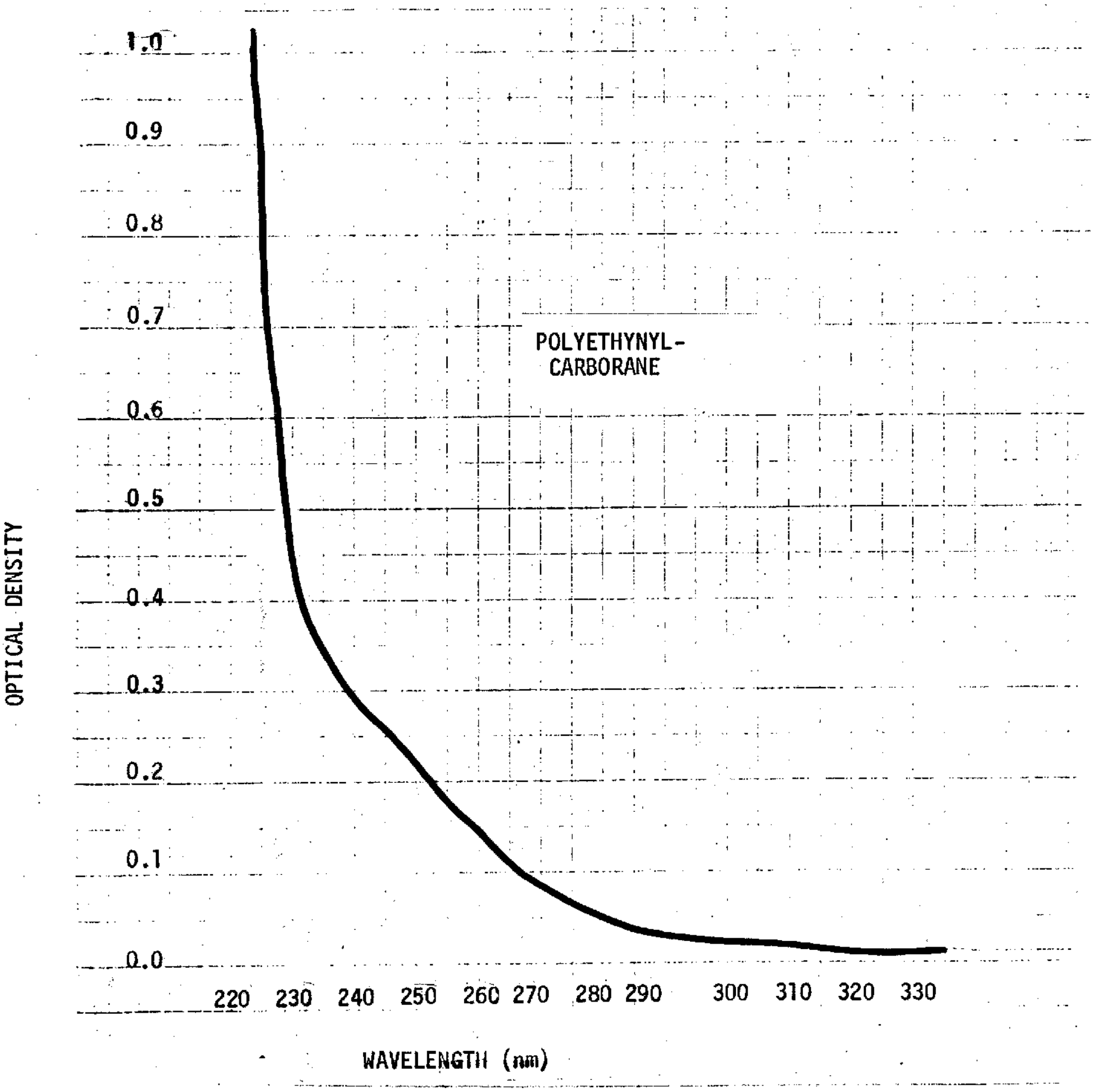

FIGURE 32. U.V. SPECTRUM OF POLYETHYNYLCARBORANE

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C - 2

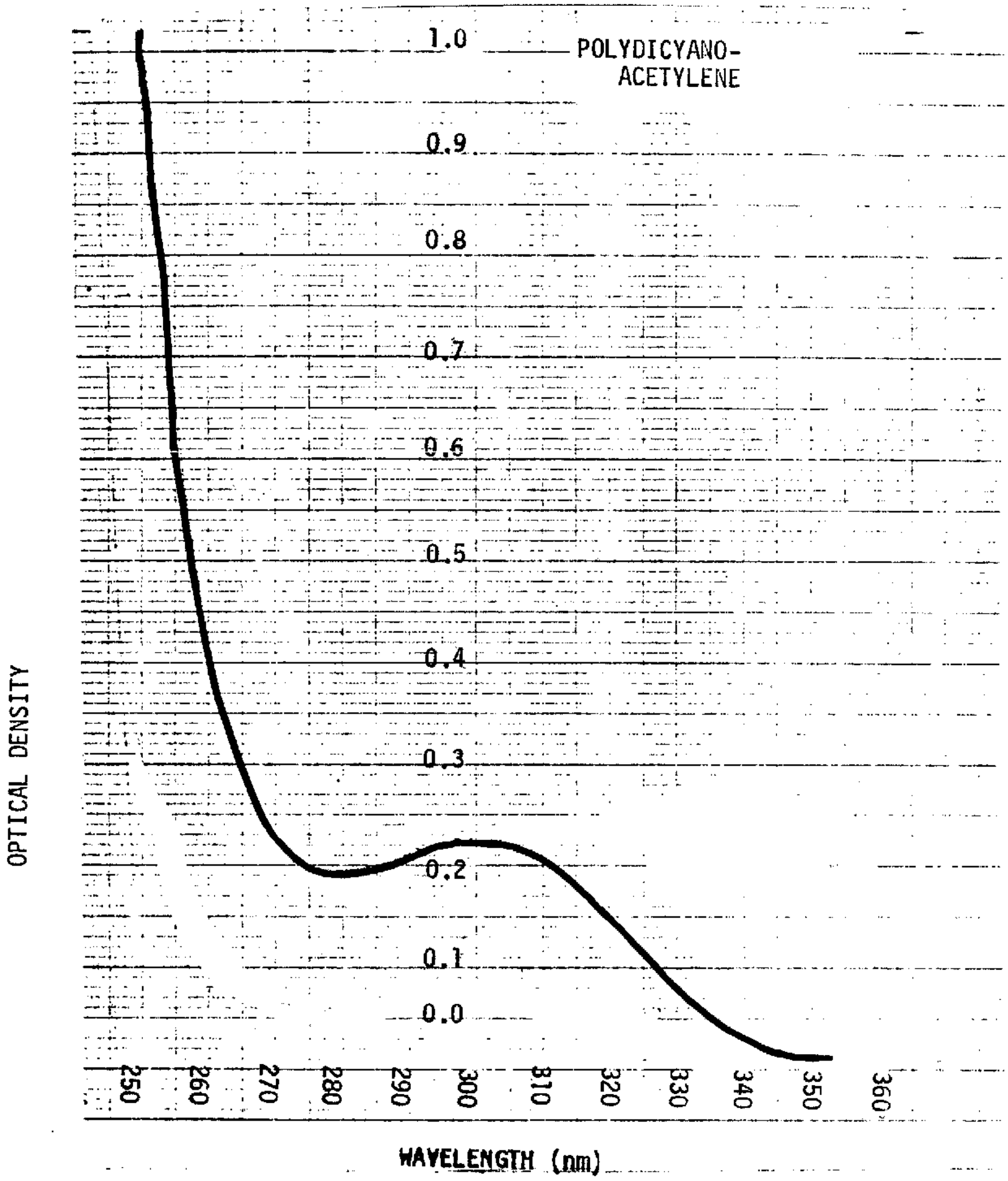


FIGURE 33. U.V. SPECTRUM OF POLYDICYANOACETYLENE

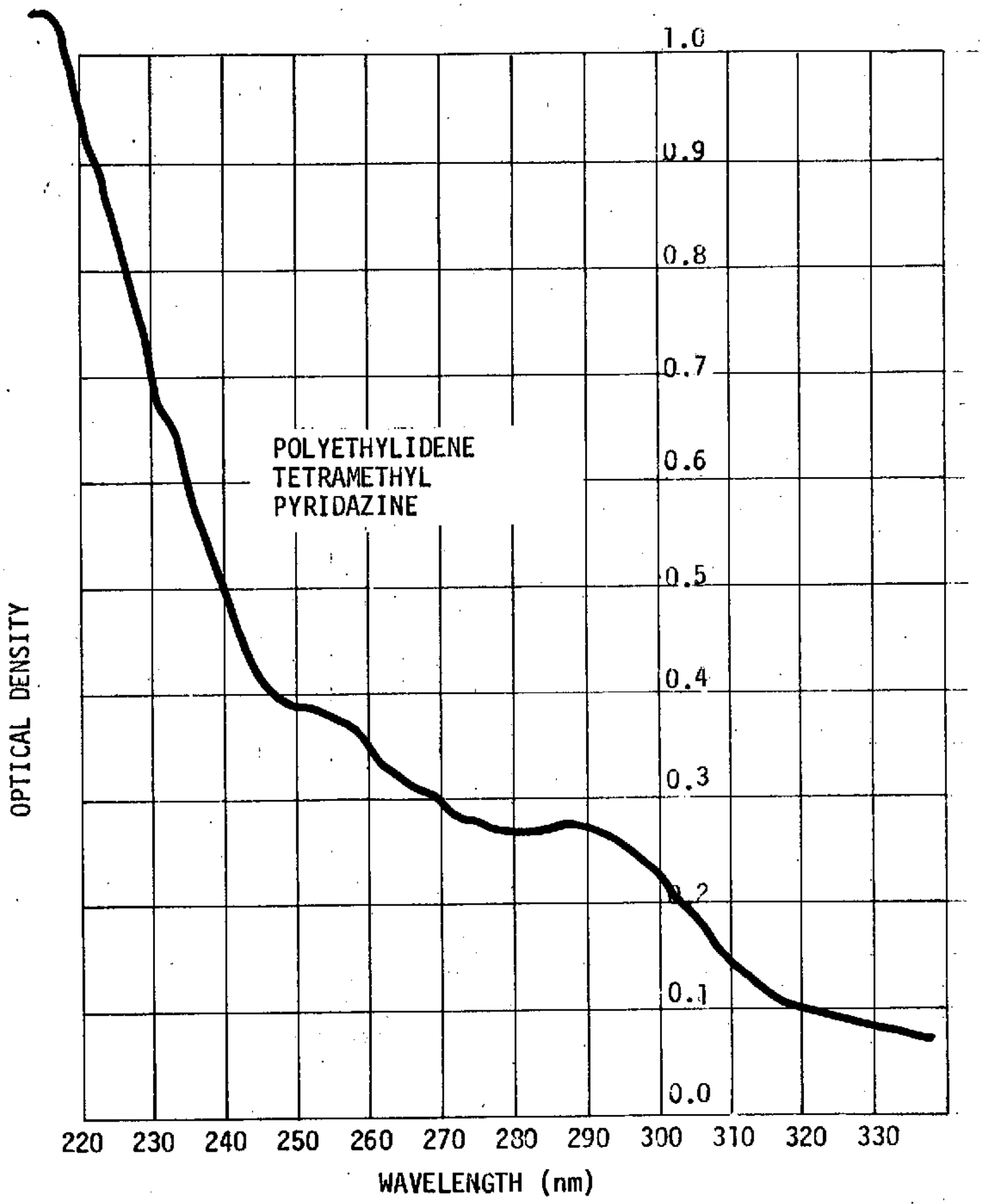
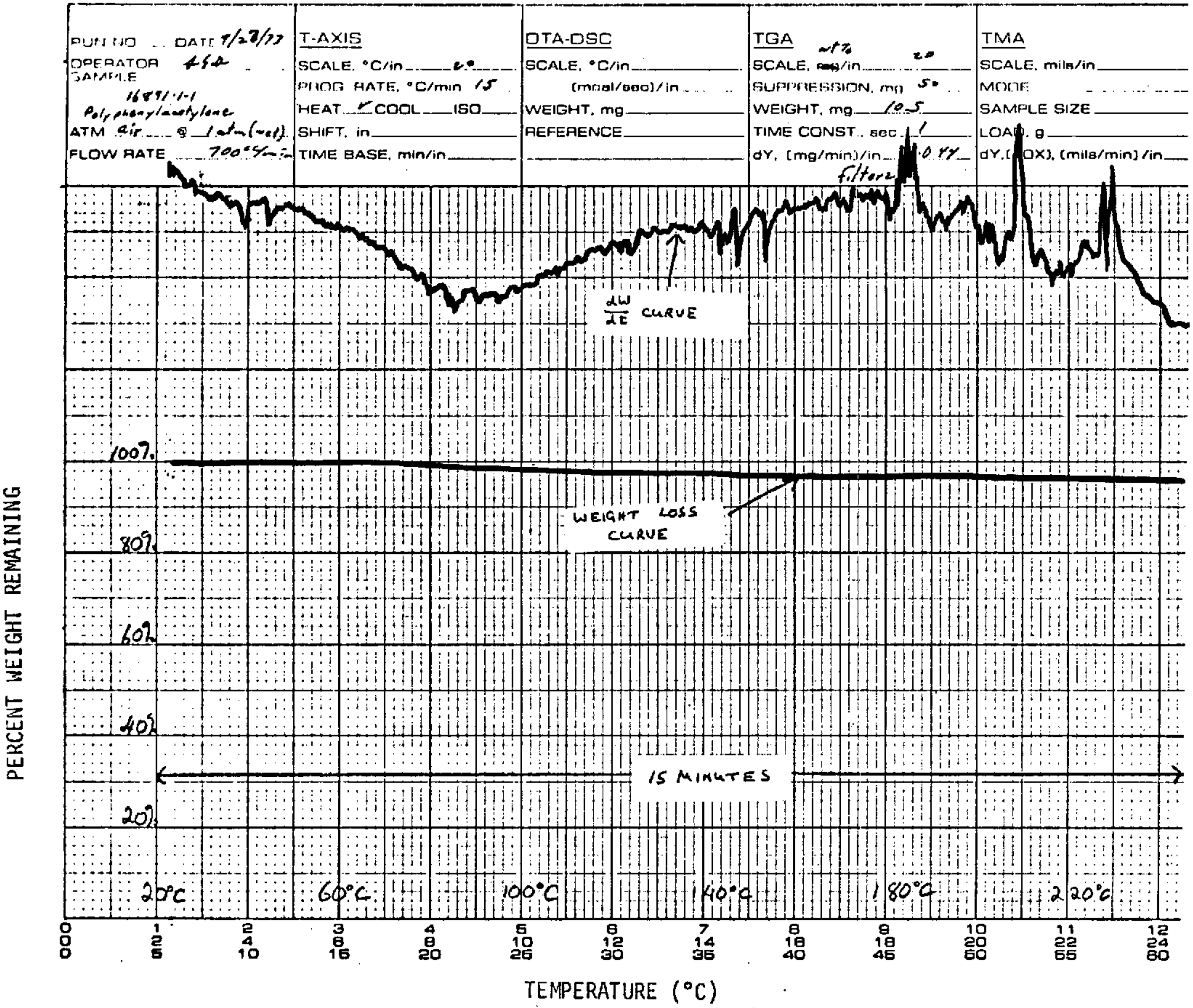


