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Gentlemen:

Attached is the Second Quarterly Report for NASw-1415, covering work done during September, October and November, 1966.

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Principal Investigator

BG:md

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RESEARCH DIVISION

Washington Research Center, Clarksville, Maryland 21029

Synthesis of Linear, Double Chain,
Ladder Polymers from Substituted Tetracosphosphonitriles

Quarterly Progress Report Covering the Period
September, October and November 1966

By

N 67 13620

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ABSTRACT

During this reporting period the thermal polymerization of β -trans- $[\phi\text{PN}(\text{NH}_2)]_4$ was investigated at temperatures ranging from 209 to 320. Highest number average molecular weight of 36,000 was obtained when the deammoniation was carried out at 265°C.

The following monomers have been prepared and are now being used for polymerization studies; $[\phi\text{PN}(\text{N}_3)]_4$, $[\phi\text{PN}(\text{NCS})]_4$ and $[\phi\text{PN}(\text{NHCH}_3)]_4$. Thermal deamination of the tetrakismonomethylamide resulted in lower molecular weight polymers. By heating the tetraazide, nitrogen is evolved and a polymeric material is produced.

RESULTS AND DISCUSSION

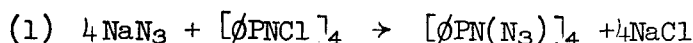
I. Preparation of Derivatives of β -trans- $[\phi\text{PNCl}]_4$

A. β -trans- $[\phi\text{PN}(\text{NH}_2)]_4$

A description of the preparation of this intermediate was given in the previous Quarterly Report.¹ High yields can be obtained by passing an excess of ammonia through a solution of β -trans- $[\phi\text{PNCl}]_4$ in tetrahydrofuran. This reaction was conducted twice during this quarter resulting in the isolation of approximately 250 g. of the tetraamide.

B. β -trans- $[\phi\text{PN}(\text{N}_3)]_4$

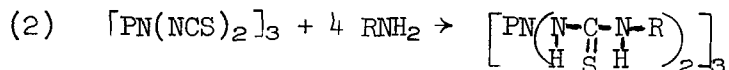
The preparation of the non-geminally substituted tetraazide has been reported², but no subsequent work was carried out. The polyazide derivatives apparently are stable only if substitutions are non-geminal, and are unstable if two azido groups are attached to a single phosphorus atom.³ The tetraazide can be prepared by the simple nucleophilic substitution of an azido group for chlorine.



Mild heating of an acetonitrile solution of $[\phi\text{PNCl}]_4$ in the presence of an excess of sodium azide causes the reaction to go to completion in a few hours. The compound β -trans- $[\phi\text{PN}(\text{N}_3)]_4$, m.p. 134-5°, was prepared in 87% yield by this process. It is assumed that the β -trans configuration was maintained since no other isomers were recovered. An infrared spectrum (Figure 1) showed the characteristic azide absorption band at about 2100 cm^{-1} .

C. β -trans- $[\phi\text{PN}(\text{NCS})]_4$

The preparation of the isothiocyanate derivative also is a relatively simple procedure. It has been reported that the ambident thiocyanate anion, $\text{N} \equiv \text{C}-\text{S}^-$, will react with phosphonitrilic chlorides to give the isothiocyanate phosphonitriles, i.e., $[\text{PN}(\text{NCS})_2]_n$.⁴ Compounds of this type have been studied and reactions of the type,



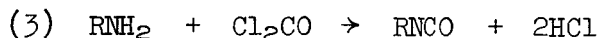
have been reported.⁵ We prepared β -trans- $[\phi\text{PN}(\text{NCS})]_4$, postulating that it would form ladder polymers when reacted with β -trans- $[\phi\text{PN}(\text{NH}_2)]_4$.

β -trans- $[\phi\text{PN}(\text{NCS})]_4$ was prepared by treating β -trans- $[\phi\text{PNCl}]_4$ with KSCN in refluxing acetonitrile. The metathesis occurred slowly as the reactants were heated. An essentially quantitative yield of product was obtained. The product, m.p. 145-7°, had an infrared spectrum as shown in Figure 2, and an elemental analysis as follows:

	<u>C</u>	<u>H</u>	<u>N</u>	<u>S</u>	<u>P</u>
Obs.	46.5	3.0	15.5	17.6	17.1
Calcd. $[\phi\text{PN}(\text{NCS})]_4$	46.7	2.8	15.6	17.2	17.8

D. β -trans- $[\phi\text{PN}(\text{NCO})]_4$

A reaction sequence similar to (2) can be postulated for an isocyanato phosphonitrile and an amino-phosphonitrile. Unlike the reaction of KSCN, the reaction of an inorganic cyanate cannot be carried out readily. Therefore, the preparation of β -trans- $[\phi\text{PN}(\text{NCO})]_4$ was attempted by adding phosgene to β -trans- $[\phi\text{PN}(\text{NH}_2)]_4$. Presumably the reaction would follow the course,



where R is the phosphonitrilic ring. A similar reaction with $\text{P}_3\text{N}_3\text{Cl}_4(\text{NH}_2)_2$ to produce $\text{P}_3\text{N}_3\text{Cl}_4(\text{NCO})_2$ is reported in the literature.⁶ The product obtained however did not appear to be a simple tetrasubstituted cyclic tetra-phosphonitrile. The infrared spectrum (Figure 3) did not show the characteristic isocyanate absorption at 2270 cm.^{-1} and the characteristic absorption at 1300 cm.^{-1} for PN tetramers had shifted. Elemental analysis of the product was as follows:

	<u>C</u>	<u>H</u>	<u>N</u>	<u>P</u>
Obs.	48.0	5.1	18.5	20.6
Calc. for $[\phi\text{PN}(\text{NCO})]_4$	51.2	3.1	17.1	18.9

These values imply that the isocyanate may have coupled with an amido group to form the -NHCONH- bridge. A molecular weight of 1640 obtained by vapor phase osmometry supports this view.

E. β -trans- $[\phi\text{PN}(\text{NHCH}_3)]_4$

Preparation of the tetrakismonomethylamide from β -trans- $[\phi\text{PNCl}]_4$ was accomplished by bubbling an excess of methylamine through a tetrahydrofuran solution of β -trans- $[\phi\text{PNCl}]_4$. This material has been reported previously as a compound exhibiting dimorphism.⁷ The product, m.p. $148-50^\circ$, was obtained in approximately 48% yield.

F. β -trans- $[\phi\text{PN}(\text{NH}_2)]_4 \cdot 2\text{HCl}$

One of the unique properties of amido phosphonitrilic compounds is their ability to coordinate with Lewis acids to give addition complexes. Coordination of HCl has been reported only for those phosphonitriles with at least one NH_2 per phosphorus.⁸⁻⁹

Passing $\text{HCl}(\text{g})$ through a benzene solution of β -trans- $(\phi\text{PNNH}_2)_4$ caused a precipitate to form. The precipitate recovered from the reaction had an infrared spectrum shown in Figure 4. This can be compared to the

infrared spectrum of starting β -trans- $[\phi\text{PN}(\text{NH}_2)]_4$ shown in Figure 5. Elemental analysis of the product showed:

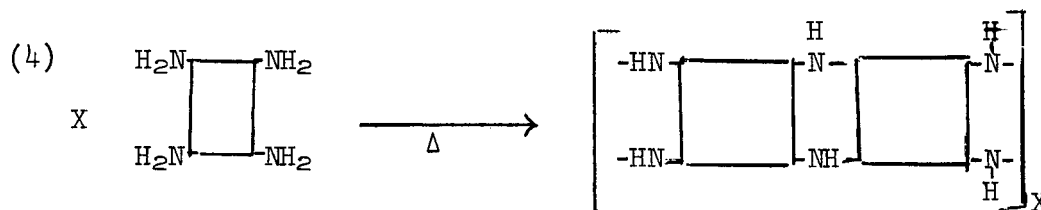
	<u>C</u>	<u>H</u>	<u>N</u>	<u>Cl</u>	<u>P</u>
Found	46.5	5.3	16.9	12.4	18.7
Calcd. for $[\phi\text{PNNH}_2]_2 \cdot 2\text{HCl}$	46.1	4.8	17.9	11.3	19.8

II. Polymerization Reactions

A. Thermal Deammoniation of β -trans- $[\phi\text{PN}(\text{NH}_2)]_4$

The thermal deammoniation of β -trans- $[\phi\text{PN}(\text{NH}_2)]_4$ to yield polymers was initially reported in the first Annual Report.¹

The following type of reaction was envisioned:



Ideally, for each mole of monomer there should be obtained no more than half a mole of NH_3 .

During the past quarter a study was conducted to determine if the molecular weight distribution of the polymer is a function of the temperature at which this condensation occurs. The study was conducted at temperatures ranging from 209 to 320°C. The data obtained are reported in Table I. The percent NH_3 evolved is based on that postulated for reaction (4). Ammonia half-life is that time required to evolve fifty percent of the expected ammonia. The polymerization product was then dissolved in 75 ml. of anhydrous chloroform and stirred overnight. That part which was soluble was used for further analysis. Molecular weights were determined for the total product that was soluble in chloroform; these proved to be fairly low. Higher molecular weight polymer was recovered by fractionally precipitating the chloroform soluble polymer. The initial precipitate, representing from 13 to 24 percent of the total chloroform soluble material, was used for a second molecular weight determination. The highest molecular weight obtained was 36,000 which represents a DP of about 70 tetramer units. It can be seen that the highest number average molecular weights were obtained when the polymerization was carried out at about 265°C. Higher temperatures result in lower molecular weight polymers, although over 90% of the available ammonia is evolved. This may result from the formation of small ring compounds, or more likely, the opening of the phosphonitrile ring.

TABLE I

Thermal Deammoniation of β -trans- $[\phi\text{PN}(\text{NH}_2)]_4$

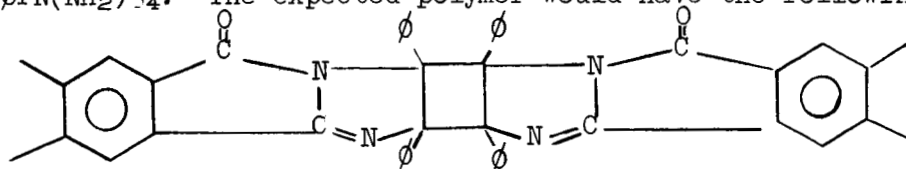
Run No.	Temp. (°C)	NH ₃ Evolution		Overall Product		High Mol. Wt. Product	
		* Life (Hrs.)	Yield %	% Sol In CHCl ₃	Mol. Wt.	Wt. %	Mol. Wt.
Prev. Typical	209	-	86	55	5,900	23	11,700
Prev. Best	219	-	75	92	13,000	13	20,000
4046-32	230	6.5	92	37	1,050	-	-
4046-33	260	3.0	96	71	2,800	18	7,150
-36	265	1.8	100	34	2,000	24	7,200
-39	265	0.5	92	84	-	18	-
-40	265	0.5	89	94	-	31	22,000
-42	265	0.5	90	95	(Sample decomposed)		
-46	260	0.5	89	59	3,750	15	35,000
-47	280	0.1	90	90	3,750	14	25,800
-48	300	0.05	90	92	1,780	13	4,260
-49	320	0.03	94	100	2,030	13	4,500

B. Copolymerization of β -trans- $[\phi\text{PNCl}]_4$ and β -trans- $[\phi\text{PN}(\text{NH}_2)]_4$.

One attempt to copolymerize a tetrachlorophosphonitrile and a tetraaminophosphonitrile led to a polymer with a molecular weight of between one and two thousand. However, the product did not have an elemental analysis that was consistent with a product that would result from elimination of HCl from these cyclics. Apparently a side reaction occurred, and this reaction will be reinvestigated.

C. Copolymerization of β -trans- $[\phi\text{PN}(\text{NH}_2)]_4$ with Pyromellitic Dianhydride

The reaction of aromatic dianhydrides such as pyromellitic dianhydride (PMDA) with tetraamines has been extensively explored by C.S. Marvel and others. We have carried out the reaction of PMDA with β -trans- $[\phi\text{PN}(\text{NH}_2)]_4$. The expected polymer would have the following pyrrole structure:



Equimolar amounts of PMDA and the tetrakisamide were dissolved in dimethylformamide. Upon heating the solution turned yellow at 80°C. and at 100°C. to a deep green color. Refluxing started at about 135°C. (BP of DMF is 152°); however, upon removal of distillate the solution was brought to reflux at 152°.

A brown solid was recovered from the reaction mixture that was soluble in chloroform. Molecular weight determinations of this product gave

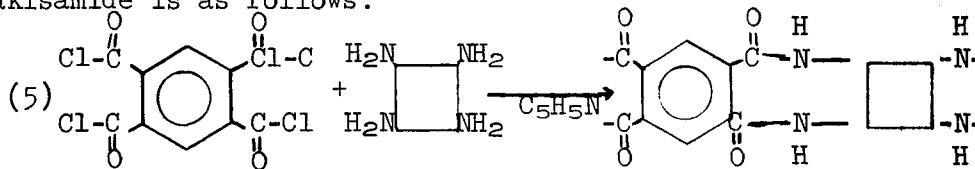
values of 1,145 and 1,460. Elemental analysis was as follows:

C, 54.47; H, 3.50; N, 12.61; P, 4.47.

The phosphorus analysis appears to be quite low with respect to nitrogen. If the phosphorus is corrected to give an N:P ratio of 2:1, then the empirical formula $C_{40.40}H_{30.88}P_4N_8O_{7.4}$ can be obtained. An infrared spectrum of the product is illustrated in Figure 6. Strong absorption bands at 1600 cm.^{-1} and 1700 cm.^{-1} may be due to $\begin{matrix} O \\ || \\ -C-NH- \end{matrix}$ and $-C=N-$ bonds.