FIGURE 34. U. V. SPECTRUM OF POLYETHYLIDENE TETRAMETHYL PYRIDAZINE



RUN NO ___ DATE 9/28/77
OPERATOR ASA
SAMPLE 1689/-1-1 Polyphenylacetylene
ATM air @ 1 atm (wet)
FLOW RATE 700 cc/min

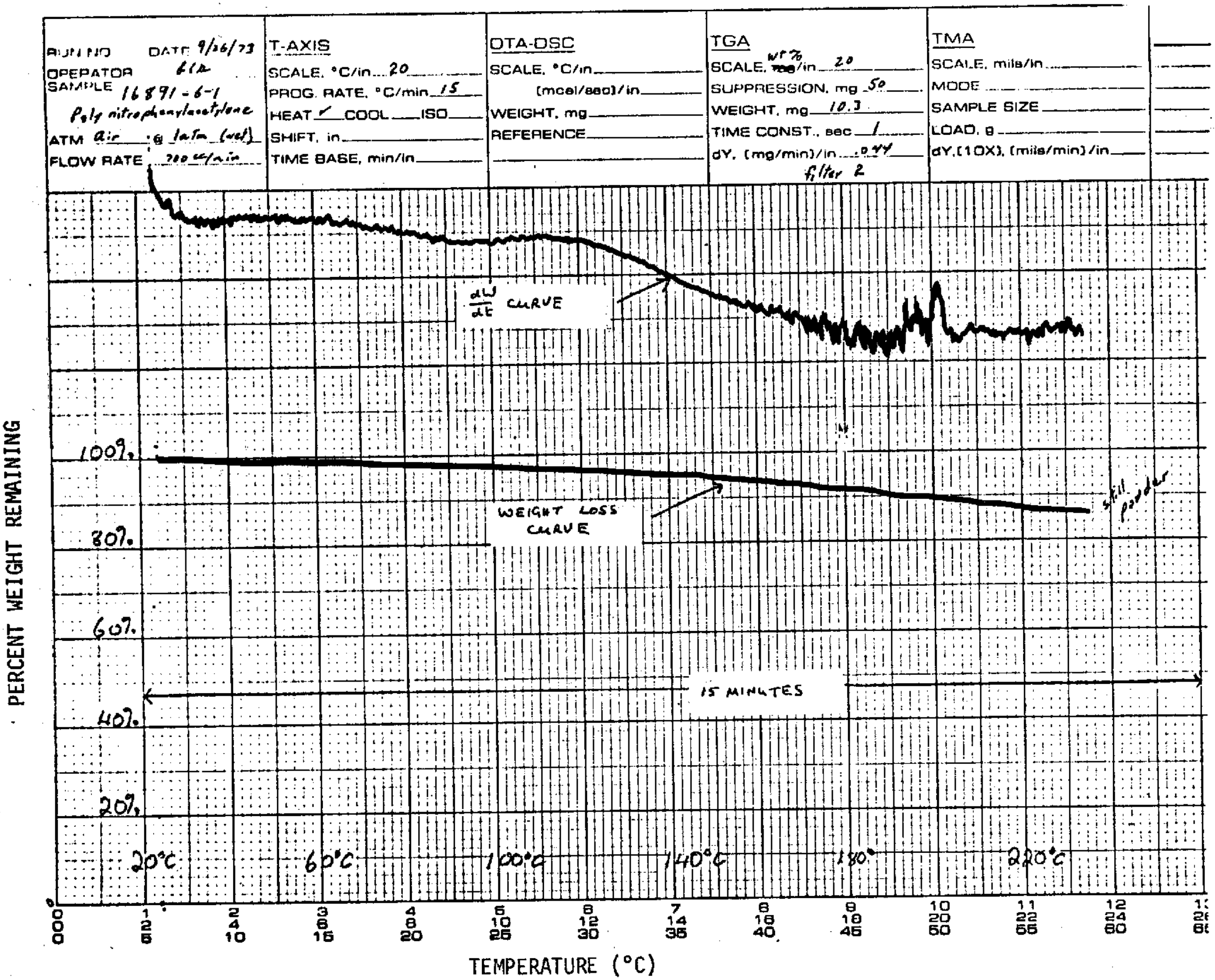
T-AXIS
SCALE, °C/in 20
PROG RATE, °C/min 15
HEAT ✓ COOL ___ ISO ___
SHIFT, in ___
TIME BASE, min/in ___