D. Reaction of Pyromellitic Tetraacid Chloride (PMTC) with β -trans- $[\phi PNNH_2]_4$.

Acid chlorides can react quite smoothly with amides if one first prepares the pyridine complex.¹⁰ The expected reaction of PMTC with β -trans-tetrakisamide is as follows:

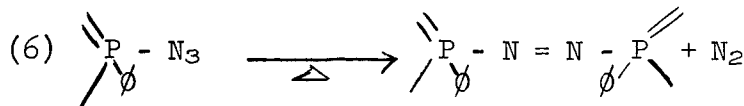


Addition of pyridine to PMTC in chloroform resulted in the formation of a blood-red soluble complex. Upon refluxing this complex with β -trans-tetrakisamide a solid precipitated after several hours. An infrared spectrum of the product (Figure 7) does not have the expected absorption at about 1600 cm.^{-1} ; however there is a shift in the band from 900 cm.^{-1} to 960 cm.^{-1} . Also present is a fairly strong absorption peak at 2650 cm.^{-1} which is usually attributed to P-OH. The product is now being analyzed.

E. Thermal Polymerization of β -trans- $[\phi P(N_3)]_4$

The behavior of the β -trans tetraazidotetraphenylphosphonitrile upon heating indicates that polymerization might be possible if azo bonds form intermolecularly as nitrogen is evolved. Data for azidophosphonitrile decompositions were recently reported by Shorts et al.¹¹

Heating β -trans- $[\phi P(N_3)]_4$ above its melting point, $134-5^\circ$, causes the slow evolution of a gas that is presumed to be nitrogen. This evolution becomes rapid if the melt is heated to 200°C . The product is a highly colored resinous material. Heating at 220° for fifteen minutes caused the evolution of 90% of the available nitrogen as based on the following reaction:



The product, however, was not soluble in chloroform or toluene. Other conditions for this condensation polymerization are being investigated.

F. Polymerization of β -trans- $[\phi\text{PN}(\text{NHCH}_3)]_4$

The thermal deamination of this phosphonitrile could be expected to give polymers similar to those produced by the tetrakisamide. Initial studies of this reaction have indicated that the intermolecular elimination of methylamine occurs at higher temperatures than that required to eliminate ammonia from $[\phi\text{PN}(\text{NH}_2)]_4$.

Investigation of this polymerization is not yet complete and the data shown in Table II represents preliminary work only.

TABLE II

Thermal Deamination of β -trans- $[\phi\text{PN}(\text{NHCH}_3)]_4$

<u>Run No.</u>	<u>Temperature</u>	<u>Time</u>	<u>% of Theory H_2NMe Evolved</u>	<u>Average Mol. Wt. of Product</u>
1	305°C	11 hrs.	85	1570
2	335	6	85	1980
3	375	4	84	2030
4	400	2.5	75	693

G. Thermal Polymerization of β -trans- $[\phi\text{PN}(\text{NH}_2)]_4 \cdot 2\text{HCl}$

Presumably, polymerization of this complex could occur with elimination of ammonium chloride. It was believed that thermal condensation would take place at lower temperatures than are required for the deamination reaction.

Heating the complex to 255° caused the slow evolution (and sublimation) of NH_4Cl and resulted in the formation of a low molecular weight polymer. The average molecular weight was only 1620. Distribution of molecular weights has not been determined as yet.

EXPERIMENTAL

I. Preparation of Derivatives of β -trans- $[\phi\text{PNCl}]_4$

A. β -trans- $[\phi\text{PN}(\text{NH}_2)]_4$

The procedure used was essentially the same as previously reported. Ammonia gas, 38 g., was passed through a solution containing 160 g. of β -trans- $[\phi\text{PNCl}]_4$ in 600 ml. of tetrahydrofuran. The excess ammonia was removed by flushing with dry N_2 and the by-produced NH_4Cl was removed by filtration. The crude product was obtained by removing the solvent and pure material, m.p. 222-223.5°, was obtained by recrystallization from THF. The yield of product was 103 g. or 75%.

B. β -trans- $[\phi\text{PN}(\text{N}_3)]_4$

A mixture containing β -trans- $[\phi\text{PNCl}]_4$, (25 g., 0.0397 mole) and sodium azide, (45 g. 0.70 mole) was placed in 250 ml. of acetonitrile. All of the phosphonitrile and some of the azide dissolved. The reaction mixture

was heated to 80°C and held at this temperature for four hours. The excess azide and by-produced sodium chloride were removed by filtration. Product was recovered by distilling off the solvent. A recrystallization from chloroform gave 23 g. of β -trans- $[\phi\text{PNN}_3]_4$ m.p. 134-5°C for a yield of 87%. A sample of the product has been submitted for elemental analysis

C. β -trans- $[\phi\text{PN}(\text{NCS})]_4$

A solution containing β -trans- $[\phi\text{PNCI}]_4$, (3 g., 4.76 mmoles) and potassium thiocyanate (1.85 g., 19.0 mmoles) in 25 ml. of anhydrous acetonitrile was heated to 80° in a nitrogen atmosphere. The temperature was maintained at 80° for four hours. After cooling, by-produced KCl was filtered and the filtrate was concentrated by evaporating most of the solvent. The crystallized product, m.p. 145-7°C, weighed 3.0 g. for a yield of 88%.

D. Attempted Preparation of β -trans- $[\phi\text{PN}(\text{NCO})]_4$

The solvent for this reaction, chloroform, was distilled from P_2O_5 to provide an anhydrous alcohol free medium for the reaction. Phosgene (2.3 g., 0.023 mole) was passed through a solution of β -trans- $[\phi\text{PN}(\text{NH}_2)]_4$, 3.0 g., 0.0054 mole, in 300 ml. of the freshly distilled chloroform. Excess phosgene was absorbed in dilute NaOH. The white precipitate that slowly formed was filtered and dried. The product, 3.0 g., had a m.p. of 297-300°.

E. β -trans- $[\phi\text{PN}(\text{NHCH}_3)]_4$

Gaseous methylamine was passed through a solution of β -trans- $[\phi\text{PNCI}]_4$ (115 g., 0.183 mole) in one liter of dry tetrahydrofuran. The precipitated methylamine hydrochloride that formed was removed by filtration and the process then repeated to insure that all tetrachlorophosphonitrile had been converted to the tetraamide. The solution was concentrated and 54 g. or .089 mole of β -trans- $[\phi\text{PN}(\text{NHCH}_3)]_4$ was recovered for a yield of 48.4%. The product was submitted for characterization by IR and elemental analyses.