DTA-DSC
SCALE, °C/in ___
(mcal/sec)/in ___
WEIGHT, mg ___
REFERENCE ___

TGA
SCALE, ~~mg~~ wt%/in 20
SUPPRESSION, mg 50
WEIGHT, mg 10.5
TIME CONST., sec 1
dY, (mg/min)/in 0.44

TMA
SCALE, mils/in ___
MODE ___
SAMPLE SIZE ___
LOAD, g ___
dY, (ΔX), (mils/min)/in ___

FIGURE 35. THERMOGRAVIMETRIC ANALYSIS OF POLY(PHENYLACETYLENE)


RUN NO DATE 9/26/73
OPERATOR GIA
SAMPLE 16891-6-1
Poly nitrophenylacetylene
ATM air @ 1atm (wet)
FLOW RATE 200 cc/min

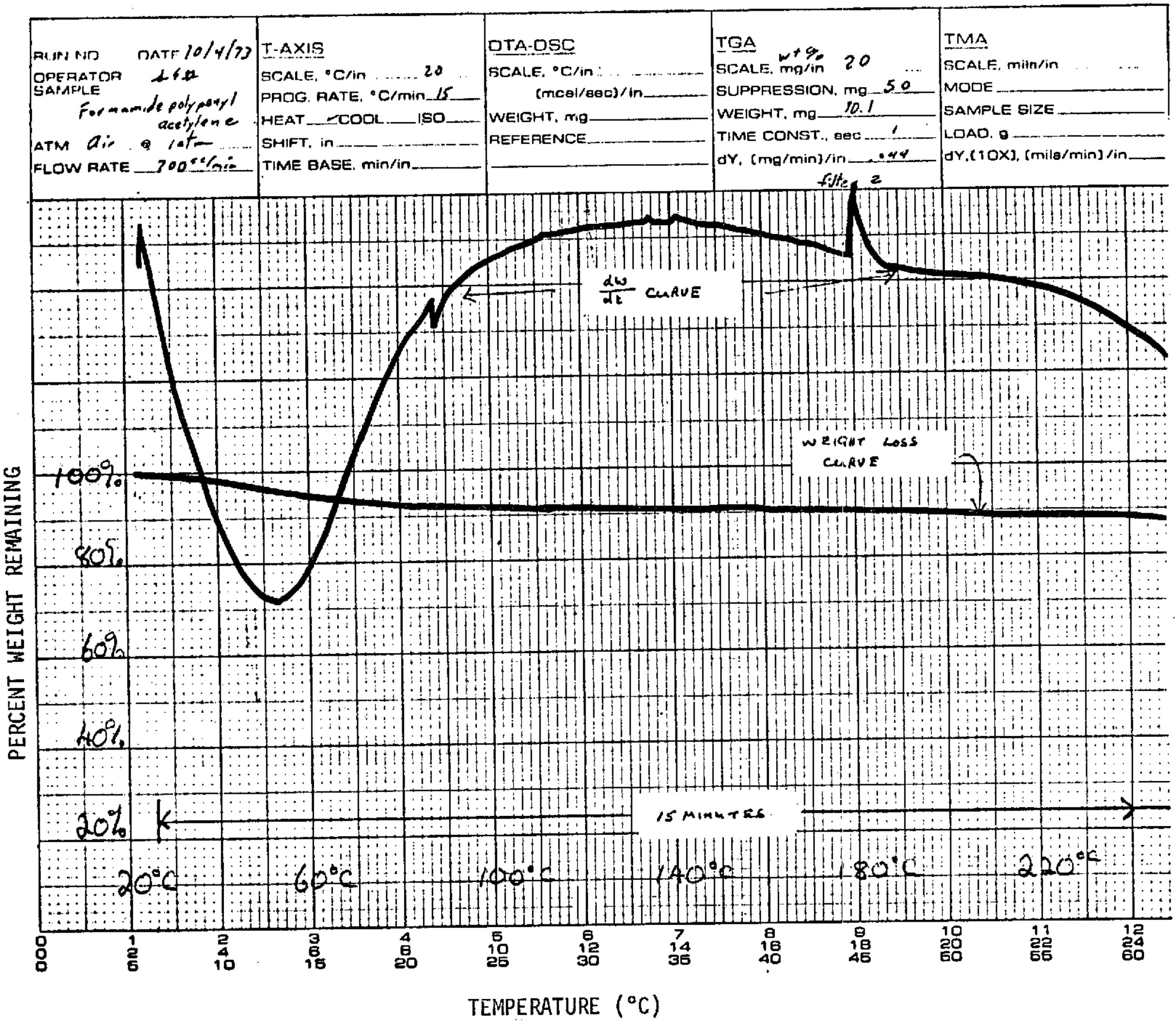
T-AXIS
SCALE, °C/in 20
PROG. RATE, °C/min 15
HEAT ✓ COOL ISO
SHIFT, in
TIME BASE, min/in

DTA-DSC
SCALE, °C/in
(mcal/sec)/in
WEIGHT, mg
REFERENCE

TGA
SCALE, ~~mg~~ wt %/in 20
SUPPRESSION, mg 50
WEIGHT, mg 10.3
TIME CONST., sec 1
dY, (mg/min)/in 0.44
filter 2

TMA
SCALE, mils/in
MODE
SAMPLE SIZE
LOAD, g
dY,(10X), (mils/min)/in

FIGURE 36. THERMOGRAVIMETRIC ANALYSIS OF POLY(NITROPHENYLACETYLENE)



RUN NO DATE 10/4/73
OPERATOR L.F.B.
SAMPLE Formamide polyphenyl acetylene
ATM air @ 1 atm
FLOW RATE 700 cc/min

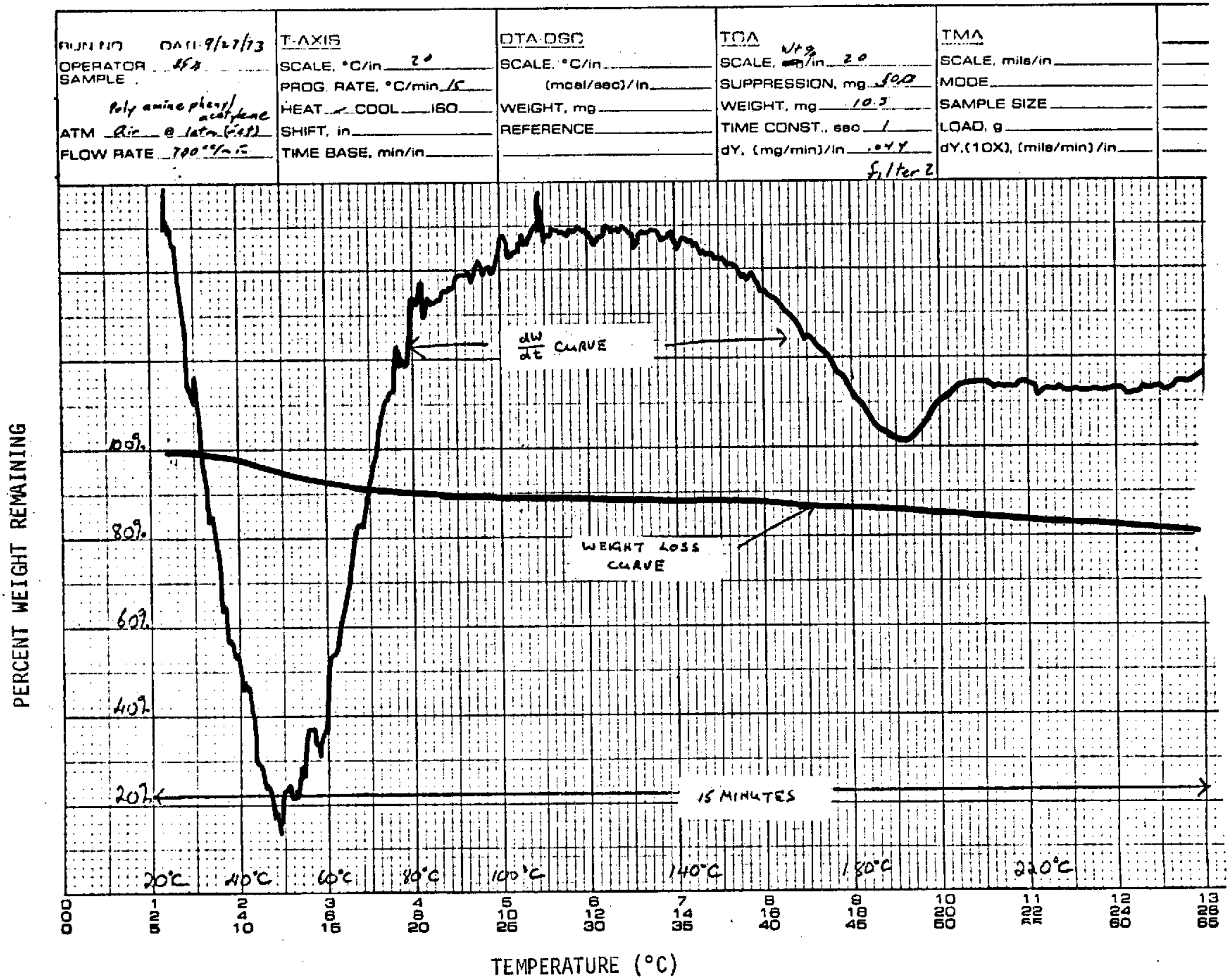
T-AXIS
SCALE, °C/in 20
PROG. RATE, °C/min 15
HEAT ✓ COOL ___ ISO ___
SHIFT, in ___
TIME BASE, min/in ___