F. β -trans- $[\phi\text{PN}(\text{NH}_2)]_4 \cdot 2\text{HCl}$

Gaseous HCl was passed through a solution of β -trans- $[\phi\text{PN}(\text{NH}_2)]_4$, 1.5 g. (2.72 mmoles) in 500 ml. of anhydrous benzene until no additional precipitate formed. The excess HCl was eliminated by passing N_2 through the reaction mixture, and the precipitate was filtered and dried to give a white powder weighing 1.5 g. Analysis indicated that the product was the dihydrochloride, thus, the yield was 88%.

II. Polymerization Reactions

A. Thermal Deammoniation of β -trans- $[\phi\text{PN}(\text{NH}_2)]_4$

The cyclic tetramer was polymerized by heating small samples, 1-5 g., in a dry nitrogen atmosphere. Samples were heated in an oil bath. Temperatures were maintained to $\pm 1^\circ\text{C}$ with a controller. The evolved ammonia was dissolved in water and titrated with standard acid. After the polymerization was

complete, the polymer was stirred with 75 ml. of anhydrous chloroform for twelve hours. The portion that dissolved was considered a useful polymer and molecular weights were obtained for this material.

By redissolving the polymer in chloroform and precipitating approximately one fifth of the solid with n-heptane, highest molecular weight fractions were obtained.

B. Copolymerization of β -trans- $[\phi\text{PNCl}]_4$ and β -trans- $[\phi\text{PN}(\text{NH}_2)]_4$.

A solution containing β -trans- $[\phi\text{PNCl}]_4$, 7.87 g., 0.0125 mole, β -trans- $[\phi\text{PN}(\text{NH}_2)]_4$, 6.90 g., 0.0125 mole, and 3.85 g., 0.05 mole, of pyridine in 200 ml. of dry chlorobenzene was heated at reflux temperature (130°C) for twenty-four hours. A product, identified as pyridine hydrochloride by its infrared spectrum was removed by filtration and a polymeric product was obtained upon concentrating the reaction mixture. A product was recrystallized from chloroform and then methylene chloride, and submitted for elemental analysis. This analysis implied the product was not simply a condensation polymer.

C. Copolymerization of $[\phi\text{PN}(\text{NH}_2)]_4$ and Pyromellitic Dianhydride (PMDA)

A solution containing 4.0 g. (7.25 mmoles) of β -trans- $[\phi\text{PN}(\text{NH}_2)]_4$ and 1.585 g. (7.25 mmoles) of PMDA in 35 ml. of dimethylformamide was heated. At 80°C the solution turned yellow and at 100°C a precipitate formed while the solution turned green. Reflux began at about 135°. A distillation head was attached to the reaction flask and some distillate removed until refluxing proceeded at 152°C.

After 1 hour the solution was cooled and filtered. A small amount of grey solid, less than 0.1 g., was removed. This solid did not melt until 300°. The filtrate was evaporated to dryness at reduced pressure of 10 mm. and 60°C. A deep brown glassy solid remained which had a softening temperature of approximately 70°C. The residue, 5.44 g., was taken up in 200 ml. of hot chloroform and filtered. Of the total sample 1.55 g. remained insoluble. This sample was sent for analysis, the results of which are given on page of the Discussion.

The chloroform filtrate volume was reduced to about 5 ml. and n-heptane was added whereupon an oil separated. This oil was washed several times with chloroform-n-heptane and then dried under a high vacuum. The oil solidified to a brown solid which is presently being analyzed.

D. Copolymer of β -trans- $[\phi\text{PN}(\text{NH}_2)]_4$ and Pyromellitic Tetraacid Chloride

Pyromellitic tetraacid chloride was obtained from Eastman DPI. To a flask containing 2.2 g. (7.26 mmoles) of the acid chloride was added 2.3 g. of pyridine in 50 ml. of anhydrous chloroform. Upon addition of the pyridine the solution turned deep red.

The solution was brought to reflux at about 64°C. and a chloroform solution of β -trans- $[\phi\text{PN}(\text{NH}_2)]_4$, 4.0 g. (7.26 mmoles) was slowly added. After several hours a precipitate formed. The solution was filtered hot after 24 hours. A grey precipitate, 3.35 g., which softened at 230°C, was recovered. This solid is now being characterized.

E. Thermal Polymerization of $[\phi\text{PN}(\text{N}_3)]_4$

The tetraazide was heated under nitrogen in the same apparatus used for the thermal polymerization of β -trans- $[\phi\text{PN}(\text{NH}_2)]_4$. A gas burette was used to collect the N_2 that evolved upon heating the tetraazide. In a typical run, 0.3 g. of β -trans- $[\phi\text{PN}(\text{N}_3)]_4$ was heated to 200° for four hours. During this period, 40 ml. of N_2 (corr. to STP) or 90% of the theoretical amount, was evolved. The product, a black resinous material, was not appreciably soluble in either chloroform or toluene.

F. Thermal Polymerization of β -trans- $[\phi\text{PN}(\text{NHCH}_3)]_4$

This material was polymerized by heating the tetramer under a nitrogen atmosphere in a small furnace fitted with a temperature controller. As in the case of the $[\phi\text{PN}(\text{NH}_2)]_4$ the evolved amine was measured by titrating with standard acid. In a typical run, a three gram sample was heated to 300°C and during an eleven hour period, 0.26 g. or 85% of the theoretically available methylamine was evolved. The product was dissolved in chloroform, and a molecular weight obtained. The highest molecular weight fractions are now being obtained by fractional precipitation from chloroform-heptane solutions.

G. Pyrolysis of β -trans- $[\phi\text{PN}(\text{NH}_2)]_4 \cdot 2\text{HCl}$

A 1.5 g. sample of β -trans- $[\phi\text{PN}(\text{NH}_2)]_4 \cdot 2\text{HCl}$ was heated under nitrogen to 255°C for twelve hours. A solid, presumed to be NH_4Cl from its infrared spectra, slowly collected on the outlet from the flask. The polymer left in the reaction vessel was a white powder. It had an infrared pattern similar to the polymers obtained by heating β -trans- $[\phi\text{PN}(\text{NH}_2)]_4$. The soluble portion amounted to about 80% of the residue and was submitted for elemental analysis and molecular weight measurement.

MANPOWER EXPENDED

The following breakdown shows the cumulative man hours expended to date:

	T h r o u g h		
	<u>September</u>	<u>October</u>	<u>November</u>
Principal Investigator	78	97	122
Department Director	21	30	38
Senior Chemist	376	584	904
Technician	1176	1336	1496
Analytical Chemist	2	4	4
Analytical Technician	2	6	6

PROGRAM PLANNING CHART

Attached is the current planning chart. Dark areas represent work accomplished.

ANTICIPATED WORK

Polymerization reactions will be carried out with monomers that have been prepared.

Efforts will be made to increase the molecular weight of polymers that have been prepared by deammoniation of β -trans- $[\text{OPN}(\text{NH}_2)]_4$.

Reactions of pyromellitic dianhydride and tetraacid chloride with the tetrakisamide will continue.