DTA-DSC
SCALE, °C/in ___
(mcal/sec)/in ___
WEIGHT, mg ___
REFERENCE ___

TGA
SCALE, ~~mg/in~~ wt % 20
SUPPRESSION, mg 50
WEIGHT, mg 10.1
TIME CONST., sec 1
dY, (mg/min)/in .44
filter 2

TMA
SCALE, mils/in ___
MODE ___
SAMPLE SIZE ___
LOAD, g ___
dY,(10X), (mils/min)/in ___

FIGURE 37. THERMOGRAVIMETRIC ANALYSIS OF POLY(FORMAMIDOPHENYLACETYLENE)



RUN NO DATE 9/27/73
OPERATOR [illegible]
SAMPLE Poly amine phenyl acetylene
ATM Air @ latm (?)
FLOW RATE 100 cc/min

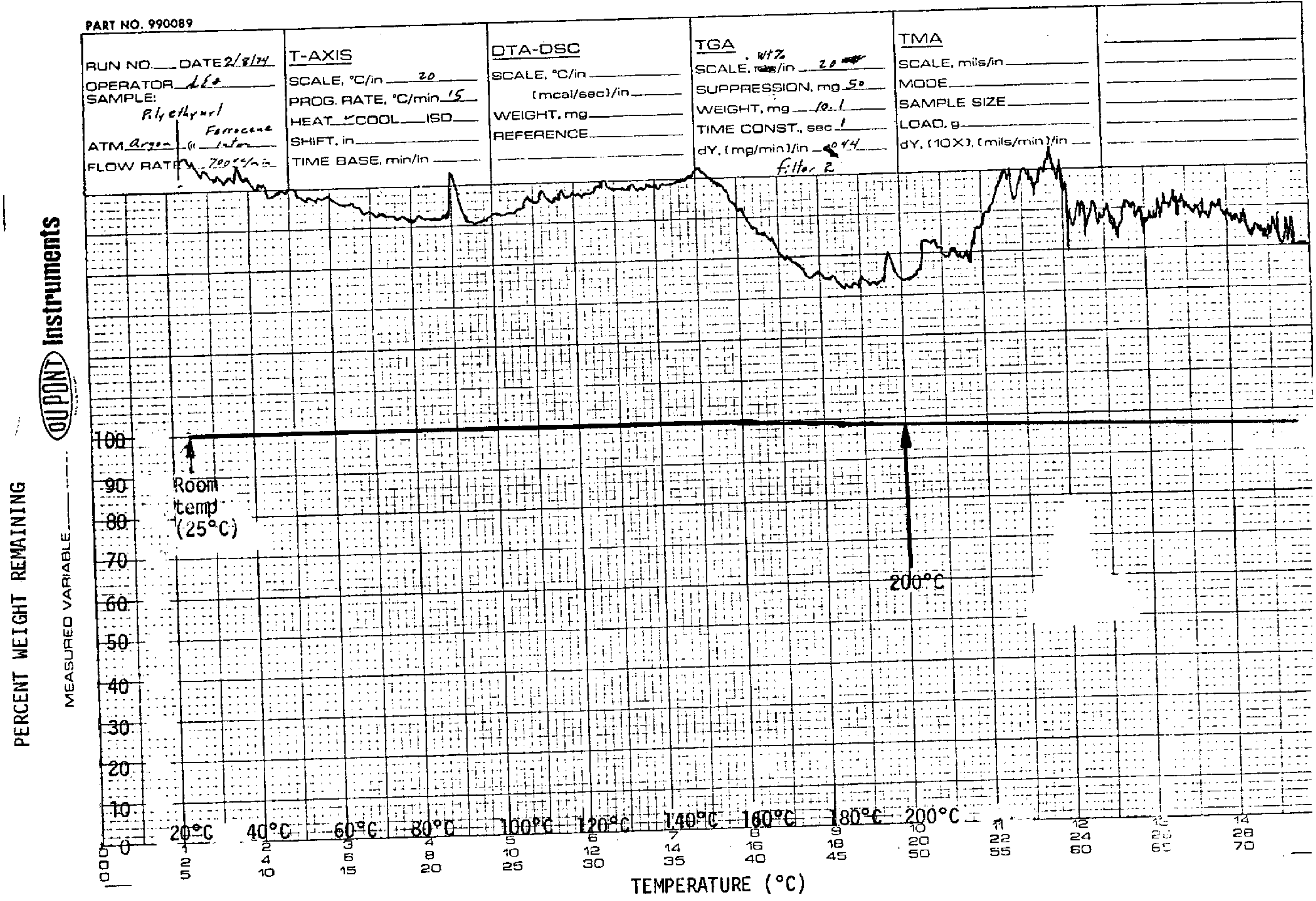
T-AXIS
SCALE, °C/in 20
PROG. RATE, °C/min 15
HEAT ✓ COOL ___ ISO ___
SHIFT, in ___
TIME BASE, min/in ___

DTA-DSC
SCALE, °C/in ___
(mcal/sec)/in ___
WEIGHT, mg ___
REFERENCE ___

TGA
SCALE, ~~mg~~ Wt%/in 20
SUPPRESSION, mg 500
WEIGHT, mg 10.3
TIME CONST., sec 1
dY, (mg/min)/in .044
filter 2

TMA
SCALE, mils/in ___
MODE ___
SAMPLE SIZE ___
LOAD, g ___
dY,(10X), (mils/min)/in ___

FIGURE 38. THERMOGRAVIMETRIC ANALYSIS OF POLY(AMINOPHENYLACETYLENE)



PART NO. 990089

RUN NO.___ DATE 2/8/74

OPERATOR LLO

SAMPLE: Polyethynyl Ferrocene

ATM Argon ((Inlet

FLOW RATE 700 cc/min

T-AXIS

SCALE, °C/in 20

PROG. RATE, °C/min 15

HEAT ✓ COOL___ ISD___

SHIFT, in___

TIME BASE, min/in___

DTA-DSC

SCALE, °C/in___

(mcal/sec)/in___

WEIGHT, mg___

REFERENCE___

TGA

SCALE, ~~mg~~ wt%/in 20

SUPPRESSION, mg 50

WEIGHT, mg 10.1

TIME CONST., sec 1

dY, (mg/min)/in .044

filter 2

TMA

SCALE, mils/in___

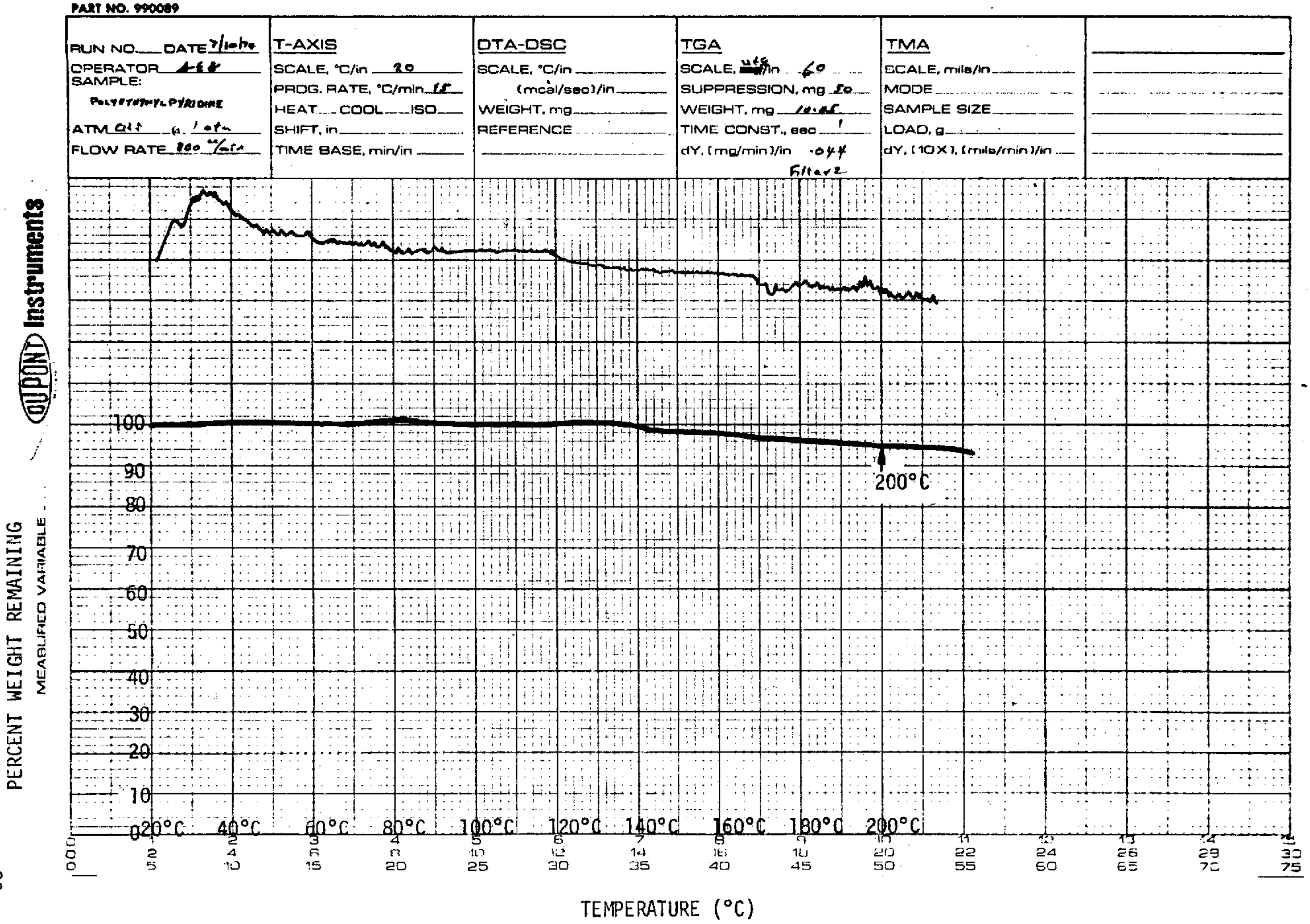
MODE___

SAMPLE SIZE___

LOAD, g___

dY, (10X), (mils/min)/in___

FIGURE 39. THERMOGRAVIMETRIC ANALYSIS CURVE FOR PURE POLY(ETHYNYLFERROCENE)



PART NO. 990089

RUN NO.___ DATE 7/10/76

OPERATOR AEK

SAMPLE: POLYETHYNYLPYRIDINE

ATM air @ 1 atm

FLOW RATE 200 cc/min

T-AXIS

SCALE, °C/in 20

PROG. RATE, °C/min 10

HEAT___ COOL___ ISO___

SHIFT, in___

TIME BASE, min/in___

DTA-DSC

SCALE, °C/in___

(mcal/sec)/in___

WEIGHT, mg___

REFERENCE___

TGA

SCALE, ug/in 60

SUPPRESSION, mg 10

WEIGHT, mg 10.65

TIME CONST., sec 1

dY, (mg/min)/in .044 Filter 2

TMA

SCALE, mils/in___

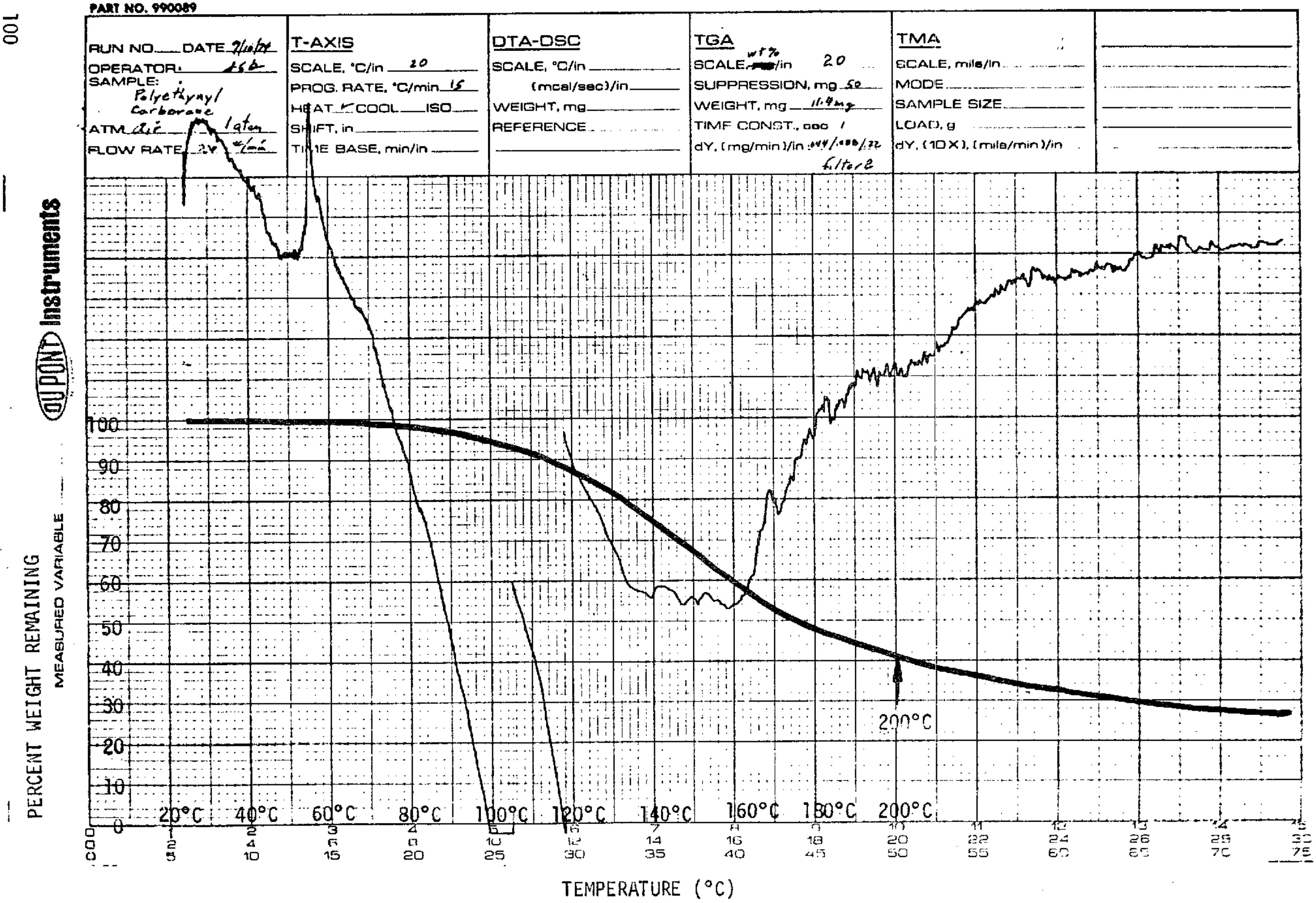
MODE___

SAMPLE SIZE___

LOAD, g___

dY, (10X), (mils/min)/in___

FIGURE 40. THERMOGRAVIMETRIC ANALYSIS CURVE FOR POLY(ETHYNYLPYRIDINE)



PART NO. 990089

RUN NO.___ DATE 7/10/74
OPERATOR: ssb
SAMPLE: Polyethynyl Carborane
ATM air 1 atm
FLOW RATE 24 cc/min

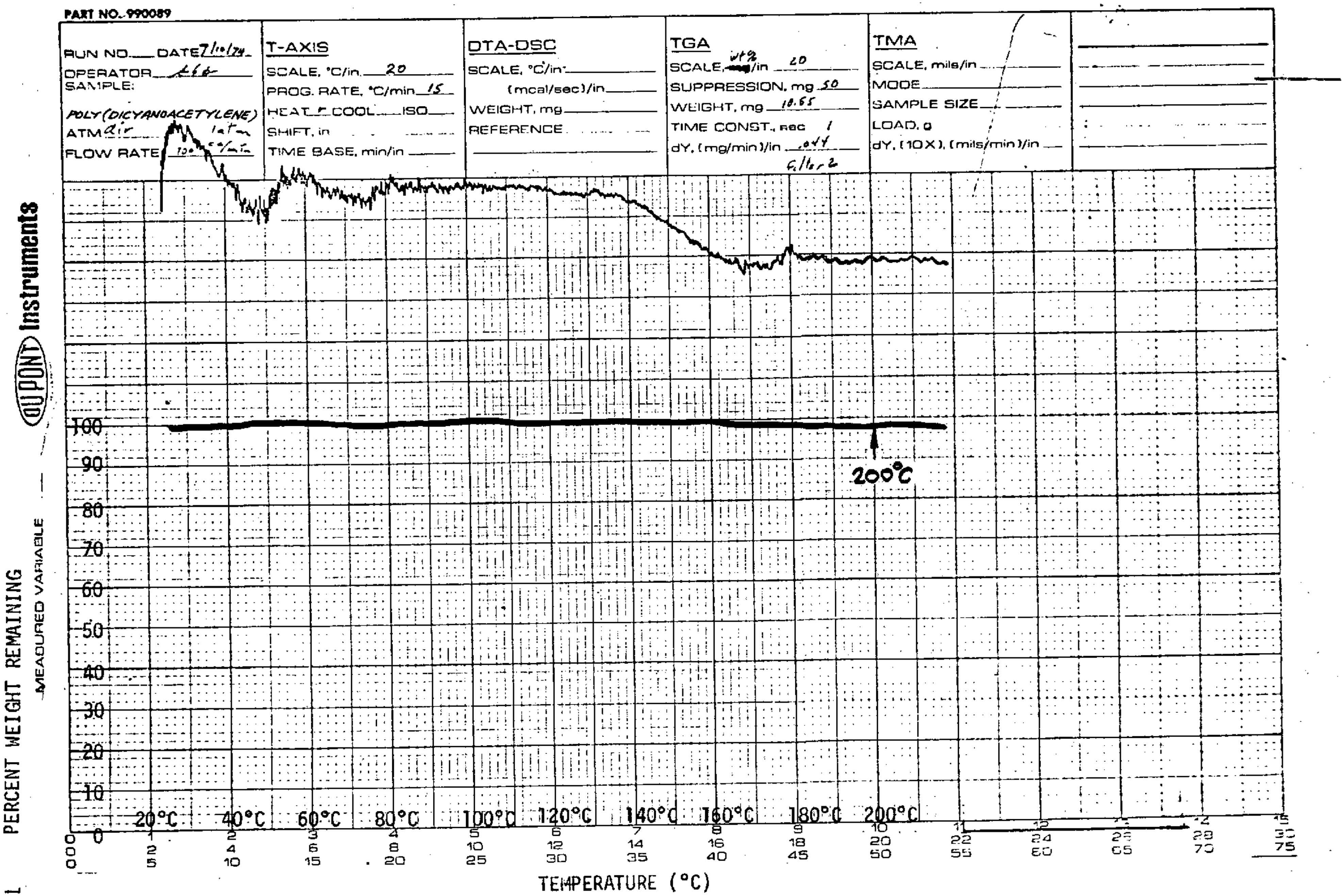
T-AXIS
SCALE, °C/in 20
PROG. RATE, °C/min 15
HEAT ✓ COOL ___ ISO ___
SHIFT, in
TIME BASE, min/in

DTA-DSC
SCALE, °C/in
(mcal/sec)/in
WEIGHT, mg
REFERENCE

TGA
SCALE, wt%/in 20
SUPPRESSION, mg 50
WEIGHT, mg 11.4mg
TIME CONST., sec 1
dY, (mg/min)/in .044/.088/.22 filter 2