DURATION OF SUBPROJECT

Sub-Project	Man Months												Total		
	Jan	Feb	Mar	Apr	May	Jun	Jul	Aug	Sept	Oct	Nov	Dec		Professional	Technician
Polymers From $[ZrEtCl]_4$													4	6	10
Isolation of $[MePnCl]_4$													3	4	7
Polymers from $[MePnCl]_4$													3	4	7
Thermal Studies of $[R_2Pn]_4$													3	4	7
													13	18	31

REFERENCES

1. Grushkin, B., Quarterly Report No. 1, NASw-1415, September 1966.
2. Grushkin, Rice, Annual Report, NASw-924, May 1965.
3. Grundman and Raetz, Z. Naturforsch, 10b, 116 (1955).
4. Otto, Audrieth, J. Am. Chem. Soc., 80, 5894 (1958).
5. Tesi, Otto, Sherif, Audrieth, J. Am. Chem. Soc., 82, 528 (1960).
6. British Patent; 888,662, January 31, 1962.
7. Grushkin, Annual Report NASw-924, May 1966.
8. Bode, Glausen, Z. Anorg. Chem. 258, 99 (1948).
9. Ray, Shaw, Chem. and Ind., 61, 1173 (1961).
10. Sonntag, Chem. Reviews, 52, 237 (1953).
11. Shorts, Bilbo and Gentry, Inorg. Chem., 5, 2140 (1966).