TMA
SCALE, mils/in
MODE
SAMPLE SIZE
LOAD, g
dY, (10X), (mils/min)/in

FIGURE 41. THERMOGRAVIMETRIC ANALYSIS CURVE FOR POLY (ETHYNYLCARBORANE)



RUN NO.___ DATE 7/10/74
OPERATOR ___
SAMPLE: POLY(DICYANOACETYLENE)
ATM air 1 atm
FLOW RATE 100 cc/min

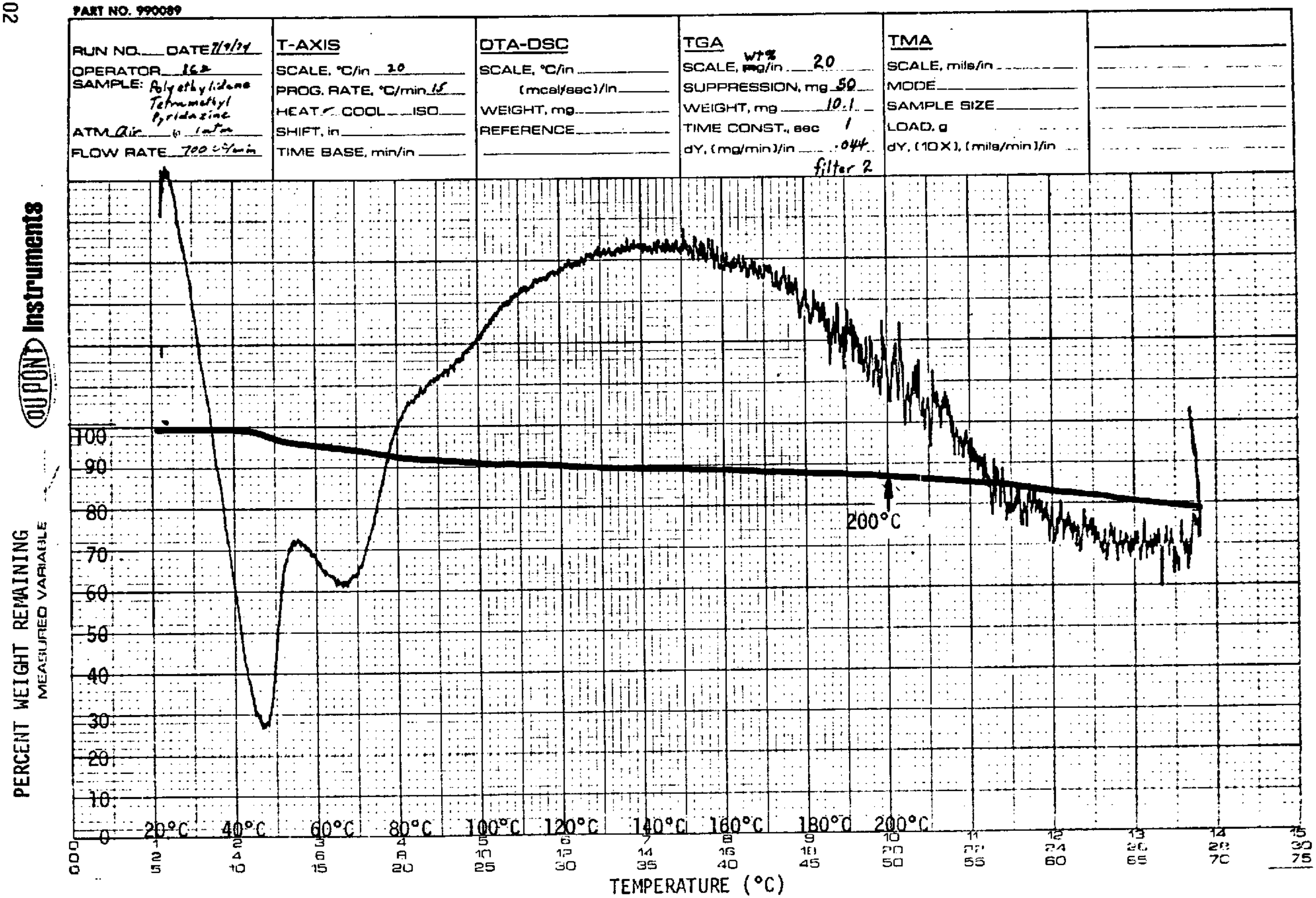
SCALE, °C/in. 20
PROG. RATE, °C/min 15
HEAT ✓ COOL___ ISO___
SHIFT, in ___
TIME BASE, min/in ___

SCALE, °C/in ___
(mcal/sec)/in ___
WEIGHT, mg ___
REFERENCE ___

SCALE, wt%/in 20
SUPPRESSION, mg 50
WEIGHT, mg 10.65
TIME CONST., sec 1
dY, (mg/min)/in .044
6/10/72

SCALE, mils/in ___
MODE ___
SAMPLE SIZE ___
LOAD, g ___
dY, (10X), (mils/min)/in ___

FIGURE 42. THERMOGRAVIMETRIC ANALYSIS CURVE FOR POLY(DICYANOACETYLENE)



PART NO. 990089

RUN NO. DATE 7/9/74
OPERATOR JGB
SAMPLE: Polyethylidene Tetramethyl Pyridazine
ATM air @ 1 atm
FLOW RATE 700 cc/min

T-AXIS
SCALE, °C/in 20
PROG. RATE, °C/min 15
HEAT ✓ COOL ISO
SHIFT, in
TIME BASE, min/in

DTA-DSC
SCALE, °C/in
(mcal/sec)/in
WEIGHT, mg
REFERENCE

TGA
SCALE, ~~mg~~ wt%/in 20
SUPPRESSION, mg 50
WEIGHT, mg 10.1
TIME CONST., sec 1
dY, (mg/min)/in .044
filter 2

TMA
SCALE, mils/in
MODE
SAMPLE SIZE
LOAD, g
dY, (10X), (mils/min)/in

FIGURE 43. THERMOGRAVIMETRIC ANALYSIS CURVE FOR POLY(ETHYLIDENETETRAMETHYL PYRIDAZINE)