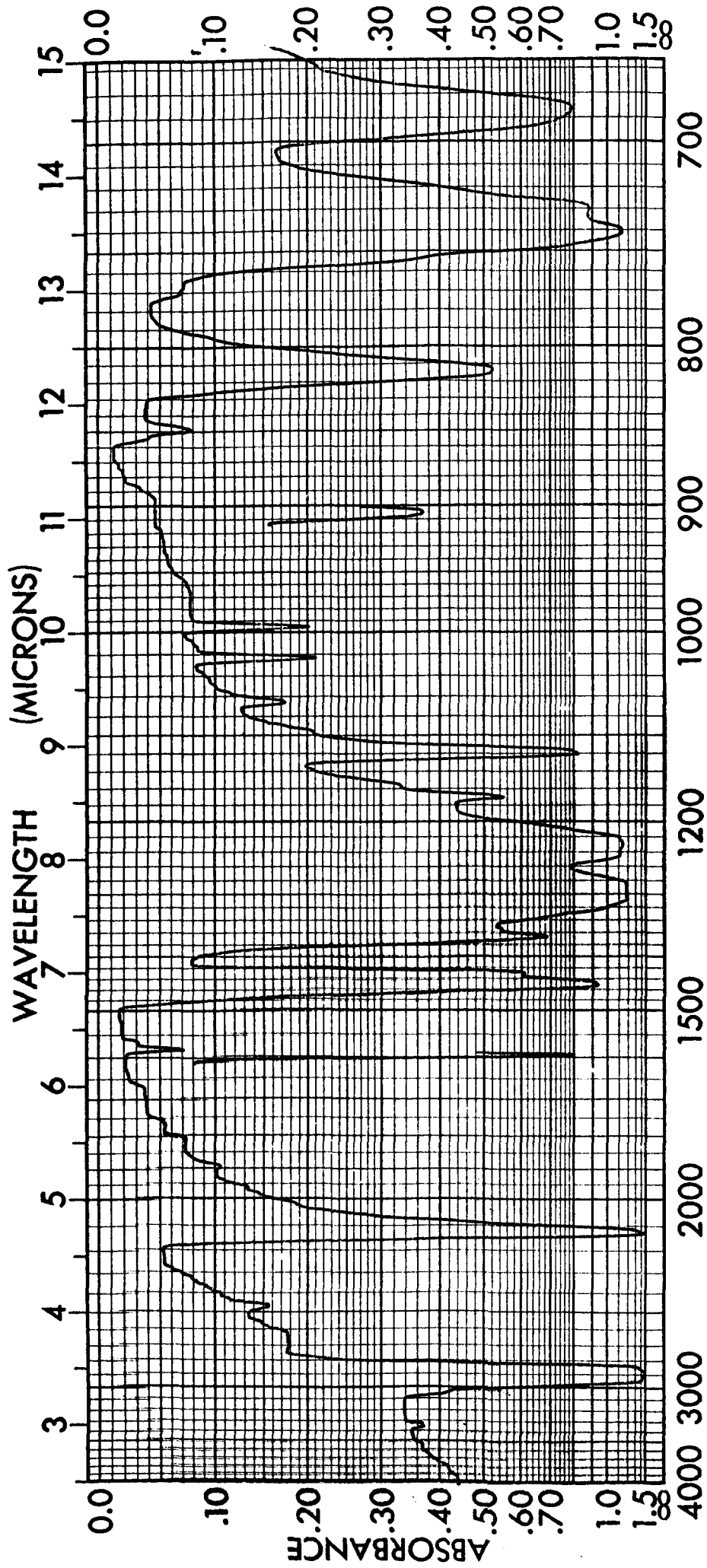


Figure 1

Infrared Spectrum of β -trans-[ϕ FN(Ns)]₄

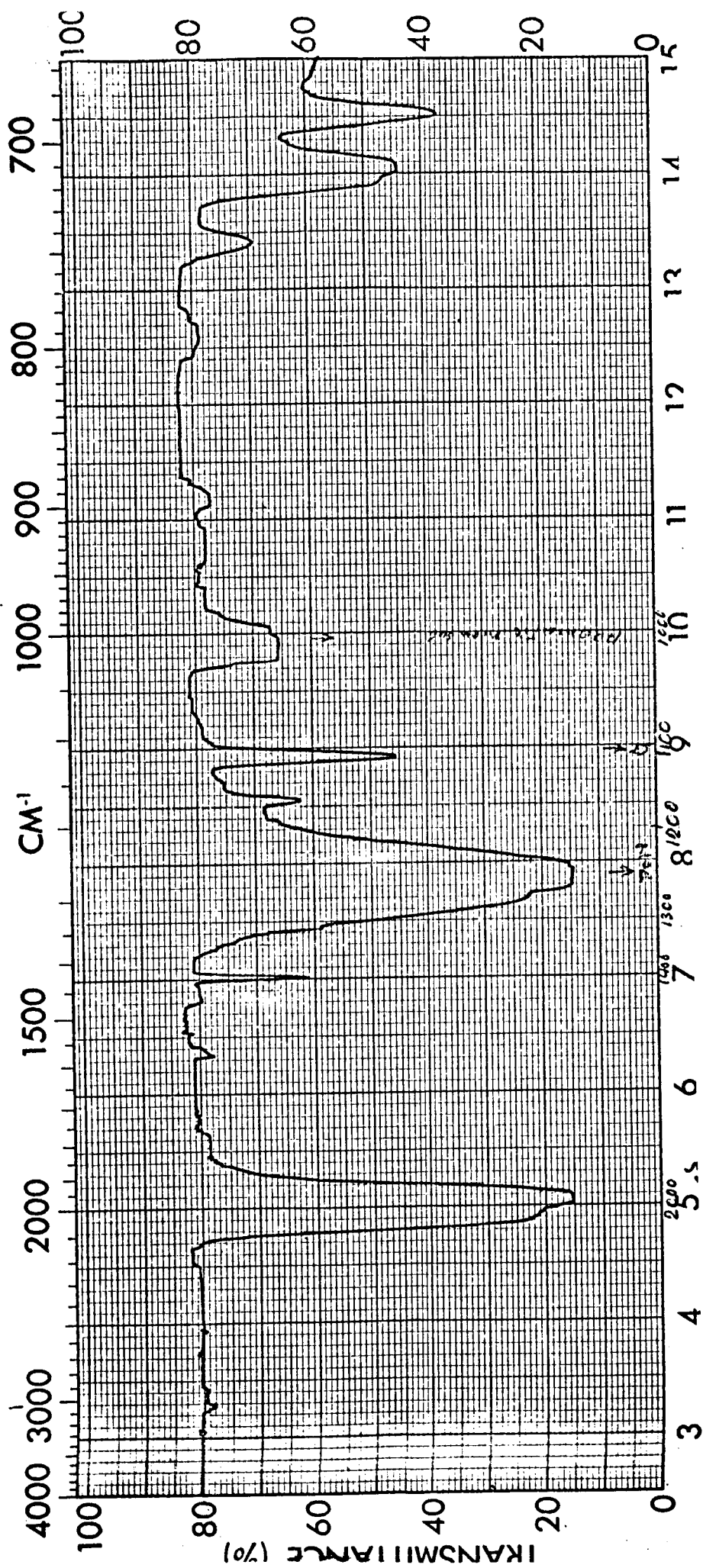


Figure 2

Infrared Spectrum of β -trans-[OPN(NCS)]₄

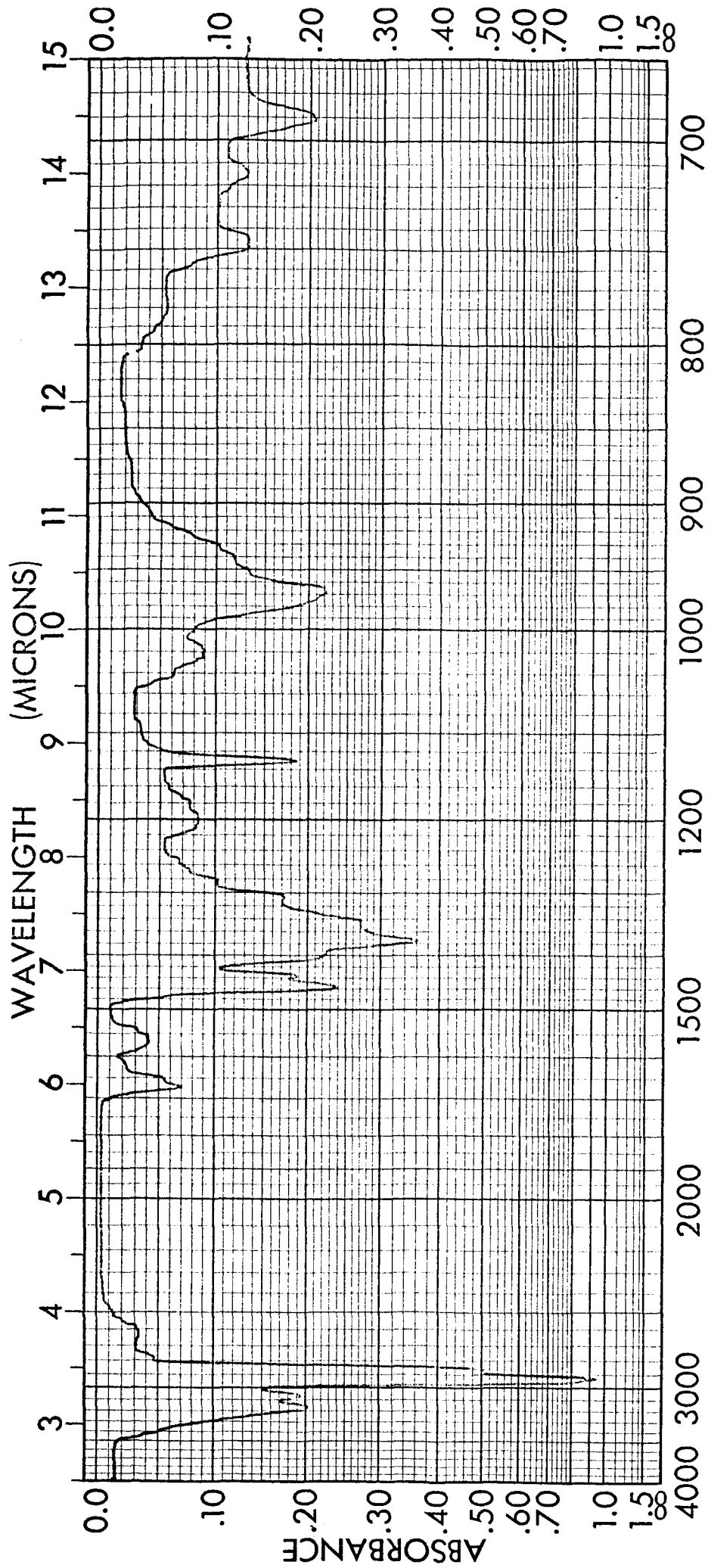


Figure 3

Infrared Spectrum of the Product of β -trans- $[\phi\text{PNN}(\text{NH}_2)]_4$ plus COCl_2