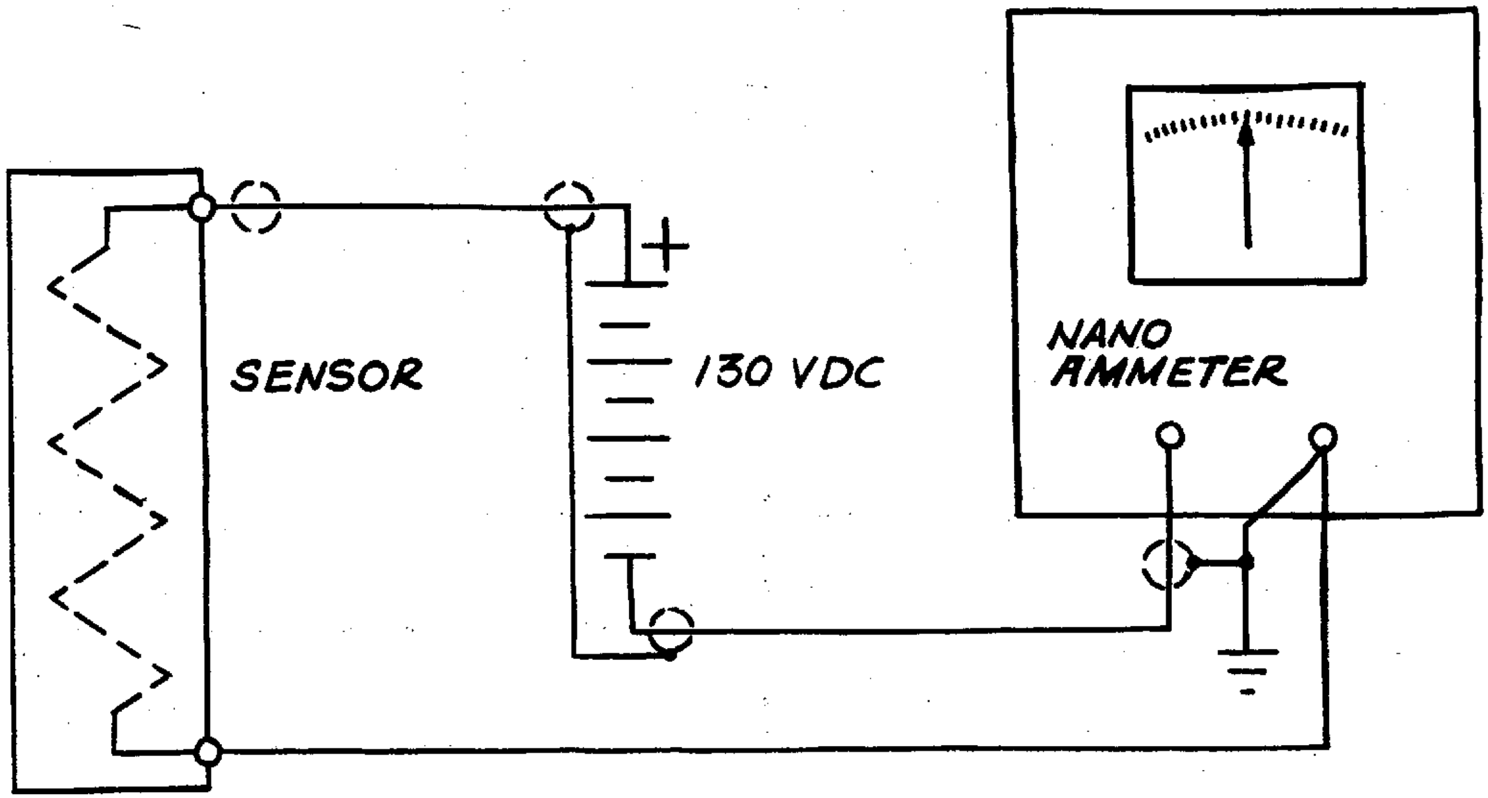


FIGURE 44. SCHEMATIC DIAGRAM OF TEST CIRCUITRY

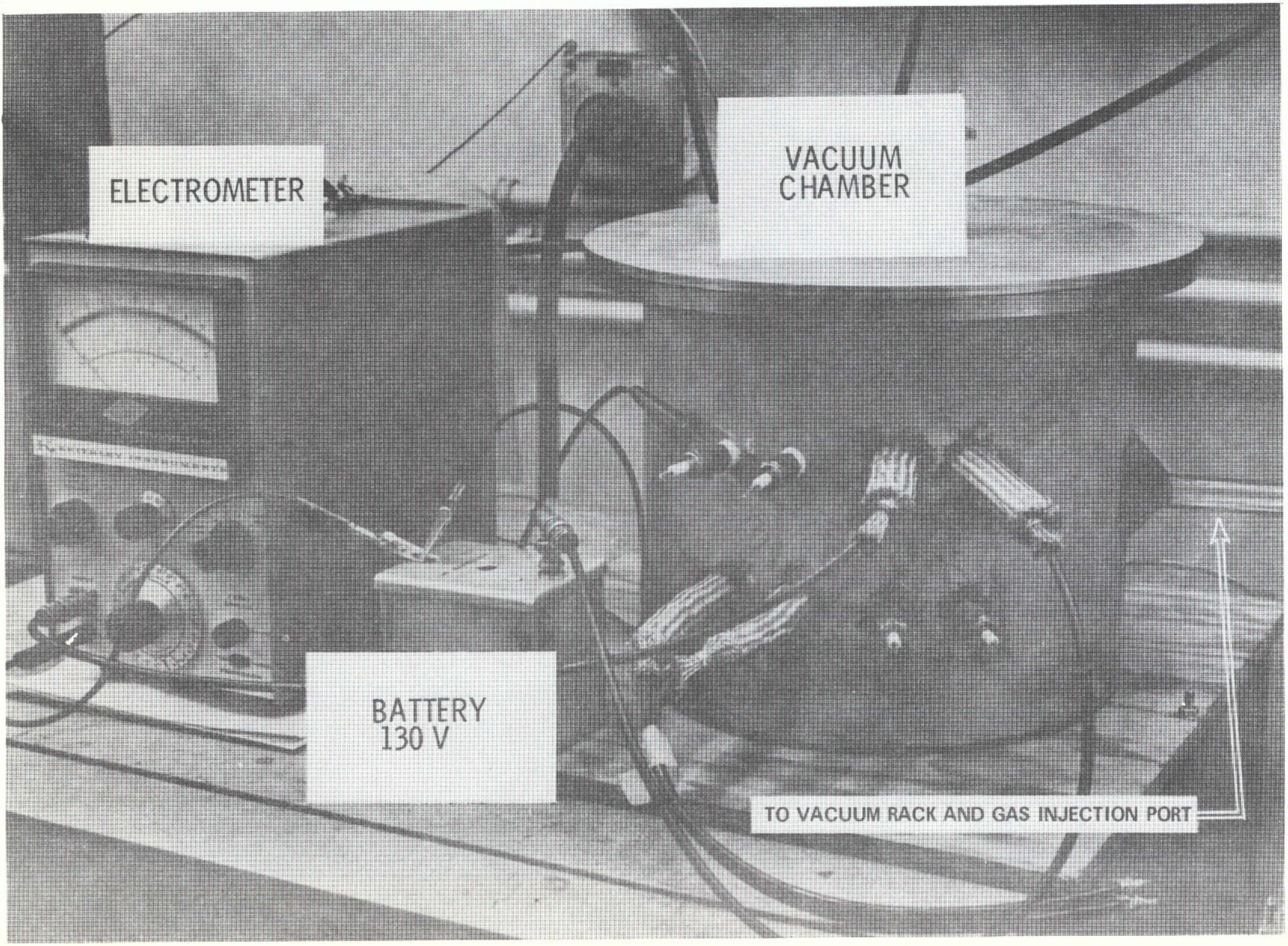


Plate 1. Vacuum Chamber and Associated Electrical Equipment

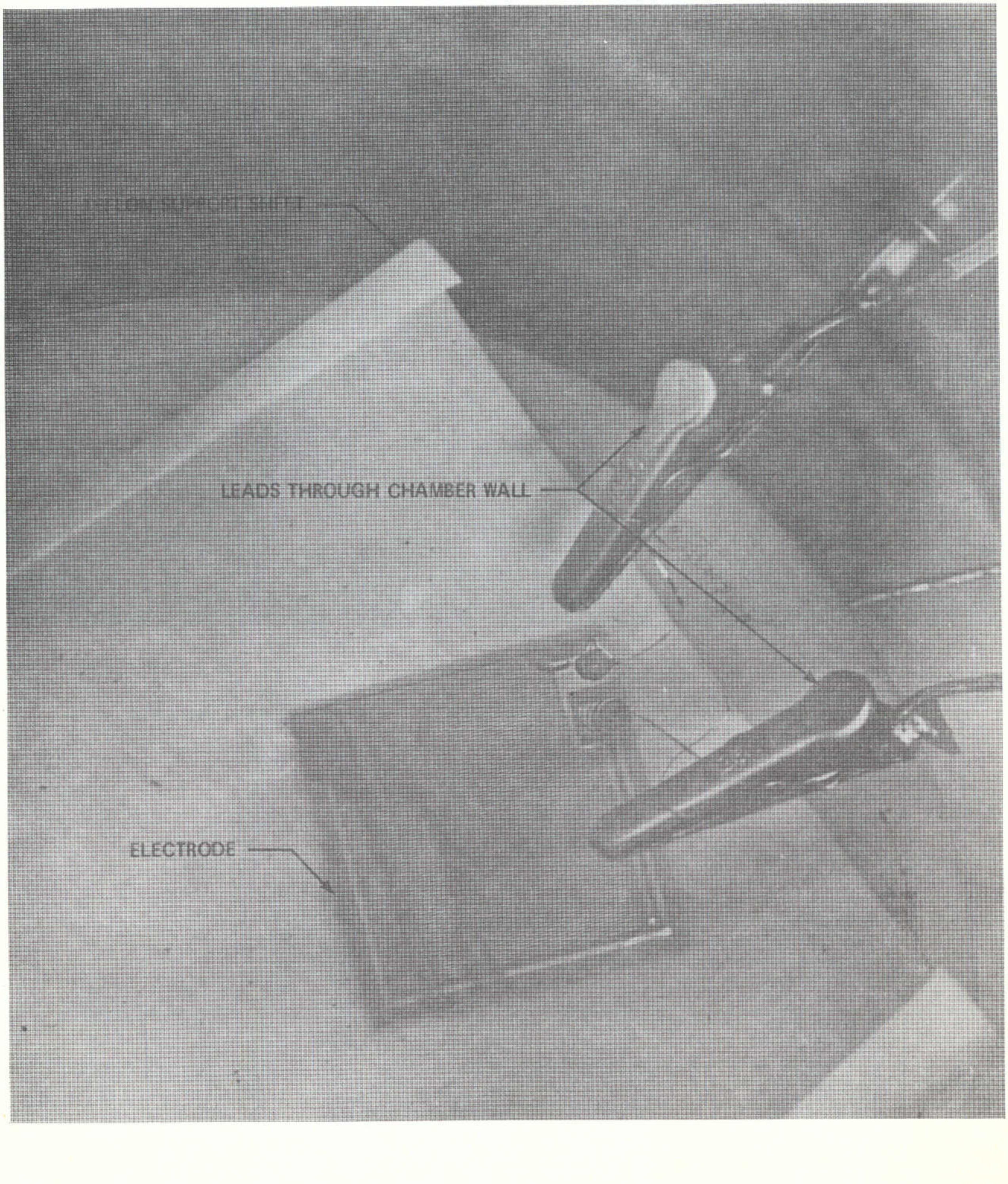


Plate 2. Interior of Chamber Showing Sensing Electrode (Polymer Coated) Attached to Electrical Leads