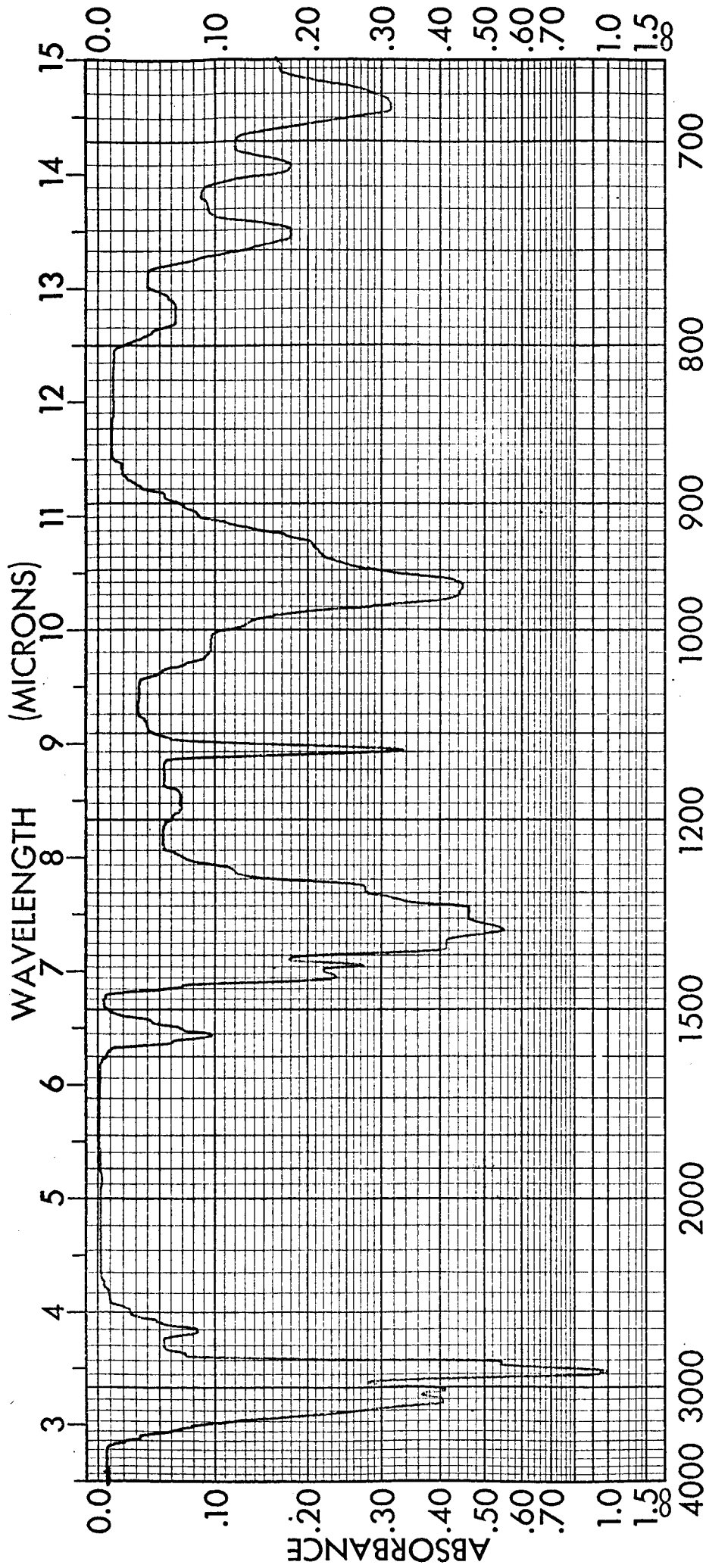


Figure 4

Infrared Spectrum of $[\phi\text{PN}(\text{NH}_2)]_4 \cdot 2\text{HCl}$

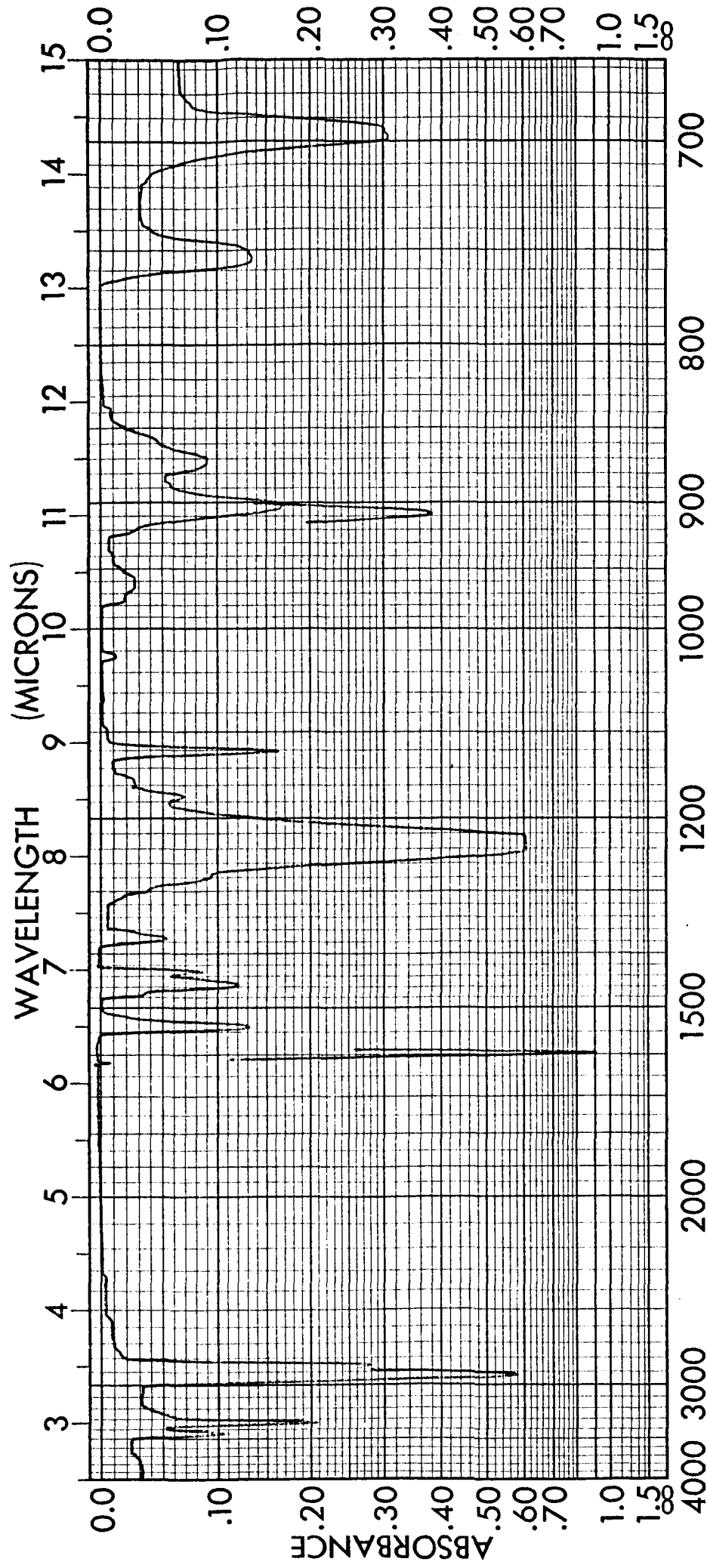


Figure 5

Infrared Spectrum of β -trans- $[\phi\text{PN}(\text{NH}_2)]_4$.