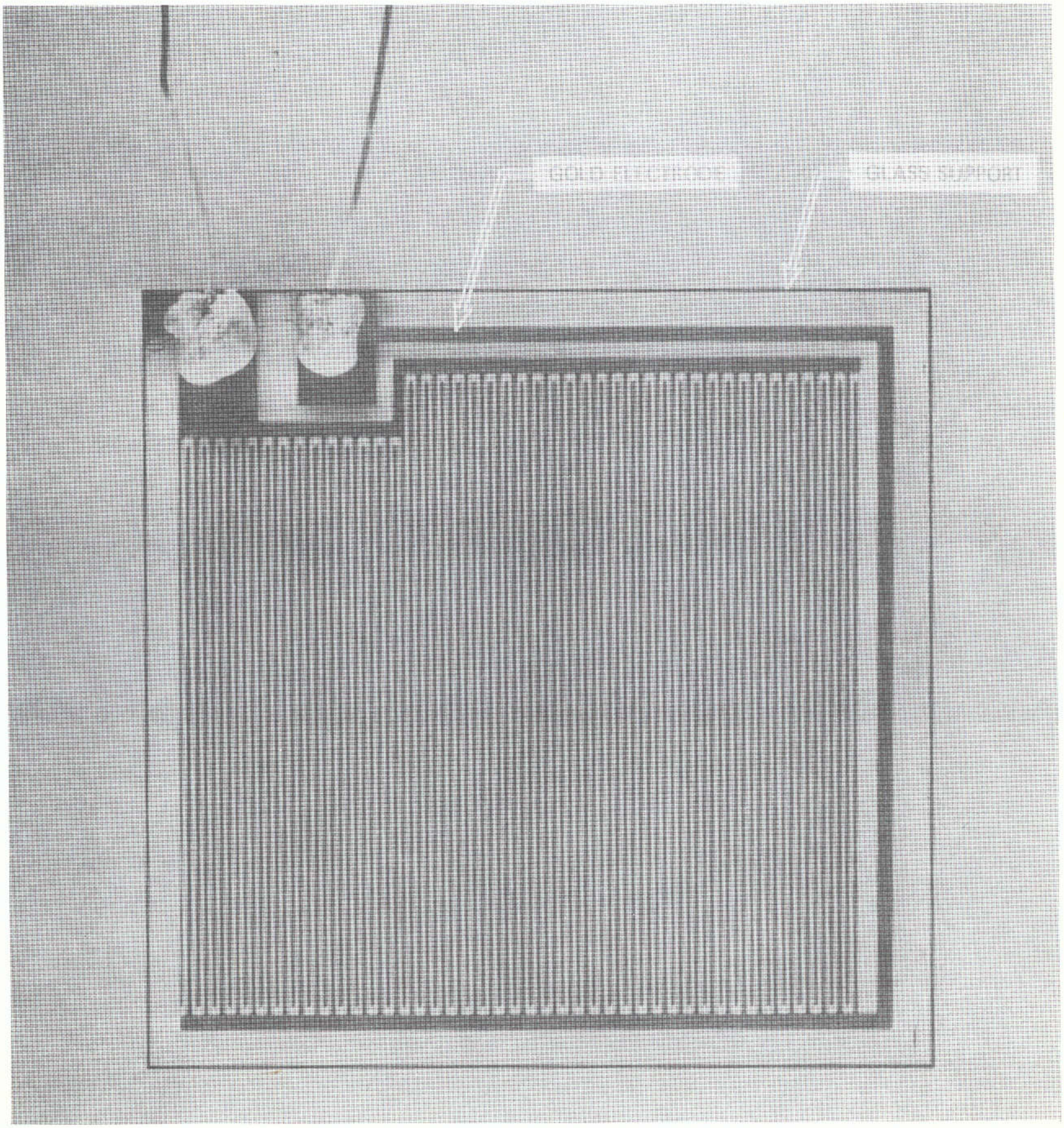


Plate 3. Close–up of Uncoated Sensing Electrode

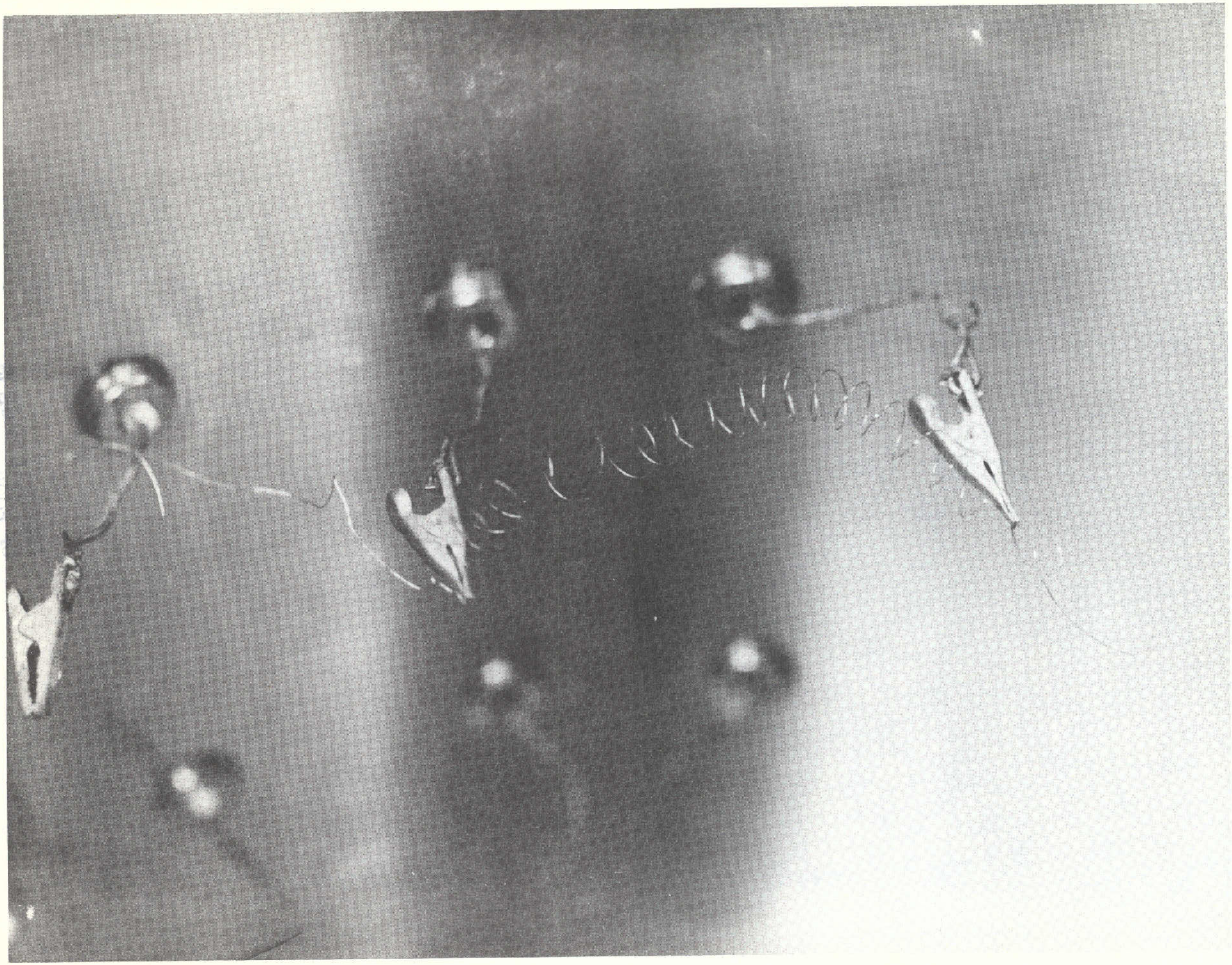


Plate 4. Ignition Coil

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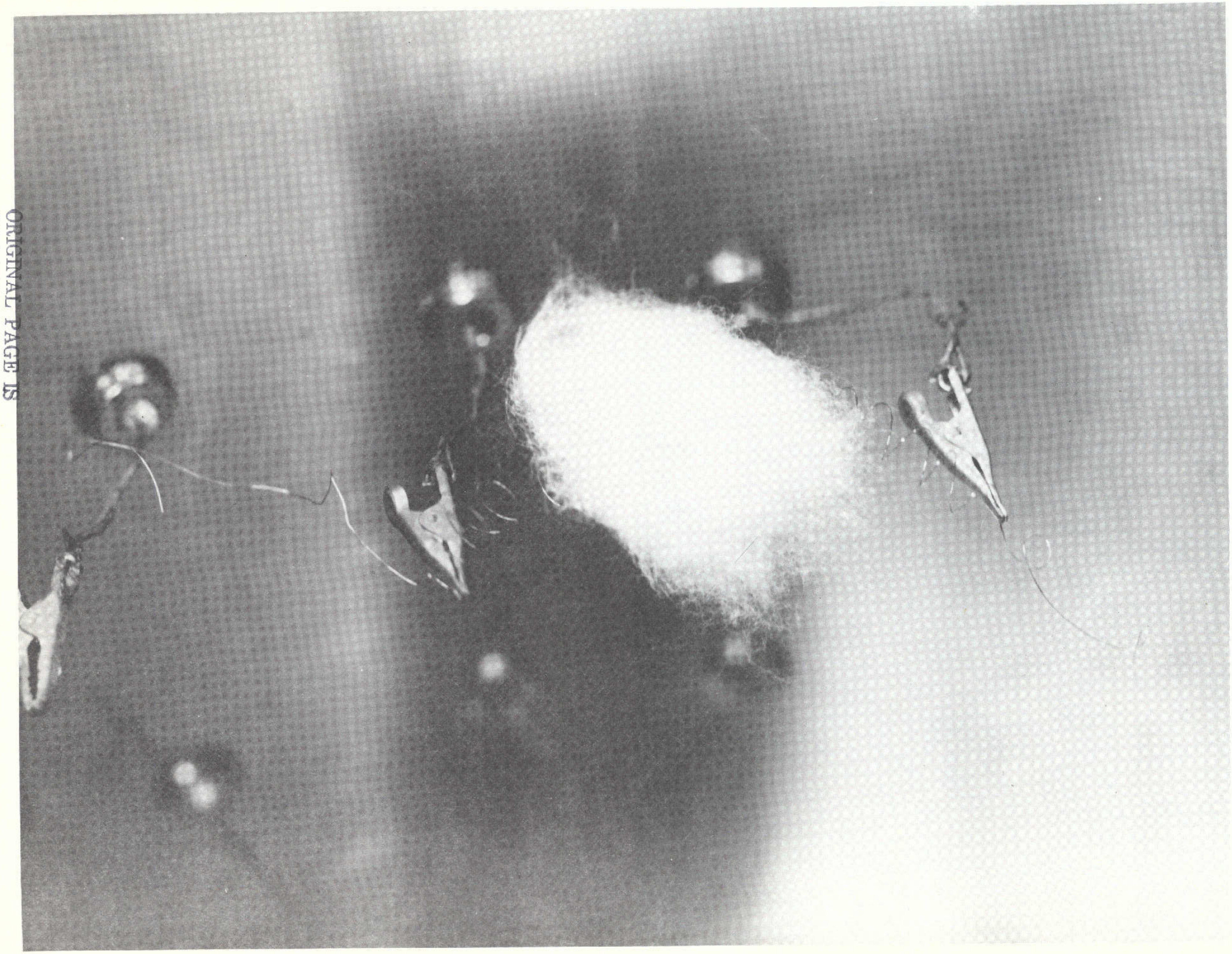

Plate 5. Coil With Cotton

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