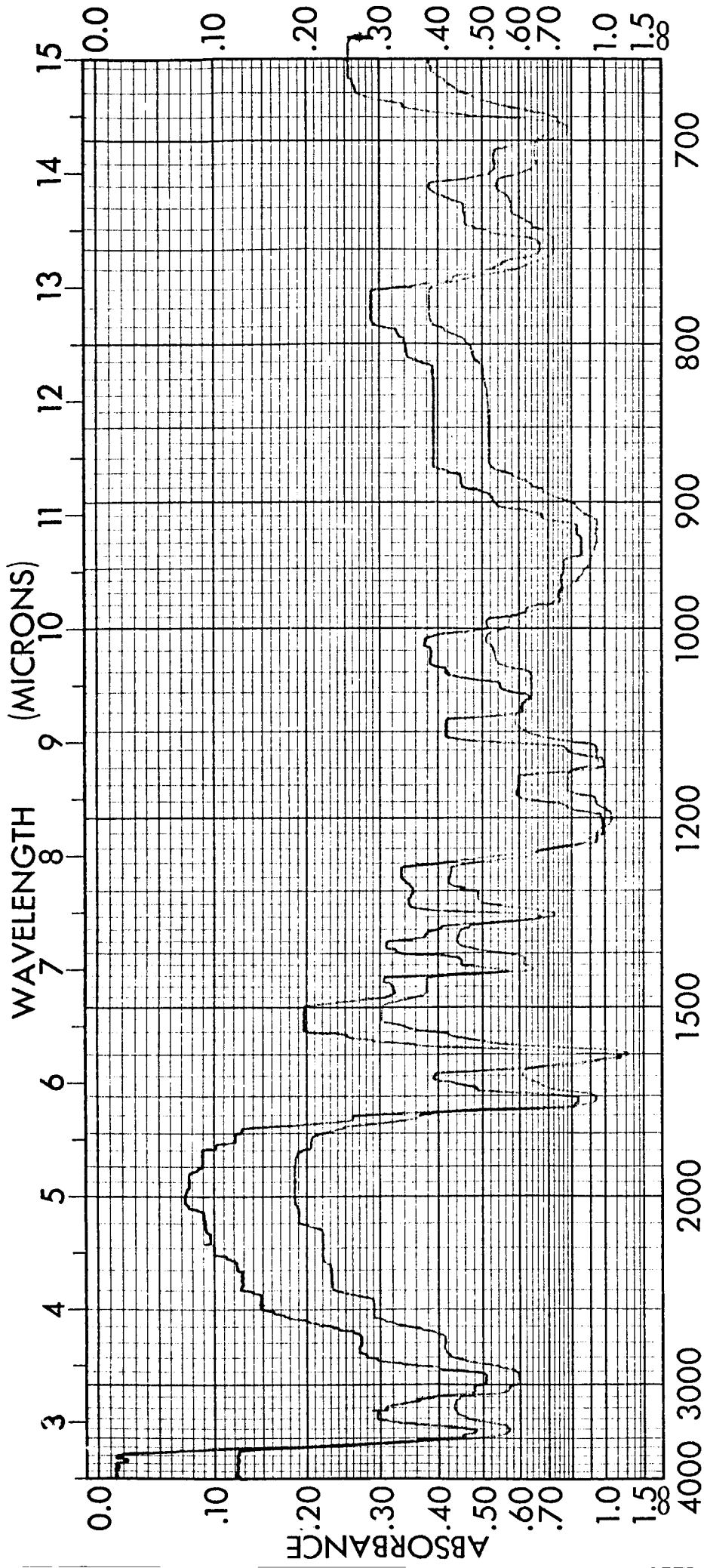


Figure 6.

Infrared Spectrum of Product from Reaction of β -trans- $[\phi\text{PN}(\text{NH}_2)]_4$ with PMDA.

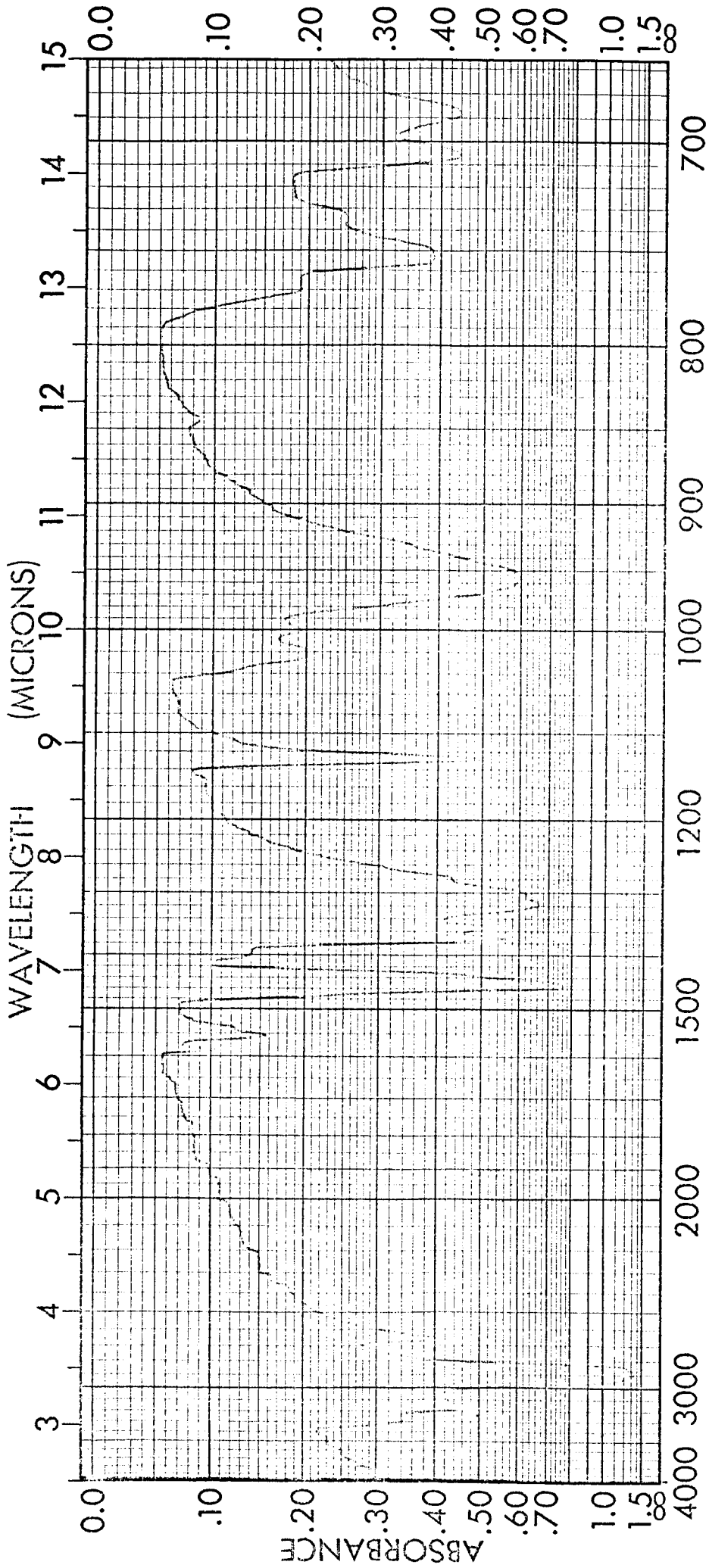


Figure 7

Infrared Spectrum of the Product from Reaction of β -trans- $[\text{O-PN}(\text{NH}_2)_4]_4$ with Pyromellitic Tetraacid Chloride.